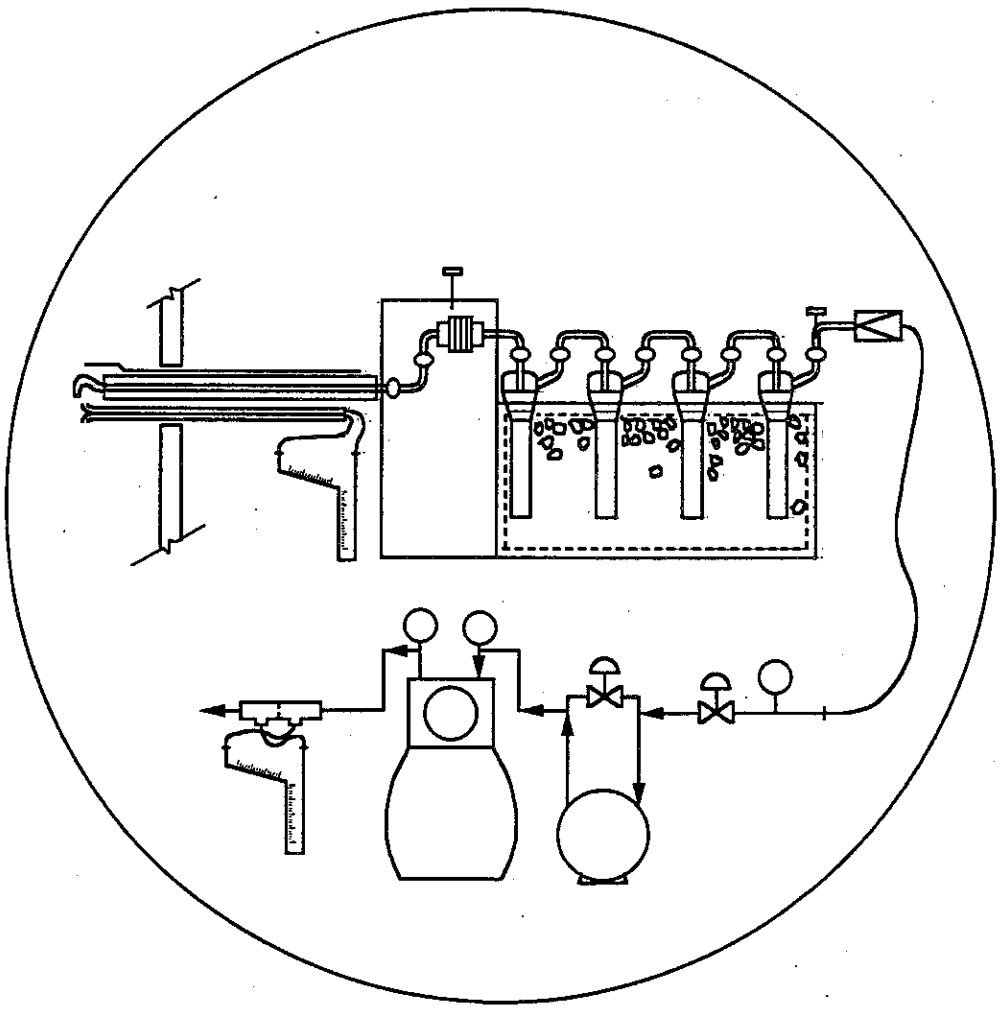
California Environmental Protection Agency

Air Resources Board

STAFF REPORT

Initial Statement of Reasons for a Proposed Public Hearing to Consider the Amendment and Adoption of Stationary Source Test Methods

August 9, 1996



State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

STAFF REPORT:
INITIAL STATEMENT OF REASONS FOR PROPOSED RULEMAKING
PUBLIC HEARING TO CONSIDER THE AMENDMENT AND ADOPTION OF STATIONARY SOURCE TEST METHODS

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I. INTRODUCTION AND RECOMMENDATIONS

A. Introduction

The Air Resources Board (ARB or Board) staff proposes to amend six existing test methods and adopt one new test method for measuring emissions from stationary sources. These emission measurement procedures can be used to determine compliance with local air pollution control or air quality management district emission regulations, to evaluate the effectiveness of air pollution control equipment, and to support control measure development for the criteria and toxic pollutant stationary source programs. In addition, the test methods can be used to develop emission inventories, including emissions information mandated by the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (stats. 1987, Chapter 1252).

Section 39607(d) of the Health and Safety Code requires the ARB to adopt test procedures to determine compliance with ARB and district nonvehicular emission standards. Since 1983, the Board has adopted 47 test methods which are applicable to a wide variety of nonvehicular, or stationary sources. The adopted test methods are referenced in Sections 94101-94147, Title 17, California Code of Regulations (CCR). However, if a district has established a test method for a specific source, Section 94100 of the CCR directs that the district test method shall be used to determine compliance with the district's emission limit for that source.

B. Public Process

The proposed new and amended test methods are the result of several years of consultation with affected industries, the U.S. Environmental Protection Agency, and the districts. We conducted a public workshop on December 12, 1995 for all of the proposed new and revised methods and a prior workshop on April 29, 1992 for most of these methods. Source test companies have requested, used, and commented on several of the proposed ARB methods. We have met with instrument manufacturers and representatives of analytical laboratories. In meetings, written correspondence, and consultation by phone, ARB staff has exchanged information with U.S. EPA staff regarding the source test methods. Finally, written comments have been received from source test companies, analytical laboratories, industrial firms, instrument manufacturers and districts regarding the proposed new and amended test methods.

C. Recommendations

We recommend that the Board adopt the following:

(1) Amendments to the California Code of Regulations (CCR) to incorporate the new and amended test methods by reference (specific amendments to the CCR are presented in Appendix 1), and

(2) One new stationary source test method and amendments to six existing test methods (the test method texts are presented in Appendix 2)

II. PROPOSED AMENDMENT AND ADOPTION OF TEST METHODS

A. Need for Adoption of New and Amended Source Test Methods

As this proposed action is part of our continuing effort to update and improve the ARB source test methods, staff has revised existing test methods and proposed one new method to reflect advances in emission measurement technology, to improve the accuracy and precision of source test data, and to measure new compounds in stationary source emission tests. Pretest planning requirements have been added to several test methods to ensure test objectives are considered in setting sampling and analytical parameters and to help avoid the need for costly retests. New procedures for low concentration laboratory analysis have been added to obtain the lowest possible reportable concentrations of toxic pollutants. For some of these procedures, the staff has added specific guidance; two examples are analysis procedures for ion chromatography and inductively coupled plasma atomic emission spectroscopy. The proposed test methods provide flexibility in the choice of sampling and analysis procedures where the alternative would improve the quality of source test data or simplify a test, without reducing the quality of test results. Finally, the revised test methods are consistent with the corresponding U.S. EPA test methods.

The proposed new and amended ARB test methods will assist district staff in evaluating source test data to demonstrate compliance to permit conditions and other district regulations. The consistency between federal and revised state source testing procedures will simplify source test planning. The pretest planning protocol will help district staff determine if a planned source test will provide meaningful data. The detailed laboratory analysis procedures will assist district staff in auditing the performance of analytical laboratories.

We have altered each of the proposed new and amended test methods to require that modifications be approved only by the ARB Executive Officer. Previously modifications to ARB test procedures were approved by either the districts or the ARB. However, source test companies and other industry representatives requested the change to provide for greater consistency in source test requirements throughout the state. The districts retain the option of adopting their own test methods, as authorized in the California Code of Regulations, Section 94100. Several districts have exercised this option: the South Coast Air Quality Management District, the Bay Area Air Quality Management District, and the San Diego County Air Pollution Control District have adopted a number of their own test methods for determining compliance with district regulations.

B. Proposed Amendment of Existing Test Methods

We propose that the following test methods be amended:

Method 5	Determination of Particulate Matter Emissions from Stationary Sources
Method 7	Determination of Nitrogen Oxide Emissions from Stationary Sources
Method 100	Procedures for Continuous Gaseous Emission Stack Sampling

Method 425 Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

Method 429 Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources

Method 431 Determination of Ethylene Oxide Emissions from Stationary Sources

C. Proposed Adoption of One New Test Method

We also propose that the following new test method be adopted:

Method 436 Determination of Multiple Metals in Emissions from Stationary Sources

The text of the proposed new and amended regulations is appended to this Staff Report in Appendix 1. The text of the proposed new and amended test methods, which the proposed regulations incorporate by reference, is appended to this Staff Report in Appendix 2.

III. ENVIRONMENTAL AND ECONOMIC IMPACTS

The proposal is not expected to have any adverse environmental impacts. Rather, the new and amended test methods will assist air quality decision-makers with improved information regarding emissions from stationary sources. The new and amended test methods will provide greater uniformity and improved quality assurance practices for source testing performed in California. As a result, source test data used in such air quality programs as permitting, emission inventory and air quality modeling will be more consistent and comparable.

The economic impacts of this proposal are expected to be minimal for source test firms and the industrial community. The business community will benefit from the expanded pretest protocol in a number of the revised test methods. The source tester can use the protocol to anticipate and correct potential deficiencies before sampling emissions, and thus prevent a costly retest. With greater uniformity between state and federal test methods, a plant operator can lower costs by consolidating the source tests needed to determine compliance to permit requirements and other emission regulations. In eliminating the provision that allows districts to modify the ARB test methods, the Board will also promote state-wide uniformity of source-testing requirements, again resulting in lower costs to industry.

IV. ALTERNATIVES CONSIDERED

We have considered two alternatives to the proposed adoption of new and revised ARB test methods. The first alternative discussed below is not to adopt the proposal; the second alternative is to rely on U.S. EPA test methods rather than on ARB test methods.

Not adopting the new and amended source test procedures would be detrimental for the following reasons:

(1) Without revision, the six existing source test methods listed above would remain inconsistent with corresponding U.S. EPA test methods. Further, these ARB methods may continue to be used without the improvements in emissions measurement technology and the more rigorous quality assurance practices contained in the proposed revisions.

(2) A number of the new and amended methods proposed in this report have already become standard practice for California source testers. Source testers use these draft ARB methods because the proposed revisions have provided necessary improvements over the older, Board-adopted methods. Currently, source testers are legally required to obtain Board or district approval to use any alternative method, including draft ARB methods, before a source test is conducted. Until the Board adopts new and amended test methods, source testers are at some risk of delay and liability for use of draft ARB test methods.

The second alternative, relying on U.S. EPA test methods rather than developing ARB test methods, would also be detrimental due to the need for test methods to support California's unique emission control programs. ARB methods contain additional guidance not in U.S. EPA methods, including pretest planning protocol and step-by-step procedures for air sampling, preparation of air samples, and sample analysis. ARB methods are needed when there are no applicable U.S. EPA methods, ARB methods are needed for their completeness, and they are needed to provide guidance and flexibility for difficult-to-test industrial processes. In addition, Health and Safety Code Section 39607 (d) requires that the ARB adopt test methods for determining compliance to district regulations. Several of the source test methods considered in this proposal were originally developed by ARB staff before U.S. EPA methods were available. Where the U.S. EPA improved upon the sampling, analysis, or quality assurance aspects of an ARB test method, we have incorporated the improvements in the proposed revisions to the ARB test method.

V. SUMMARY OF PROPOSED NEW AND EXISTING TEST METHODS WITH MAJOR REVISIONS

In this section we have summarized each existing test method which contains major revisions and the proposed new test method. For each test method, the discussion includes emission sources, sampling and analysis procedures, proposed revisions, and the need for use of the ARB method instead of the corresponding U.S. EPA method. The U.S. EPA methods are footnoted to the complete citation found in the Reference Section of this Staff Report: Initial Statement of Reasons.

A. ARB Method 100, Procedures for Continuous Gaseous Emission Stack Sampling

1. Background

Adopted in 1983, Method 100 has been used to test for compliance with district rules and permit conditions for gaseous criteria pollutants throughout California. Method 100 has been used to test a variety of industrial sources, including combustion equipment such as internal combustion engines, steam boilers and gas turbines, as well as cement kilns, and nitric acid plants. The ARB Method 100 is a source test procedure by which a sample from an exhaust stream is continuously extracted, conditioned and analyzed by instruments. Continuous gas analyzers are used to measure emissions of sulfur dioxide, oxides of nitrogen, hydrocarbons, carbon monoxide, carbon dioxide, and the diluent oxygen. Stack gas flow rates and moisture are also measured in order to determine the mass emission rate of air pollutants.

2. Proposed Revisions

Method 100 was updated to improve the quality of the data collected and to reflect improvements in emission measurement technology. The proposed revisions are required in the State Implementation Plan as quality assurance procedures. The U.S. EPA staff has preliminarily reviewed the proposed revisions and indicated that these revisions are acceptable. These quality assurance procedures include a field calibration check for each gas analyzer and a limit on the drift of the measurement system during a source test. In addition, a sampling system check is required to determine that there are no losses of the component of interest in the sampling system which would cause a low measurement, or low bias, in the test results for that component.

The above quality assurance procedures require more field calibration gases at a variety of concentrations. As an alternative to the added cost and hazards of transporting additional calibration gas cylinders, the revised Method 100 allows the use of a gas dilution system in the field. Formerly, only one calibration gas cylinder was needed to calibrate the gas analyzer for each of the six stack gas constituents that are typically measured. With the revised method, the tester must also use a second cylinder to check instrument response at the mid-range of each of the six analyzers. In contrast, a gas dilution system dilutes a high-level calibration gas to any lower concentration needed and eliminates the need for additional gas cylinders of the same constituent. Thus, use of a gas dilution system will reduce the number of calibration gas cylinders which must be transported to a test location. Fewer gas cylinders will lower cost of a source test and reduce the safety risks associated with the presence of pressurized gas cylinders. Performance specifications for a gas dilution system are included in the appendix to the revised method.

We surveyed the ARB-certified source test companies to determine the possible economic impacts of these revisions. Our survey indicated that the cost of a Method 100 source test would increase by about 10%, or about $300 per test for the improved quality assurance practices. These quality assurance procedures are already standard practice for a number of source test companies. Despite the small

added cost, source testers supported the changes that would make ARB Method 100 more consistent with U.S. EPA test methods.

3. Need for ARB Method

Source testers can use one test method, ARB Method 100, to simultaneously obtain data for the six most commonly measured stack gas components. In contrast to the ARB multi-pollutant method, the corresponding U.S. EPA procedures for instrument monitoring of these stack gases are contained in six single-pollutant and diluent source test methods.[1] With the proposed revisions, ARB Method 100 will have performance standards consistent with those of the U.S. EPA test methods. In addition, the performance specifications for a gas dilution system in ARB Method 100 are similar to the requirements in U.S. EPA's gas dilution system calibration method, Method 205.[2] Source testers not only benefit from the ease of using ARB Method 100, but also find guidance in ARB Method 100 not in the U.S. EPA methods regarding specifications for gas analyzers, determination of gas concentration stratification and stack flowrate, and calculation of mass emission rates.

B. ARB Method 425, Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

1. Background

ARB Method 425 was adopted in 1987 and later amended in 1990. Method 425 has been used to measure total chromium and hexavalent chromium emissions from glass melting furnaces and chrome plating tanks as well as from stationary diesel engines and utility boilers. The sampling method consists of the capture of a particulate sample in impingers, or chilled glass vessels which are filled with a sodium hydroxide solution, and a downstream filter. The sample is extracted and analyzed for total chromium using graphite furnace atomic absorption spectroscopy. Alternately, for high total chromium concentrations the test method allows flame atomic absorption spectroscopy if the total chromium concentration is within the detection range of that method. Hexavalent chromium is determined using either manual colorimetry or ion chromatography.

2. Proposed Revisions

Health researchers have determined that even very low concentrations of hexavalent chromium can create serious health risks. Because chromium concentrations need to be documented at very low concentrations, the ARB staff has revised Method 425 to obtain the lowest possible reportable concentrations of total and hexavalent chromium. Pretest procedures were added to the revised method to help the source tester plan for collecting sufficient material to provide reportable levels of hexavalent and total chromium. In addition, we have provided detailed instructions for low concentration analysis of hexavalent chromium using ion chromatography. The quality assurance procedures have also been expanded.

Finally, more comprehensive requirements have been set for recording data, calculating emissions, and reporting test results.

3. Need for ARB Method

ARB Method 425 is adequate to test for both total and hexavalent chromium at a range of concentrations and at a variety of sources. In contrast, one corresponding U.S. EPA method, Method 306,[3] is intended to measure only high concentrations of total chromium at electroplating facilities. A second U.S. EPA method, proposed Method SW-846 0061,[4] is intended to measure hexavalent chromium in an acid gas environment, such as at a hazardous waste incinerator. U.S. EPA's Method SW-846 0013 for hexavalent chrome includes expensive and difficult-to-use sampling equipment. No side-by-side comparison testing of the U.S. EPA and ARB sampling trains has been performed to demonstrate improved collection efficiency of hexavalent chromium in the U.S. EPA sampling train. Due to the high cost to fabricate and operate a sampling train to meet the requirements of SW-846 0013, few source testers in California have chosen to use the U.S. EPA alternative.

C. ARB Method 429, Determination of Polycyclic Aromatic Hydrocarbons (PAH) Emissions from Stationary Sources

1. Background

ARB Method 429 was adopted in 1989 for determining emissions of polycyclic aromatic hydrocarbons (PAH) from stationary sources. The test method has been widely used to determine PAH emissions from a variety of combustion processes, including municipal waste incinerators, medical waste incinerators and wood-fired boilers. In the method, particulate and gaseous phase PAH are collected on a filter, on an adsorbent resin, and in solution-filled impingers. The sample is recovered, extracted, and analyzed using isotope dilution mass spectrometry combined with high resolution gas chromatography.

Since adoption of ARB Method 429, the staff has presented proposed revisions for review and comment at three workshops. The first two workshops were held in July and December of 1990. In March 1991, a summary of these two workshops and the resulting revisions were mailed to workshop participants and other interested source testers and laboratory analysts for further review and comment. A final workshop was held on December 12, 1995. We have received written comments from analytical laboratories, source testing firms, and air pollution control districts.

2. Proposed Revisions

We are proposing revisions to Method 429 in response to both public comment and the results of ARB method development work. The proposed revisions clarify some sampling and analytical procedures, improve the method's accuracy and precision and increase the method's flexibility. In addition, three new compounds have been added to the list of target PAH to increase the number of target compounds from 16 to 19 compounds. These compounds include 2-methylnaphthalene, benzo(e)pyrene, and perylene.

Significant revisions were made to pretest preparation, sample recovery and preservation, sample analysis, calculations, and reporting requirements. The pretest preparation describes procedures that must be followed to optimize sampling and analytical parameters. Typically, PAH background levels are detectable for about four of the 19 target compounds. The revised procedures for the preparation of the sampling media will reduce the background levels of PAH, resulting in the ability to report lower levels of each compound.

Reducing the background levels of PAH will also be achieved by changing the solvent used to recover the samples after sampling is completed and by changing the solvent used to extract the recovered samples. In addition to changes in sample recovery, revisions in the sample preservation and handling procedures make the storage time and storage temperature requirements less burdensome for the tester and the laboratory analyst, without significantly affecting the accuracy and precision of the method.

The revised Method 429 also contains modifications in the sample analysis procedure. As adopted in 1989, the test method required separate analysis of two samples from specific components of a single sampling train. The proposed revisions allow the analysis of a single composite sample from each sampling train, thereby reducing the cost of the test method. The adopted method allowed the use of high resolution mass spectrometry as an alternative analytical procedure to low resolution mass spectrometry, but the method did not contain instructions for the procedure or performance criteria. The revised Method 429 now contains such instructions and performance criteria.

The calculations and reporting requirements are described in more detail in the amended method and all terminology has been revised to be consistent with the isotope dilution methods for dioxins in ARB Method 428 and U.S. EPA Method 23.[5]

3. Need for ARB Method

Only ARB Method 429 has sampling and analysis procedures specifically for determining PAH from air samples. The staff recommends the analysis procedure of ARB Method 429 procedure over the two applicable U.S. EPA analysis methods, EPA Methods 8270 [6] and 1625 [7] for semivolatile organic compounds. ARB Method 429 contains an isotope dilution procedure to account for the possible loss of target compounds in sample preparation prior to sample analysis. In contrast, the U.S. EPA Method 8270 for PAH analysis does not include isotope dilution. Although the U.S. EPA Method 1625 does contain isotope dilution, this EPA method was designed to analyze waste water specifically, and does not contain a procedure for preparing air samples. The ARB staff included a solids extraction procedure in ARB Method 429 for extracting the PAH compounds from the sampling filter and the adsorbent resin.

D. ARB Method 431, Determination of Ethylene Oxide Emissions from Stationary Sources

1. Background

Adopted in 1989, ARB Method 431 is prescribed in the ARB's "Ethylene Oxide Airborne Toxic Control Measure for Sterilizers and Aerators" to determine the efficiency of an emission control device. The method is used to determine the emissions of ethylene oxide from sterilizers at a variety of locations, including hospitals, other medical facilities, and medical device manufacturers.

The ARB toxic control measure for sterilizers requires that Method 431 be used to sample the inlet and outlet of the control device to measure control efficiency. A typical sterilizer operates in three phases: sterilization, sterilant evacuation, and aeration, with emissions occurring primarily during the evacuation cycle. The source tester uses Method 431 to measure volumetric flow rate and repeatedly extract gas samples during the evacuation cycle. The samples are directly analyzed onsite using gas chromatography with flame ionization detection. Total precontrolled and controlled emissions of ethylene oxide for the sterilizer are calculated from concentration and flowrate data.

2. Proposed Revisions

We revised Method 431 to provide the flexibility needed to more accurately and safely measure sterilizer emissions from the variety of sterilizers and control devices operating in California. Due to the fact that a sterilizer operates as a cyclic process, the emissions measurement process is complicated by varying emissions and flowrates over time. The method was revised to allow the use of an integrated sampling procedure to more accurately measure emissions for unsteady flowrates and pollutant concentrations. The integrated sample is collected in a Tedlar bag and either is analyzed on-site or is transported to a laboratory for analysis within twenty-four hours. A semi-continuous sampling configuration was also included in the revised method for sterilizers with a pulsed evacuation cycle.

The revised method now allows the source tester to choose the appropriate ARB or U.S. EPA flow measurement methods, including the use of a pitot tube for large ducts.

A source tester who directly measures pollutant levels at the inlet to a control device may be exposed to hazardous levels of ethylene oxide. To insure the safety of test personnel, ARB staff has included an optional calculation method to determine the mass of ethylene oxide delivered to a control unit in place of actual measurement of inlet conditions. The revised method retains the requirement that the concentration of ethylene oxide emitted from the control unit will be measured and analyzed.

Both alternatives in the revised method, the allowance of integrated sampling and the estimation of ethylene oxide at the control inlet, will reduce the cost of an ethylene oxide source test. The test cost will be reduced if the integrated sample is analyzed at an off-site laboratory, because neither a chemist nor the field gas chromatograph will be needed at the test site. The estimation method for precontrolled emissions is cost-effective, since only controlled emissions will be directly sampled and analyzed if precontrolled emissions are estimated.

3. Need for ARB Method

ARB Method 431 is needed to provide an accurate, yet flexible, emissions measurement method for both industrial and medical facility sterilizers in California. The ARB's revised Method 431 is consistent with the U.S. EPA test procedure, which was included in the U.S. EPA control requirements for ethylene oxide sterilizers.[8] However, the U.S. EPA sterilizer regulation and source test method apply only to large industrial users of ethylene oxide, and not to many of the medical sterilizers operating in California.

E. Proposed ARB Method 436, Determination of Multiple Metals Emissions from Stationary Sources

1. Background

Draft ARB Method 436 has been used by source testers in California since 1989 to assess emissions of up to 19 metals from combustion equipment including hospital incinerators, tire incinerators, cement kilns and crude oil stream generators. We developed Method 436 to allow source testers to simultaneously collect data for a number of metals, rather than performing a separate test for each metal of interest. ARB Method 436, for example, could be performed at a hazardous waste incinerator in place of the combined performance of ARB Method 104 for beryllium, Method 424 for cadmium, and Method 433 for nickel.

2. Proposed Method

In the method, a sample from the emission stack is withdrawn isokinetically using a modified ARB Method 5 sampling train. (The Method 5 sampling train is discussed in Section VI.) Particulate emissions are captured on a heated filter, and gaseous emissions are collected in a series of nitric acid, hydrogen peroxide and potassium permanganate impingers. The samples are analyzed using inductively coupled plasma atomic emission spectroscopy (ICPAES) or direct aspiration atomic absorption spectroscopy. Graphite furnace atomic absorption spectroscopy can also be used for some metal species if greater analytical sensitivity is needed than can be obtained using ICPAES. Mercury levels are determined using cold vapor atomic absorption spectroscopy.

ARB staff updated the draft method to include pretest planning protocol, improve quality assurance, add additional target metals and improve the sampling

and analysis procedures. In addition, we revised the sampling and analysis procedures of Method 436 to be consistent with procedures of U.S. EPA Method 29,[9] U.S. EPA's multiple metals test method.

3. Need for ARB Method

ARB draft Method 436 includes the sampling procedures, analytical methods and quality assurance procedures of U.S. EPA Method 29. Thus, the U.S. EPA and the ARB methods both provide for the analytical precision needed to report the lowest possible concentrations for each metal species. However, only the ARB method contains pretest procedures to assist the tester to collect a sufficient amount of material to obtain reportable data for trace concentrations of metal species. Also, ARB Method 436 does not permit determination of total particulate on the same sample, as does U.S. EPA Method 29. This is because most California districts require particulate determination on the filter and in the impingers, while U.S. EPA only considers the filter catch. Determination of impinger particulate would interfere with the metals analysis.

VI. SUMMARY OF EXISTING TEST METHODS WITH PROPOSED MINOR REVISIONS

We have briefly summarized below the existing methods for which we are proposing minor revisions.

A. ARB Method 5, Determination of Particulate Matter Emissions from Stationary Sources

ARB Method 5 was adopted in 1983 and subsequently amended in 1986 and 1988. The method is used to extract particulate matter emissions from an emission stack and to collect the particulate matter on a glass fiber filter and in chilled impingers. To insure that a representative particulate sample has been extracted, the particulate matter is collected isokinetically, or at a rate equal to the stack gas velocity. The tester measures stack gas flowrate, stack moisture, and mass of the particulate sample to determine the mass emission rate from the stack in units of pounds per hour or grams per hour.

The proposed revisions will make ARB Method 5 more consistent with U.S. EPA Method 5[10] and U.S. Method 202, Determination of Condensible Particulate Emissions from Stationary Sources.[11] Revisions to ARB Method 5 include the addition of field calculations for maintaining an isokinetic sampling rate, expanded instructions for recovery of sample material collected in the impingers, and minor editorial corrections.

B. ARB Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources

ARB Method 7 has not been revised since its adoption in 1983. The method is a wet chemistry reference method used to measure the oxides of nitrogen from a grab sample. The oxides of nitrogen are extracted into solution and quantified using a manual colorimetric procedure with phenoldisulfonic acid. ARB staff added the requirement to obtain and analyze U.S. EPA audit samples to make the method consistent with U.S. EPA Method 7.[12]

VII. REFERENCES:

1. The following test methods are in CFR 40, Part 60, Appendix A:

   EPA Method 3A, Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)

   EPA Method 6C, Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

   EPA Method 7E, Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

   EPA Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources

   EPA Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

   EPA Method 25B, Determination of Total Gaseous Organic Concentration Using a Nondispersive Infrared Analyzer.

2. EPA Method 205, Verification of Gas Dilution Systems for Field Instrument Calibrations, CFR 40, Part 51, Appendix M.

3. EPA Method 306 and 306A, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, CFR 40, Part 63, Appendix A.

4. SW-846 0061, November 1986, 3rd edition, U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, CFR Title 40, Part 266, Appendix IX.

5. EPA Method 23, Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources, CFR 40, Part 60, Appendix A.

6. EPA Method 8270B, Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique, SW-846, November 1986, 3rd Edition, U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, CFR 40, Part 261.

7. EPA Method 1625, Revision B - Semivolatile Organic Compounds by Isotope Dilution Gas Chromatography/Mass Spectrometry, CFR 40, Part 136, Appendix A.

8. Ethylene Oxide Emissions Standard for Sterilization Facilities, December 6, 1994, CFR 40, Part 63.360.

9. EPA Method 29, Determination of Metals Emissions from Stationary Sources, CFR 40, Part 60, Appendix B.

10. EPA Method 5, Determination of Particulate Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

11. EPA Method 202, Determination of Condensible Particulate Emissions from Stationary Sources, CFR 40, Part 51, Appendix M.

12. EPA Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

STAFF REPORT:

Initial Statement of Reasons for Proposed Rulemaking
Public Hearing to Consider the Amendment and
Adoption of Stationary Source Test Methods

APPENDIX 1

Proposed Amendments to the California Code of Regulations

PROPOSED AMENDMENTS TO THE CALIFORNIA CODE OF REGULATIONS

Note: ~~Graphic screen~~ indicates deleted text; Underline indicates inserted text.

Amend Section 94105, Title 17, California Code of Regulations to read as follows:

94105. Method 5 - Particulate Matter Emissions.

The test method for determining particulate matter emissions is set forth in the Air Resources Board's Method 5, Determination of Particulate Matter Emissions from Stationary Sources, adopted June 29, 1983, as last amended ~~January 7, 1988~~ [Insert date of amendment], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Amend Section 94107, Title 17, California Code of Regulations to read as follows:

94107. Method 7 - Nitrogen Oxides.

The test method for determining nitrogen oxide emissions is set forth in the Air Resources Board's Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources, adopted June 29, 1983, as last amended [Insert date of amendment], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Amend Section 94114, Title 17, California Code of Regulations to read as follows:

94114. Method 100 - Continuous Sampling.

The test method for continuous gaseous emission stack sampling is set forth in the Air Resources Board's Method 100, Procedures for Continuous Gaseous Emission Stack Sampling, adopted June 29, 1983, as last amended [Insert date of amendment], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Amend Section 94135, Title 17, California Code of Regulations to read as follows:

94135. Method 425 - Total Chromium and Hexavalent Chromium Emissions from Stationary Sources.

The test method for determining total chromium and hexavalent chromium emissions from stationary sources is set forth in the Air Resources Board's Method 425, Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources, adopted January 22, 1987, as last amended ~~September 12, 1990~~, [Insert date of adoption], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Amend Section 94141, Title 17, California Code of Regulations to read as follows:

94141. Method 429 - Polycyclic Aromatic Hydrocarbon (PAH) Emissions.

The test procedure for determining polycyclic aromatic hydrocarbon emissions is set forth in the Air Resources Board's Method 429, Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources, adopted September 12, 1989, as last amended [Insert date of amendment], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Amend Section 94143, Title 17, California Code of Regulations to read as follows:

94143. Method 431 - Ethylene Oxide Emissions.

The test procedure for determining ethylene oxide emissions is set forth in the Air Resources Board's Method 431, Determination of Ethylene Oxide Emissions from Stationary Sources, adopted September 12, 1989, as last amended [Insert date of amendment], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

Adopt new Section 94161, Title 17, California Code of Regulations as follows:

94161 Method 436 - Multiple Metal Emissions.

The test procedure for determining multiple metal emissions is set forth in the Air Resources Board's Method 436, Determination of Multiple Metals in Emissions from Stationary Sources, adopted [insert date of adoption], which is incorporated herein by reference.*

Note: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, 39666 and 40001, Health and Safety Code.

*The incorporated test procedure is available upon request from the Air Resources Board's Public Information Office, 2020 L Street, Sacramento, California, 95814, telephone (916) 322-2990. The Air Resources Board may also be contacted at its Internet home page: http://www.arb.ca.gov.

STAFF REPORT:

Initial Statement of Reasons for Proposed Rulemaking
Public Hearing to Consider the Amendment and
Adoption of Stationary Source Test Methods

APPENDIX 2

Proposed New and Amended Test Methods for Stationary Sources

State of California
California Environmental Protection Agency
Air Resources Board

Proposed Amendment*

Method 5

Determination of Particulate Matter Emissions from Stationary Sources

Adopted: June 29, 1983
Amended: March 28, 1986
Amended: January 7, 1988
Amended: _____

* including new Table of Contents, Appendix A, and other changes
Note: This document consists of the text of the proposed amendment to Method 5. Proposed deletions are noted by graphic screen and proposed additions are noted by underline.

Method 5

Determination of Particulate Matter Emissions from Stationary Sources

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METHOD 5

DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

1 PRINCIPLE AND APPLICABILITY

1.1 **Principle.** Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 120 ± 14°C (248 ± 25°F) or such other temperature as specified by an applicable subpart of the standards or approved by the Executive Officer Control Agency's Authorized Representative for a particulateparticular application. The particulateparticulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

Since the definition of particulate matter is not consistent in all rules, the particulate matter catch shouldshall be itemized by weight as follows: (1) Filter Catch, (2) Probe Catch, (3) Impinger Catch, and (4) Solvent Extract to allow adjustment of the particulate matter determination to be consistent with the applicable regulation.

The number of sampling runs must be sufficient to provide minimal statistical data and shall be at least three (3), unless explicitly stated otherwise in the applicable rule.

1.2 **Applicability.** This method is applicable for the determination of particulate emissions from stationary sources.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

2 APPARATUS

2.1 **Sampling Train.** A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (See EPA Method 5 Bibliography); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (See EPA Method 5 Bibliography). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 **Probe Nozzle.** Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be ≤ 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Executive Officer Control Agency's Authorized Representative. If made of stainless steel, the

nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 **Probe Liner.** Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of 120 ±14°C (248 ±25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Executive Officer Control Agency's Authorized Representative for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F); quartz liners shall be used for temperatures between 480 and 900°C (900 and 1,650°F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Executive Officer Control Agency's Authorized Representative. The softening temperature for borosilicate is 820°C (1,508°F), and for quartz it is 1,500°C (2,732°F).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[1] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative.

2.1.3 **Pitot Tube.** Type S, as described in Section 2.1 of Method 2, or other device approved by the Executive Officer Control Agency's Authorized Representative. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 **Differential Pressure Gauge.** Inclined manometer or equivalent device (two), as

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[1] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

described in Section 2.2 of Method 2. One manometer shall be used for velocity head (ΔP) readings, and the other, for orifice differential pressure readings.

2.1.5 **Filter Holder.** Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g. stainless steel, Teflon, Viton) may be used, subject to approval of the Executive Officer ~~Control Agency's Authorized Representative~~. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 **Filter Heating System.** Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 ± 14°C (248 ± 25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Executive Officer ~~Control Agency's Authorized Representative~~ for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 **Impinger train.** The following system shall be used to determine the stack gas moisture content and condensibles: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (1/2 in) ID glass tube extending to about 1.3 cm (1/2 in) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the impinger train) may be used, subject to the approval of the Executive Officer ~~Control Agency's Authorized Representative~~. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the impinger train, each to within 1 ml or 1 g may be used, subject to the approval of the Executive Officer ~~Control Agency's Authorized Representative~~. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the impinger train by: (1) monitoring the temperature and pressure at the exit of the impinger train and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20°C (68°F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the impinger train, it is recommended that silica gel (or equivalent) still be used between the impinger system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.8 **Metering System.** Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.9 **Barometer.** Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 **Gas Density Determination Equipment.** Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Executive Officer Control Agency's Authorized Representative).

2.2 **Sample Recovery.** The following items are needed:

2.2.1 **Probe-Liner and Probe-Nozzle Brushes.** Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 **Wash Bottles - Two.** Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 **Glass Sample Storage Containers.** Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage). Alternatively, polyethylene bottles may be used.

2.2.4 **Petri Dishes.** For filter samples, glass or polyethylene, unless otherwise specified by the Executive Officer ~~Control Agency's Authorized Representative~~.

2.2.5 **Graduated Cylinder and/or Balance.** To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 **Plastic Storage Containers.** Air-tight containers to store silica gel.

2.2.7 **Funnel and Rubber Policeman.** To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 **Funnel.** Glass or polyethylene, to aid in sample recovery.

2.3 **Analysis.** For analysis, the following equipment is needed.

2.3.1 **Glass Weighing Dishes.**

2.3.2 **Desiccator.**

2.3.3 **Analytical Balance.** To measure to within 0.1 mg.

2.3.4 **Balance.** To measure to within 0.5 g.

2.3.5 **Beakers.** 250 ml.

2.3.6 **Hygrometer.** To measure the relative humidity of the laboratory environment.

2.3.7 **Temperature Gauge.** To measure the temperature of the laboratory

environment.

3 REAGENTS

3.1 Sampling. The reagents used in sampling are as follows:

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (≤ 0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative.

3.1.3 Water. When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative.

3.2 Sample Recovery

3.2.1 Acetone - reagent grade, ≤ 0.001 percent solids residue, in glass bottles - is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low residue values (≤ 0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.2.2 Reagents for Recovery of Back Half / Impinger Catch ONLY

3.2.2.1 Water, distilled, maximum solids residue as per 3.2.1.

3.2.2.2 Methylene Chloride, reagent grade, maximum solids residue as per 3.2.1.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Executive Officer ~~Control Agency's Authorized Representative~~.

3.3.3 Reagents for Analysis of Back Half / Impinger Catch ONLY

3.3.3.1 Water, distilled, same as 3.2.2.1.

3.3.3.1 Methylene Chloride, same as 3.2.2.2.

4 PROCEDURE

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testors should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively, (unless otherwise specified by the Executive Officer ~~Control Agency's Authorized Representative~~), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Executive Officer ~~Control Agency's Authorized Representative~~.

4.1.2 **Preliminary Determinations.** Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Executive Officer Control Agency's Authorized Representative. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using the Approximation Method described in Method 4, Section 1.2 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min. (or some greater time interval as specified by the Executive Officer Control Agency's Authorized Representative), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximately average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Executive Officer's Control Agency's Authorized Representative's approval must first be obtained.

4.1.3 **Preparation of Collection Train.** During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the

impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Executive Officer Control Agency's Authorized Representative, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is required. The following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum; alternatively, the

probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run. Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be not greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Executive Officer Control Agency's Authorized Representative) and a

temperature around the filter of 120 ±14°C (248 ±25°F), or such other temperature as specified by the Executive Officer ~~Control Agency's Authorized Representative~~.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic condition (Note: During the period before sampling begins point the nozzle downstream. Rotate the nozzle upstream immediately before the sampling pump is turned on.)

Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If C_P and M_d are outside the above stated ranges do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Executive Officer ~~Control Agency's Authorized Representative~~, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or

when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature less than 20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see Section 4.1.4.2) The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Executive Officer Control Agency's Authorized Representative.

Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Executive Officer Control Agency's Authorized Representative for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Executive Officer Control Agency's Authorized Representative for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impinger or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Executive Officer~~Control Agency's Authorized Representative~~ and shall be used when specified by the Executive Officer~~Control Agency's Authorized Representative~~; in these cases save a water blank and follow the Executive Officer's~~Control Agency's Authorized Representative's~~ directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. (See note, Section 2.1.7.)

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.2.1 **Determination of the Particulate Concentration.** The particulate matter concentration is determined by isokinetically aspirating a measured volume of the stack gas, catching the particulate in a filter, in the probe, connecting tubing, and in the impingers, and dividing the weight of the particulate catch by the volume of gas.

For ~~the APCD~~some rules, matter that is liquid at standard temperature must be included. This liquid matter is assumed to pass as a gas through the filter and to then condense in the impinger water. The weight of this liquid particulate is determined by recovering the impinger liquid, extraction with methylene chloride, and evaporation of the aqueous and solvent phases to constant weight. ~~Solvent extraction using methylene chloride followed by an aqueous phase extraction.~~ Caution must therefore be used not to let any acetone or other organic material contaminate ~~non-water rinse enter~~ the impinger water.

For ~~the APCD~~some rules, the combined weight of the particulate matter caught in the probe, the filter and the impingers is used in the determination of particulate matter concentration. For some rules only the combined weight of the particulate matter caught in the probe and filter is used in the determination. Accordingly, ~~it is advisable to~~ report the weight of the impinger catch separately so that ~~both the APCD and the ARB~~particulate determinations can be made as appropriate for the applicable rule. The total particulate matter catch ~~may~~must be itemized by weight as follows: (1) Filter Catch, (2) Probe Catch, (3) Impinger Catch, and (4) Solvent Extract.

4.2.1.1 Recovery of Back Half and Impinger Catch Particulate
Prior to the test all sampling train glassware shall be cleaned with soap and tap water, and rinsed using tap water and subsequently water, acetone, and methylene chloride conforming to recovery solvent specifications. It is important to completely remove silicone grease from areas which will be exposed to methylene chloride during sample recovery and glass joints shall not be greased if the back half and impinger catch particulate is recovered.

Reserve at least 200 ml of water from the same stock originally used to fill the impingers as a field blank, placing it in an appropriately labeled sample container; use water from the same stock for rinses described below.

If water in the impingers is not visibly discolored and no material is apparent floating in or adhering to impingers, only water shall be used for recovery rinsing. Quantatively transfer all liquid from the first three impingers into a clean sample container(s) (glass or plastic); rinse each impinger and the connecting glassware, including the probe extension (downstream of the filter) and any graduated cylinder used to measure liquid volume, twice with water. Recover the rinse water and add it to the same sample container(s). Mark the liquid level on the container(s).

If water in the impingers is visibly discolored or material is visible floating in or adhering to impingers, methylene chloride shall be used to ensure complete recovery of material. Recover impinger liquid and rinse with water as above. If necessary, reassemble and cap or stopper the impinger assembly and transport to a facility equipped with an appropriate laboratory hood system. Reserve at least 200 ml of methylene chloride used as a blank, placing it in an appropriately labeled glass sample container. In the laboratory hood, follow the water rinses with two rinses of methylene chloride; save the rinse products in a clean glass sample container. Mark the liquid level on the container.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at 105°C (220°F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Executive Officer Control Agency's Authorized Representative. The tester may also opt to oven dry the sample at 105°C (220°F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Executive Officer Control Agency's Authorized Representative, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest

0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Note - At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If the evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

4.3.1 Impinger Catch and Extract

4.3.1.1 The impinger catch consists of the water and organic solvent[2] rinsings from the sample train connections between the filter and impingers, plus the impinger contents. ~~These are usually received in 1 to 4 one pint wide mouth Mason jars.~~

Field Blanks of water and methylene chloride described in 4.2.1 shall be analyzed for solids content by evaporation. The impinger catch and impinger catch extract residue weights shall be corrected based on these analyses and the total volume of each reagent used. Accordingly, determine the amount of water and solvent in the sample containers before proceeding. ~~The methylene chloride used in the extraction shall also have a blank run on it similar to those run for the water and acetone. The methylene chloride extraction is to be corrected the same way the acetone rinse is.~~

The residues of the ~~impinger catch~~ solvent extract and impinger catch are to be weighed to a constant weight as defined earlier.

4.3.1.2 Combine the catch in a separatory funnel of suitable size. The Mason jar is to be rinsed with methylene chloride into the separatory funnel.

4.3.1.3 Extract the aqueous catch three times with 50 ml portions of methylene chloride (CH_2Cl_2). Each time, extract for 30 seconds with vigorous shaking, then allow the layers to separate (which may sometimes take up to 15 minutes due to emulsion formation). Drain the CH_2Cl_2 layers into a beaker of suitable size through a short stem funnel containing a cotton plug, to remove droplets of water from CH_2Cl_2 extract. Save ~~the~~ aqueous layer for use in

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[2] Methylene Chloride (CH_2Cl_2) unless the source being evaluated dictates otherwise, then an alternate solvent may be used subject to approval of the Executive Officer ~~usually benzene is used~~.

Sec. 4.3.1.8.

4.3.1.4 Rinse the funnel and cotton with fresh CH_2Cl_2 and concentrate the combined CH_2Cl_2 extract to about 25 ml under a stream of clean filtered air at room temperature in a hood.

4.3.1.5 Quantitatively transfer the concentrated extract to a tared 50 ml beaker and evaporate to dryness under the above conditions and place in a desiccator for one hour.

4.3.1.6 Weigh the extract residue to the nearest 0.1 mg.

4.3.1.7 Record the gross and tare weights and report the net weight as "Impinger Catch Extract".

4.3.1.8 From Sec. 4.3.1.3 quantitatively transfer the aqueous phase to a suitable size beaker and concentrate to about 25 ml on a hot plate or steam bath with the aid of the clean filtered air stream.

4.3.1.9 Quantitatively transfer the aqueous concentrate to a tared 50 ml beaker and evaporate to dryness on a steam bath.

4.3.1.10 Place the beaker containing the residue in a 105°C oven for one hour and then let cool in a desiccator.

4.3.1.11 Weigh the residue to the nearest 0.1 mg.

4.3.1.12 Record the gross and tare weights and report the net weight as "Impinger Catch".

4.4 Quality Control Procedures. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional for the tester.

4.4.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 5.3, determine the $\Delta H_@$ for the metering system orifice. The $\Delta H_@$ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528°R and 29.92 in. Hg. The $\Delta H_@$ is calculated as follows:

$$\Delta H_@ = 0.0319\ \Delta H\ (T_m/P_{bar})\ \theta^2 / (Y^2 V_m^2) \qquad \text{Equation 5-9}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average dry gas meter temperature, °R.
P_{bar} = Barometric pressure, in. Hg.

θ = Total sampling time, min.
Y = Dry gas meter calibration factor, dimensionless.
V_m = Volume of gas sample as measured by dry gas meter, dcf.
0.0319 = (0.0567 in. Hg/°R) x $(0.75 \text{ cfm})^2$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the $\Delta H_@$ pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperature and the barometric pressure. Calculate a dry gas meter calibration check value, Y_c as follows:

$Y_c = (10 / V_m) [0.0319 T_m]^2 / [P_{bar}]$ Equation 5-10

$Y_c = (10 / V_m) [0.0319 T_m / P_{bar}]^{1/2}$ Equation 5-10

Where:

Y_c = Dry gas meter calibration check value, dimensionless.
10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c > 1.03Y$ $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

4.4.2 **Calibrated Critical Orifice.** A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a quality control check, such procedure being subject to approval by Executive Officer Control Agency's Authorized Representative.

5 CALIBRATION

Maintain a laboratory log of all calibrations.

5.1 **Probe Nozzle.** Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 **Pitot Tube.** The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 **Metering System.** Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to

the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

After each field use, the calibration of the metering systems shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Executive Officer ~~Control Agency's Authorized Representative~~. Wherever a wet test meter is specified, a standard dry gas meter may be used instead, provided that the procedure and frequency of calibration of the standard dry gas meter used conforms to the specifications of EPA Method 5 (i.e. 40 CFR 60 Appendix A Method 5) Section 7.1, "Dry Gas Meter as a Calibration Standard".

Note - If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5.5. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity or equivalent may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the dry gas meter. Also note the barometric pressure, and the temperatures of the wet test meter, the inlet of the dry gas meter, and the outlet of the dry gas meter. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m^3 (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5-6 and calculate Y, the dry gas meter calibration factor, and $\Delta H_@$, the orifice calibration factor, at each

orifice setting as shown on Figure 5-6. Allowable tolerances for individual Y and $\Delta H_@$ values are given in Figure 5-6. Use the average of the Y values in the calculations in Section 6. Before calibrating the metering system, it is suggested that a leak-check be conducted for. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm): at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

5.3.2 **Calibration After Use**. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test) with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the dry gas meter calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as previously detailed. Alternative procedures e.g., rechecking the orifice meter coefficient may be used, subject to the approval of the Executive Officer Control Agency's Authorized Representative.

5.3.3 **Acceptable Variation in Calibration**. If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 **Probe Heater Calibration**. The probe heating system shall be calibrated before its initial use in the field. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical simple flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

5.5 **Temperature Gauges**. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 **Leak Check of Metering System** Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing

attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6 Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentrations, mg/g.

C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "i th" component change (i = 1,2,3,...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min. (cfm).

m_a = Mass of residue of acetone after evaporation, mg.

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18.0 g/g-mole. (18.0 lb/lb-mole).

m_a = Mass of residue of acetone after evaporation, mg.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_{barr} = Same as P_{bar}

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R). Note: T_m will depend on type of meter used and sampling configuration.

T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in. H_2O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n th) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2). Average dry gas meter temperature for temperature- compensated meters shall be taken as the compensation temperature regardless of meter inlet and outlet temperature.

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg) by using Equation 5-1.

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{(P_{bar}+\Delta H/13.6)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar}+\Delta H/13.6}{T_m}$$

Equation 5-1

where:

K_1 = T_{std} / P_{std} = 0.3858 °K / mm Hg for metric units.
= 17.65 °R / in Hg for English units.

Note: Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted

prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$V_m - (L_p - L_a)\theta$$

(b) Case II. One or more component changes made during sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_i \quad - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

6.4 Volume of water vapor.

$$V_{w(std)} = V_{lc}\frac{\rho_w R T_{std}}{M_w P_{std}} = K_2 V_{lc} \qquad \text{Equation 5-2}$$

where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04707 ft^3/ml for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Equation 5-3}$$

Note: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F).

6.6 Acetone Blank Concentrations.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Equation 5-4}$$

Calculate solids concentrations for water and methylene chloride in similar fashion.

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Equation 5-5}$$

Calculate solids residue weights for water and methylene chloride in similar fashion.

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). Note - Refer to Section 4.1.5 to assist in calculations of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_s = (0.001 g/mg)\ (m_n / V_{m(std)}) \qquad \text{Equation 5-6}$$

6.10 Conversion Factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205 X 10-3
g/ft^3	g/m^3	35.31

6.11 Isokinetic Variation

6.11.1 Calculation From Raw Data.

$$I = \frac{100\ T_s\ [K_3 V_{lc} + (V_m / T_m)\ (P_{bar} + \Delta H / 13.6)]}{60\ \Theta\ v_s\ P_s\ A_n}$$ Equation 5-7

$$I = \frac{100\ T_s\ [K_3 V_{lc} + (YV_m / T_m)\ (P_{bar} + \Delta H / 13.6)]}{60\ \Theta\ v_s\ P_s\ A_n}$$ Equation 5-7

where:

K3 = 0.003454 mm Hg-m^3/ml-°K for metric units.
= 0.002669 in. Hg-ft^3/ml-°R for English units.

6.11.2 Calculation from Intermediate Values

$$I = \frac{100 T_s\ V_{m(std)}\ P_{std}}{T_{std}\ v_s\ \Theta\ A_n\ P_s\ 60\ (1 - B_{ws})}$$

$$= K_4 \frac{T_s\ V_{m(std)}}{P_s\ v_s\ \Theta\ A_n\ (1 - B_{ws})}$$ Equation 5-8

where:

K_4 = 4.320 for metric units.
= 0.09450 for English units.

Acceptable Results. If 90 percent < I < 110 percent the particulate concentration concentration results are acceptable. If there is a high bias to the results, i.e. I < 90 percent, then the results are defined as at or below the determined value and the Executive Officer/Control Agency's Representative may opt to accept the results. If there is a low bias to the result i.e., I > 110 percent, then results are defined as at or above the determined value and the Executive Officer/Control Agency's Representative may opt to accept the results. Otherwise reject the results and repeat the test.

7 Alternative Test Methods

Alternative test methods may be used as long as they are equivalent to Method 5 and approved in writing by the ARB Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

8 Bibliography

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5. Smith, W.S., et al. Stack Gas Sampling Improved and Simplified with New Equipment. APCA Paper No. 67-119. 1967.

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9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 617-622.

1. EPA Method 5, Determination of Particulate Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

Figure 5.1 Schematic of Method 5 Sampling Train

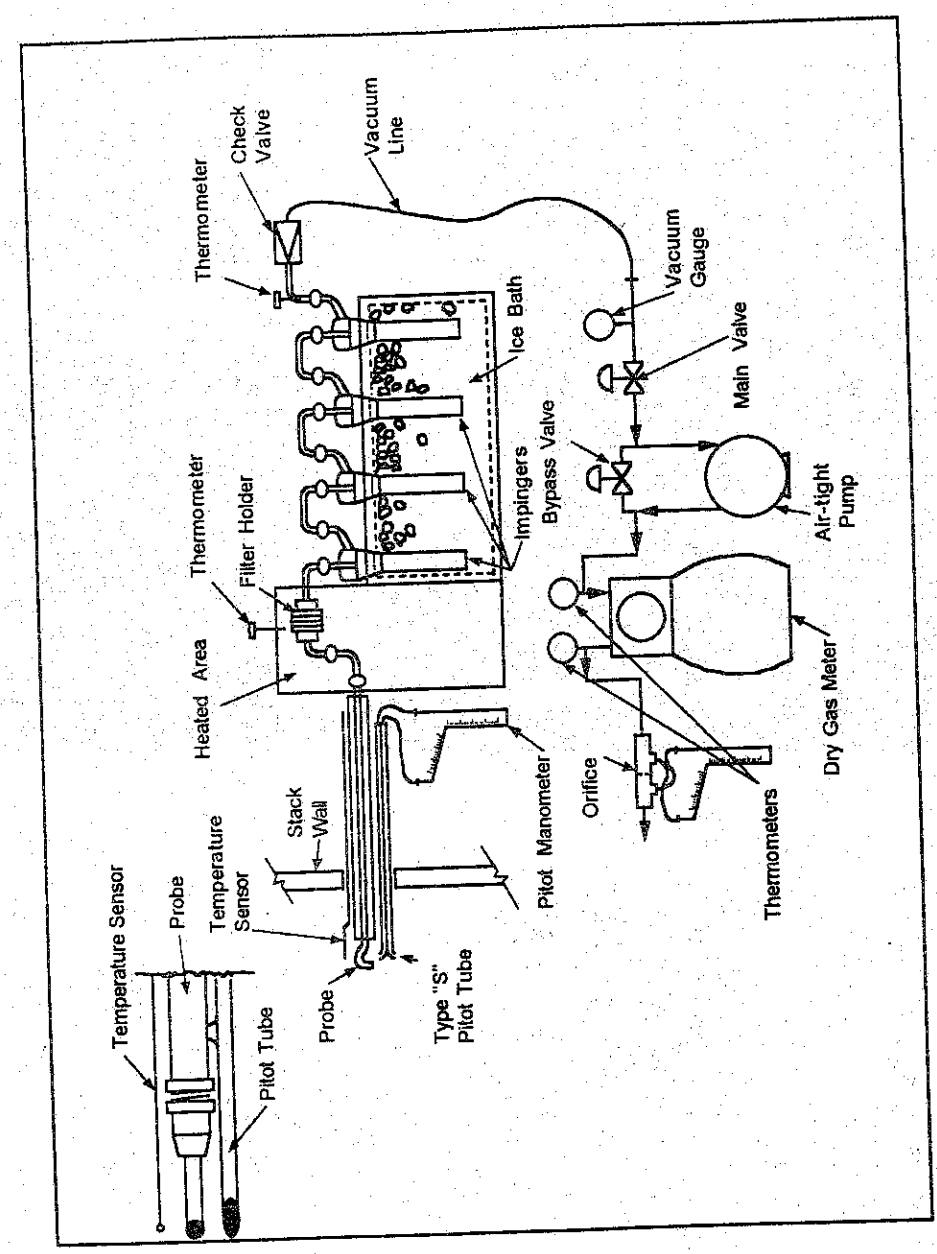

Figure 5.2
Particulate Field Data

FIELD DATA RECORD

Run No._____
Location_____
Date_____
Operator_____
Meter Box No._____
Local Time:
Start_____ Stop_____

Pitot Tube Factor _____
Probe Tip Dia, in. _____
Probe Length _____
Sample Train Leak Test:
Before _____ After _____
Pitot Tube Leak Test:
Before _____ After _____

Project No. _____
Plant Name _____
Ambient Temp °F _____
Meter Temp °F _____
Bar. Press "Hg _____
Stack Press, "H_2O _____
Assumed Moisture, % _____
Heater Box Setting, °F _____
Probe Heater Setting, °F_____

Point	Clock Time	Dry Gas Meter, CF	Pitot ΔP in. H_2O	Meter Temp °F		Orifice ΔH in. H_2O Desired	Orifice ΔH in. H_2O Actual	Impinger Temp °F	Filter Box Temp °F	Stack Temp °F	Pump Vacuum in. Hg
				in	out						
Total											
Average											
			Avg.								

Figure 5.3
Analytical Data

Plant_____
Date_____
Run No._____
Filter No._____
Amount of liquid lost during transport _____

Acetone: blank volume, ml _____ wash volume, ml _____
blank concentration, mg/mg (equation 5-4)_____ blank, mg (equation 5-5) _____

	Final Weight, mg	Tare Weight, mg	Weight Gain, mg
Container 1 (filter)			
Container 2 (probe)			
TOTAL			
		Less Acetone Blank	
		Weight of Particulate Matter	

Water: blank volume, ml _____ wash volume, ml _____
blank concentration, mg/mg (equation 5-4)_____ blank, mg (equation 5-5) _____

	Final Weight, mg	Tare Weight, mg	Weight Gain, mg
Impinger Catch			
		Less Water Blank	
		Impinger Catch: Weight of Particulate Matter	

Solvent: blank volume, ml _____ wash volume, ml _____
blank concentration, mg/mg (equation 5-4)_____ blank, mg (equation 5-5) _____

	Final Weight, mg	Tare Weight, mg	Weight Gain, mg
Impinger Catch Extract			
		Less Solvent Blank	
		Impinger Catch Extract: Weight of Particulate Matter	

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGERS	SILICA GEL	
FINAL	(ml)		(g)
INITIAL	(ml)		(g)
LIQUID COLLECTED	(ml)	(ml)	(g)
TOTAL VOLUME COLLECTED			(ml)

~~Convert water weight to liquid volume using volume(ml) = weight(grams) / 1(gram/ml).~~

Figure 5.4

Leak Check of Meter Box

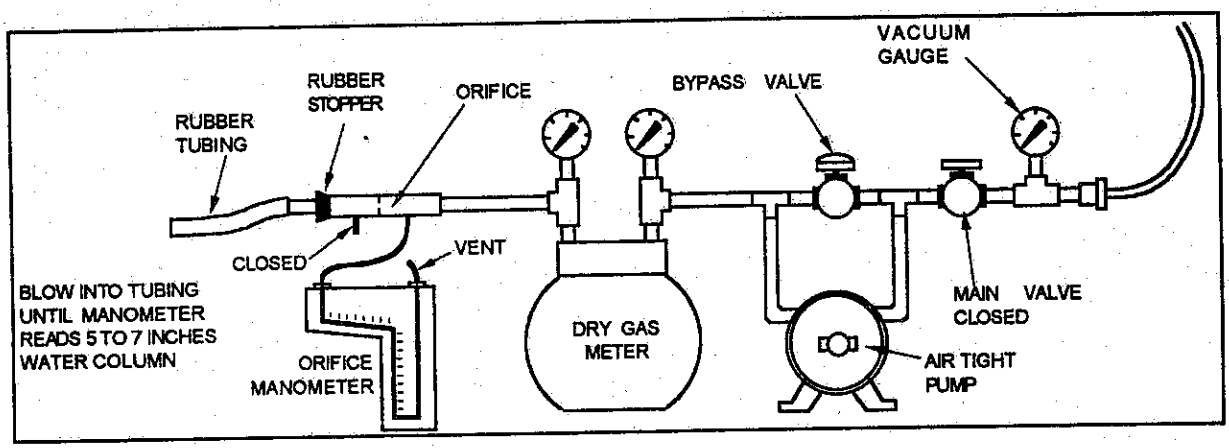

Figure 5.5

Equipment Arrangement for Metering System Calibration

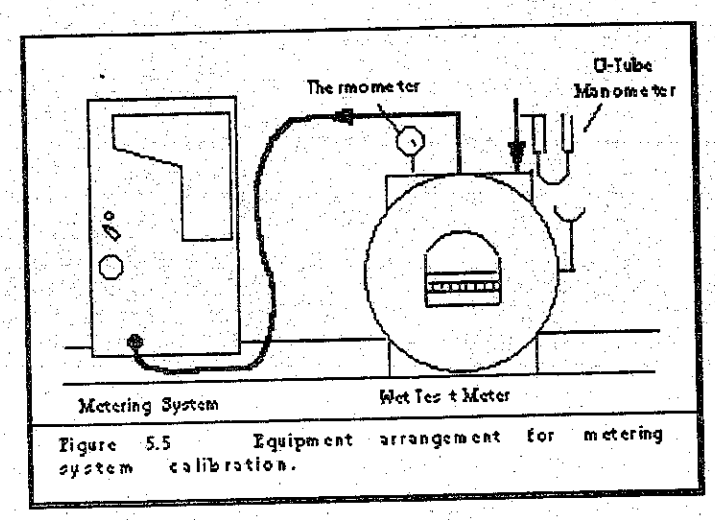

Figure 5.5 Equipment arrangement for metering system calibration.

Figure 5.6

Example Data Sheet for Calibration of Metering System (English Units)

Date _____ Metering System Calibraton

Identification_____

Barometric Pressure, P_b = _____ in. Hg

Orifice Manometer Setting ΔH in. H_2O	Spirometer (wet meter) gas volume V_w ft^3	Dry gas Meter volume V_m ft^3	Spirometer (wet meter) temperature t_w °F	Dry Gas Meter Inlet temperature t_i °F	Dry Gas Meter Outlet temperature t_o °F	Dry Gas Meter Average temperature t_m °F	Time θ min

Calculations

$$Y = \frac{V_w P_b (t_m + 460)}{V_m (P_b + \Delta H / 13.6)(t_w + 460)}$$

$$\Delta H_@ = \frac{0.0319\ \Delta H}{P_b (t_o + 460)} \left[\frac{(t_w + 460)\ \theta}{V_w} \right]^2$$

ΔH in. H_2O	Y	$\Delta H_@$
Average		

Y = Ratio of reading f wet test meter to dry test meter; tolerance for individual values +/- 0.02 from average.

$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68 oF and 29 92 inches of mercury, in. H2O; tolerance for individual values +/- 0.20 from average.

PROPOSED

Appendix A of Method 5

Guidelines for Field Calculation of Target Values for D_n and ΔH

Section 4.1.5 of Method 5 requires that an isokinetic sampling rate be maintained during sampling, normally within +/-10% of the true isokinetic rate. No specific procedures are specified for adjustment of sampling rate. Rather the intent is that the departure from true isokinetic be calculated as specified by Section 6.11 after the completion of sampling. Some departure from true isokinetic is recognized as inevitable, in part because stack conditions during sampling including moisture content may vary and can not be anticipated completely or accommodated instantaneously.

The principle means of keeping sampling rates near true isokinetic are:

(1) selection of an appropriate nozzle diameter D_n
(2) adjustment of console valves to keep ΔH (orifice meter differential pressure in inches of water) at or near a calculated appropriate value.

Rapid and reliable calculation of target values for these parameters in the field is facilitated by use of nomographs, special slide rules or pre-programmed portable calculators or computers. Calculators and computers are becoming more popular for this purpose but the references cited in EPA Method 5 pertain only to the basis and use of nomographs originally developed by EPA. The purpose of this appendix is to present equations which can be programmed into a portable calculator or computer. Because different programming languages are used by or available on different calculators and computers it is impractical and beyond the scope of this appendix to present complete programs for the execution of these calculations.

Estimation of Orifice Differential Pressure from Pitot Pressure

$$\Delta H = [\ 846.72\ D_n^4\ \Delta H_@ C_p^2 (1-B_{ws})^2 (M_d / M_s)(T_m / T_s)(P_s / P_m)\ ]\ \Delta p$$

Estimation of Ideal Nozzle Diameter

$$D_n = [\ 0.035\ Q_m\ P_m\ (1-B_{ws})\ /(T_m C_p (1-B_{ws}))]^{0.5}\ [T_s M_s\ /(P_s \Delta p)]^{0.25}$$

Nomenclature

The nomenclature for these equations is the same as as defined in Section 6.1 of Method 5 except that

P_m = meter pressure = $P_{barr} + \Delta H / 13.6$,

Q_m = orifice meter flow rate
= $[0.9244 / \Delta H_@\ ]^{0.5}\ [T_m \Delta H / (P_m M_m)]^{0.5}$

M_m = molecular weight of metered gas stream, approximately the same as M_d.

Equations are from the APTI Course 450 instructor's manual.

State of California
California Environmental Protection Agency
Air Resources Board

Proposed Amendment*

Method 7

Determination of Nitrogen Oxide Emissions from Stationary Sources

Adopted: June 29, 1983
Amended: _____

* including new Table of Contents and other changes
Note: This document consists of the text of the proposed amendment to Method 7. Proposed deletions are noted by ~~graphic screen~~ and proposed additions are noted by underline.

METHOD 7

Determination of Nitrogen Oxide Emissions from Stationary Sources

TABLE OF CONTENTS

PROPOSED AMENDMENT OF METHOD 7

Determination of Nitrogen Oxide Emissions from Stationary Sources

1 PRINCIPLE AND APPLICABILITY

1.1 Principle: A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimeterically using the phenoldisulfonic acid (PDS) procedure.

The number of sampling runs must be sufficient to provide minimal statistical data and shall be at least three (3), unless explicitly stated otherwise in the applicable rule.

1.2 Applicability: This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x (as NO_2) per dry standard cubic meter, without having to dilute the sample.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative.

2 Apparatus

2.1 Sampling (see Figure 7-1): Other grab sampling systems or equipment, capable of measuring sample volume to within ±2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within ±5 percent will be considered acceptable alternatives, subject to approval of the ~~Control Agency's Authorized Representative~~Executive Officer. The following equipment is used in sampling:

2.1.1 Probe: Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

2.1.2 Collection Flask: Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask Valve: T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature Gauge: Dial-type thermometer, or other temperature gauge, capable of measuring 1°C (2°F) intervals for -5 to 50°C (25 to 125°F).

2.1.5 Vacuum Line: Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Vacuum Gauge: U-tube manometer, 1 meter (36 in.), with 1-mm (0.1-in.) divisions, or other gauge capable of measuring pressure to within ± 2.5 mm Hg (0.10 in. Hg).

2.1.7 Pump: Capable of evacuating the collection flask to a pressure equal to or less than 77 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze Bulb: One-way.

2.1.9 Volumetric Pipette: 25 ml.

2.1.10 Stopcock and Ground Joint Grease: A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

2.1.11 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg.) In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase, or vice versa for elevation decrease.[1]

2.2 Sample Recovery: The following equipment is required for sample recovery.

2.2.1 Graduated Cylinder: 50 ml with 1-ml divisions.

2.2.2 Storage Containers: Leak-free polyethylene bottles.

2.2.3 Wash Bottle: Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH: To cover the pH range of 7 to 14.

2.3 Analysis: For the analysis, the following equipment is needed:

2.3.1 Volumetric Pipettes: Two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml for each sample and standard.

2.3.2 Porcelain Evaporating Dishes: 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallow-form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene

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[1] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

beakers (Nalge No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath: Low-temperature ovens or thermostatically controlled hot plates kept below 70°C (160°F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper: Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

2.3.6 Graduated Cylinder: 100 ml with 1-ml divisions.

2.3.7 Volumetric Flasks: 50 ml (one for each sample and each standard) 100 ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000 ml (one).

2.3.8 Spectrophotometer: To measure absorbance at 410 nm.

2.3.9 Graduated Pipette: 10 ml with 0.1-ml divisions.

2.3.10 Test Paper for indicating pH: To cover the pH range of 7 to 14.

2.3.11 Analytical Balance: To measure to within 0.1 mg.

3 REAGENTS

Unless otherwise indicated, it is intended that all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. Two reagents are required:

3.1.1 Water. Deionized distilled to conform to ASTM Specification D1193-77, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Absorbing Solution. To prepare the absorbing solution, cCautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery: Two reagents are required for sample recovery:

3.2.1 Water: Same as in 3.1.1

3.2.2 Sodium Hydroxide (1N): Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

3.2.2 Water: Deionized, distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyzt, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis: For the analysis, the following reagents are required:

3.3.1 Fuming Sulfuric Acid: 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

3.3.2 Phenol: White solid.

3.3.1 Water: same as in 3.1.1

3.3.2 Sulfuric Acid: Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

3.3.3 Potassium Nitrate: Dried at 105 to 110°C (220 to 230°F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.4 Standard KNO_3 Solution: Dissolve exactly 2.198 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1,000-ml volumetric flask.

3.3.5 Working Standard KNO_3 Solution: Dilute 10 ml of the standard solution to 100 ml with deionized, distilled water. One milliliter of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

3.3.7 Water: Deionized, distilled as in Section 3.2.2.

3.3.6 Phenoldisulfonic Acid Solution: Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide - HANDLE WITH CAUTION), and heat at 100°C (212°F) for 2 hours. Store in a dark, stoppered bottle.

3.3.7 Concentrated Ammonium Hydroxide: Reagent grade.

3.3.8 Quality Assurance Audit Samples: Nitrate samples in glass vials prepared by EPA's Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park,

North Carolina 27711 or by others as approved by the Executive Officer. Each set will consist of two vials having solutions of unknown concentrations. Only when making compliance determinations, obtain an audit sample set from from the quality assurance management office at each EPA regional office or the responsible enforcement agency or another source approved by the Executive Officer. (Note: The tester should notify the source of audit samples at least 30 days prior to the test date and sufficiently far in advance to allow for audit sample delivery).

4 PROCEDURES

4.1 Sampling

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly greased with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg [0.4 in. Hg] over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg [3 in. Hg] absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_f), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced

into the flask by one of three methods; (1) before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample recovery: Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis:

4.3.1 Note the level of the liquid in the container and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer, to correct the final results.

4.3.2 Immediately prior to the analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml, or more, deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper).

If the sample contains solids these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask, rinse the evaporating dish

with three, approximately, 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volmetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled\ water.

4.3.3 Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds A_4, the absorbance of the 400 μg NO_2 standard (see Section 5.2.2).

4.4 Audit Sample Analysis

4.4.1 Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: it is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is the EPA AREAL QA Source Branch listed in Section 3.3.8.) The same analysts, analytical reagents and analytical system shall be used for both the compliance samples and the audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

4.4.2 Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dsm^3 and compliance results in total μg NO_2 by telephone to the source of the audit samples). Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the responsible enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

4.4.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual audit concentrations. If the 10-percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see note in Section 4.4.1).

4.4.4 Failure to meet the 10-percent specification may require retests until the problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Executive Officer may waive the reanalysis requirement, further audits, or retests and

accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Executive Officer may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

5 CALIBRATION

5.1 Flask Volume. The volume of the collection flask-flask valve combination must be known prior to sampling. Assemble the flask and flask valve and fill with water, to the stopcock. Measure the volume of water to ± 10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination.

5.2.1.1 Calibrate the wavelength scale of the spectrophotometer every six months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

5.2.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2): to a series of five 50-ml volumetric flasks. To each flask, add 25

ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 25 to 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be reported on each day that samples are analyzed. Calculate the spectophotometer calibration factor as follows:

$$K_c = 100\,(A_1 + 2A_2 + 3A_3 + 4A_4) / (A_1^2 + A_2^2 + A_3^2 + A_4^2) \quad \text{Equation 7-1}$$

where:

K_C = Calibration factor

A_1 = Absorbance of the 100-μg NO_2 standard

A_2 = Absorbance of the 200-μg NO_2 standard

A_3 = Absorbance of the 300-μg NO_2 standard

A_4 = Absorbance of the 400-μg NO_2 standard

5.2.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. These calculated concentration values should not differ from the actual concentrations (i.e., 100, 200, 300, and 400 μg NO_2) by more than 7 percent for three of the four standards.

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6 CALCULATION. Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Nomenclature

A = Absorbance of sample.

C = Concentration of NO_x as NO_2, dry basis corrected to standard conditions, mg/dscm (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of NO_x as NO_2 in gas sample, μg.

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure, 760 of flask, mm Hg (29.92 in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{sc} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

2 = 50/25, the aliquot factor. (If other than a 25 ml aliquot was used for analysis, the corresponding factor must be substituted.)

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{sc} = \frac{T_{std}}{P_{std}}(V_f - V_a)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$
$$= K_1(V_f - 25ml)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Equation 7-2

where:

K_1 = 0.3858 °K / mm Hg for metric units
= 17.65 °R / in. Hg for English units

6.3 Total μg NO_2 Per Sample.

$$m = 2 K_c A F \qquad \text{Equation 7-3}$$

Note: If other a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

6.4 Sample concentration, dry basis, corrected to standard conditions.

$$C = K_2 \, m/V_{sc} \qquad \text{Equation 7-4}$$

where:

K_2 = 10^3 (mg/m^3)/(μg/ml) for metric units
= 6.243×10^{-5} (lb/scf)/(μg/ml) for English Units

6.5 Relative error (RE) for QA audit samples, percent.

$$RE = 100 (C_d - C_a)/C_a \qquad \text{Equation 7-5}$$

where:

C_d = Determined audit sample concentration, mg/dsm^3,
C_a = Actual audit sample concentration, mg/dsm^3.

7 ALTERNATIVE TEST METHOD

Alternative test methods may be used as long as they are equivalent to Method 7 and approved in writing by the ARB Executive Officer. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

8 BIBLIOGRAPHY

1. Standard Methods of Chemical Analysis. 5th ed. New york, D. Van Nostrand Co., Inc. 1962. Vol. I, p. 329-330.

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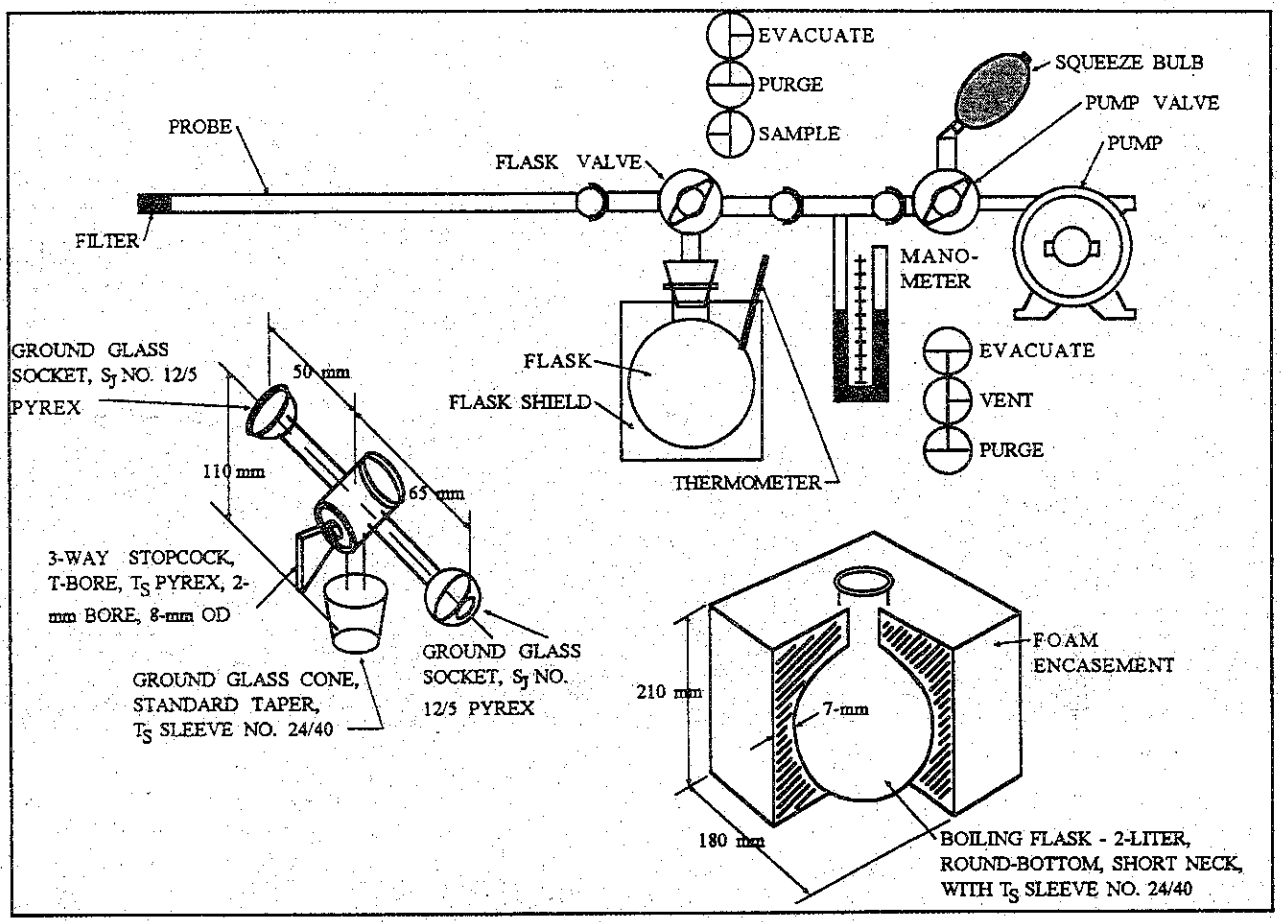
4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior, RI. 3687, February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

1. EPA Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

FIGURE 7.1
SAMPLING TRAIN, FLASK VALVE AND FLASK



State of California
California Environmental Protection Agency
Air Resources Board

Method 100

Procedures for Continuous Gaseous Emission Stack Sampling

Adopted: June 29, 1983
Amended: _____

It is proposed that the content of ARB Method 100, Procedures for Gaseous Emission Stack Sampling, adopted June 29, 1983, be deleted and replaced by the following revised content. For the text of the current test procedure, which is proposed to be replaced, contact Mr. George Lew, Air Resources Board, Monitoring and Laboratory Division, P.O. Box 2815, Sacramento, California 95812, telephone (916) 263-1630.

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METHOD 100

Procedures for Continuous Gaseous Emission Stack Sampling

1 OVERVIEW

1.1 PRINCIPLE

A sample of an exhaust gas stream is extracted, conditioned and analyzed continuously by instruments. The measurements made by the continuous analyzers are used to determine average emission concentrations. By measuring the stack gas flowrate and moisture, and using this information with the average emission concentration, mass emission rates can be determined.

1.2 APPLICABILITY

This method is applicable for determining emissions of oxides of nitrogen, carbon monoxide, carbon dioxide, sulfur dioxide, total hydrocarbons, and oxygen from stationary source flowing gas streams in ducts, stacks and flues. This procedure does not supersede the New Source Performance Standards requirement for permanently installed continuous emissions monitoring instruments.

This test procedure is an alternative method to appropriate U.S. EPA reference methods, in particular, EPA methods 3A, 6C, 7E, 10, and 25A and B. This procedure should be used only on those sources where equivalency to the reference methods has been established or the specific regulations for the source specify this procedure.

1.3 SAFETY

This method does not address the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices including the safe handling of compressed gases, flammable gases and any hazardous compounds and to determine the applicability of regulatory limitations prior to use of this method.

1.4 ALTERNATIVE TEST PROCEDURES

Any modification of this method beyond those expressly permitted shall be subject to approval by the Executive Officer of the Air Resources Board or his or her authorized representative.

1.5 DEFINITIONS

1.5.1 Range

The upper limit of the gas concentration measurement range displayed on the data recorder. The range is selected so that the sample gas concentration is between 10 and 95 percent of the range for each pollutant of interest.

1.5.2 Calibration Gas

A known concentration of a gas in an inert diluent gas.

1.5.3 Analyzer Calibration Error

The difference between the known concentration of a calibration gas and the concentration measured by the gas analyzer when the calibration gas is introduced directly to the gas analyzer.

1.5.4 Sampling System Bias

The difference between the concentration measured by a gas analyzer when a known concentration calibration gas is introduced at the sampling probe and when the same gas is introduced directly to the analyzer.

1.5.5 Zero Drift

The difference between the concentration measured by the gas analyzer for zero gas before the sample run and the concentration measured by the analyzer for zero gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

1.5.6 Calibration Drift

The difference between the concentration measured by the gas analyzer for a calibration gas before the sample run and the concentration measured by the analyzer for that same calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

1.5.7 Response Time

The time required for the data recorder to display 95% of the difference in gas concentration on the data recorder after a step change in gas concentration, such as a switch from zero gas to calibration gas.

1.5.8 Interference Check

Determination of the concentration measured for a known concentration of a component in the sample gas other than the target gas component being measured by the gas analyzer.

1.6 SOURCE TEST PERFORMANCE SPECIFICATIONS

The following specifications must be met for data from a test run to be considered valid:

1.6.1 Analyzer Calibration Error

± 2 percent or less of the range when introducing zero or calibration gas.

1.6.2 Zero Drift

± 3 percent or less of the range during a test run.

1.6.3 Span Drift

± 3 percent or less of the range during a test run.

1.6.4 Sampling System Bias

± 5 percent or less of the range when introducing zero or calibration gas.

1.6.5 Interference Check

For each analyzer, ± 5 percent or less of the range.

2 EQUIPMENT

2.1 SAMPLE TRANSFER SYSTEM

A schematic of the sampling train is shown in Figure 100.1.

2.1.1 Probe Nozzle

Quartz, borosilicate glass, stainless steel, porcelain or aluminum oxide may be used for the probe nozzle.

2.1.2 Probe Filter

An internal or external probe filter may be used. As necessary, provisions should be made for back flushing the filter to remove particulate build-up.

2.1.3 Probe

The probe shall have an inside diameter of 6 mm or larger and shall be constructed of quartz, borosilicate glass, stainless steel, aluminum oxide or porcelain.

2.1.4 Sample Line

The sample line is constructed of teflon or other material which does not absorb or otherwise alter the sample gas.

2.1.5 Probe Calibration System

Calibration gases for a sampling system bias check are introduced at the probe. Depending on the configuration of the probe, calibration gas is injected at an internal probe filter, at the probe tip, or directly behind the probe outlet.

2.1.6 Sample Conditioner

The sample conditioner shall be capable of reducing the sample gas temperature to 15° C (60° F), or to 11° C (20° F) lower than the ambient temperature, whichever is lower. All parts of the conditioner exposed to the sample shall be glass, stainless steel or teflon. The sample gas shall not be bubbled or dispersed through the condensate such that minimum contact shall be maintained between any condensate and the sample gas. A temperature gauge shall be used to determine the temperature of the condenser outlet.

If needed, a glass filter is used at the inlet or the outlet of the conditioner to prevent the accumulation of particulate material.

2.1.7 Sample System Heaters

If needed to prevent condensation of water or hydrocarbons, or the reaction of other stack constituents, a probe heater may be used. If necessary, use a heated sample line, heated filters, and a heated analyzer. Heaters shall heat the sample to a minimum of 120°C (248°F) or to a temperature above the dewpoint of the target constituent, whichever is greater. Perform no sample conditioning that lowers the sample temperature.

2.2 GAS ANALYZERS AND DATA ACQUISITION

2.2.1 Specifications

Specifications for the acceptance of gas analyzers for use of Method 100 are listed in Table 100.1. The vendor must provide test data demonstrating that the following performance requirements are met: minimum detection limit, noise

level, response time, repeatability, linearity, interference, sensitivity to temperature change, and 24 hour zero and calibration drift limits.

The analyzers shall be housed in a temperature-controlled, vibration-free environment.

2.2.2 Carbon Dioxide and Carbon Monoxide

Nondispersive infrared analyzers are acceptable.

2.2.3 Oxygen

A paramagnetic analyzer or an electrochemical (fuel cell) analyzer is acceptable.

2.2.4 Total Hydrocarbons

An analyzer using a flame ionization detector (FID) or a nondispersive infrared analyzer (NDIR) is acceptable. Propane or methane is usually used as a span gas. (Note: Compound-specific calibration curves must be determined for use of either the FID or the NDIR analyzer to measure specific organic compounds.)

2.2.5 Oxides of Nitrogen

An analyzer using chemiluminescence is acceptable. The NO_2 to NO converter must have at least a 90% efficiency in converting nitrogen dioxide (NO_2) in the sample gas to nitric oxide (NO). A NO_2 to NO converter is not necessary if data are presented to demonstrate that the NO_2 portion of the exhaust gas is less than 5 percent of the total NO_x concentration. A low temperature (maximum 350°C) converter must be used when NH_3 is present. A high temperature (650°C) stainless steel converter may be used when no NH_3 is present.

If data are not available to demonstrate that the concentration of NO_2 in the sample gas is less than 5% of the total NO_x concentration, a test of the efficiency of NO_2 converter must be conducted prior to each source test.

2.2.6 Sulfur Dioxide

An analyzer using infrared or ultraviolet absorption or fluorescence is acceptable.

2.2.7 Other Analyzers

An analyzer operating by measurement principles not listed in Table 100.1 may be used, if its performance meets the requirements of Table 100.1.

2.2.8 Data Acquisition System/Data Recorder

Provide a permanent record of gas analyzer data using a strip chart recorder, a data logger or other electronic data acquisition system. If a data recorder is not used, a real-time hardcopy of test data must be provided upon request. Any data acquisition system must have a resolution of 0.5 percent of the analyzer range. Data reporting includes the following information: pollutant, source, analyzer range, date, time, zero offsets, person operating instruments, and any other pertinent data.

2.3 MEASUREMENT OF STACK FLOWRATE, MOISTURE, AND OTHER PARAMETERS

2.3.1 Stack Gas Flowrate and Moisture Measurement

Stack gas flowrate and moisture content can be determined using equipment specified by ARB Test Methods 1 through 4. Stack gas velocity can be determined from a pitot tube measurement as outlined by Methods 1 and 2. Two possible alternatives are:

(1) A simultaneous traverse of stack gas concentration and velocity,

(2) A pre and a post test velocity traverse. (Repeat the velocity traverse whenever aware of a change in process conditions which may affect emissions.)

Note: If the pitot tube and the sampling probe are used in combination in a testing assembly, care must be taken that any aerodynamic effects on the pitot tube are eliminated. Otherwise, the pitot tube must be calibrated with the other components of the test assembly in place. (See ARB Method 2, Section 4.1.1.)

Alternate methods of flowrate measurement, including consideration of fuel rate, combustion stoichiometry and oxygen concentration in the stack gas and applicable F-factors listed in 40 CFR Part 60 Appendix A, Method 19, must be approved by the Executive Officer of the Air Resources Board or his or her authorized representative.

2.3.2 Barometer

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg. shall be used.

2.3.3 Vacuum Gauge or Flowmeter

Use a vacuum gauge or a flowmeter for leak check of the sampling train.

3 CALIBRATION GASES

3.1 Calibration Gases

The calibration gases must be certified according to EPA Traceability Protocol[1]. Alternately the calibration gases must be certified to an analytical accuracy of ±2 percent, traceable to a reference material approved by the National Institute of Standards and Technology (NIST), and recertified annually.

Multi-component gas mixtures certified according to EPA Protocol are acceptable. Multi-component gas mixtures which meet the following requirements are also acceptable: the concentration of each component gas must be certified to an analytical accuracy of ±2 percent, each component must be traceable to a NIST standard, and the mixture must be recertified semi-annually.

For each pollutant to be measured, use the following three calibration gases:

3.1.1 High-Range Gas

The concentration should be between 80 and 100 percent of the analyzer range.

3.1.2 Mid-range Gas

The concentration should be between 40 and 60 percent of the analyzer range.

3.1.3 Zero Gas

Purified air or, if appropriate, nitrogen with a contaminant concentration less than 0.25% of the analyzer range for the appropriate pollutant gas may be used.

3.2 GAS DILUTION SYSTEM

An approved gas dilution system can be used to provide low-level calibration gases from a high-level calibration gas. The calibration gas used with a gas dilution system must be an EPA Protocol gas. Alternately the gas used with a diluter must be certified to an analytical accuracy of ±1 percent, NIST-traceable, and recertified annually. See Appendix 100.1 for the performance specifications of a gas dilution system. An approved gas dilution system may be used for all analyzer calibrations and sampling system bias checks.

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1 "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," EPA-600/R93/224, Revised September 1993.

4 ON-SITE PREPARATION FOR SAMPLING

4.1 CLEANING/ASSEMBLY OF SAMPLE TRAIN

The sample train may be cleaned prior to being transported to the field. When at the testing site, assemble the cleaned sample train as shown in Figure 100.1.

4.2 CALIBRATION OF CONTINUOUS ANALYZERS

Allow analyzers to warm up according to manufacturer's instructions. Adjust system components to achieve the individual analyzer sampling rates recommended by the instrument manufacturer. Alternately introduce zero and calibration gases to the instruments and make all necessary adjustments to calibrate the analyzer and the data recorder.

Conduct the analyzer calibration error check by sequentially introducing the three calibration gases (high-range, mid-range and zero gas) and recording the analyzer response to each calibration gas. Make no adjustments to the sampling/analysis system except those necessary to achieve the proper calibration gas flowrate. The test run will be considered invalid if the analyzer calibration error for any calibration gas exceeds ±2 percent of the range. If needed, take corrective action until acceptable performance is achieved.

4.3 PRETEST LEAK CHECK

Perform a leak check on the vacuum side of the assembly at the maximum pump vacuum. Correct any leaks found and repeat the leak check and correction procedure until no leak is detected.

4.4 SAMPLE SYSTEM BIAS CHECK

A pretest sampling system bias check is required for each gas analyzer.

Perform the sampling system bias check by alternately introducing at the probe the zero gas and either the high-range or mid-range calibration gas, whichever calibration gas is closest in concentration to the sample gas. Record the gas concentrations displayed by the analyzer. During the sampling system bias check operate the system at the normal sampling rate and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rate. Determine the sampling system response time.

If the difference between the gas concentrations for the analyzer calibration error check and the sample system bias check exceeds ±5% of the range for either the zero or upscale calibration gas, the bias check is invalid. If needed, take corrective action before repeating the sample system bias check. If the analyzer is adjusted, repeat the analyzer calibration error check before repeating the bias check.

4.5 DETERMINATION OF SAMPLING TRAVERSE POINTS

Select gas sampling traverse points according to the guidelines given in ARB Methods 1 and 2 for velocity traverses. Multipoint gas sampling must be performed unless data are available to demonstrate that the mean pollutant concentration is less than 10% different from that at any single point.

5 SAMPLE COLLECTION

Insert the sample probe assembly into the stack and block off the remainder of the sample port opening. Set the probe at the predetermined position and begin data acquisition. If a traverse is required, the sampling time at each traverse point is constant. Sample for at least the sampling system response time plus one minute, allowing enough time for the system to be flushed and the instruments to respond fully. Move probe to next position and repeat. Continue until the stack has been fully traversed.

A test shall include at least three sample runs. Each sample run shall be the length of time specified in the applicable emission limit regulation. As a minimum, the sampling time must be such that the emission test is conducted during representative operating conditions of the source. For a test duration exceeding two hours, conduct sampling system bias checks every two hours. Record performance check data. As necessary, back flush through the probe to prevent particulate build-up on the probe filter. Periodically check the sample conditioner and remove condensate as needed.

If adjustments to the sampling train are necessary during the sample run, conduct a system bias check before any adjustments are made. After any adjustments are made to the analyzer, the analyzer calibration error check shall be conducted. After all adjustments are made to the sampling system, the sampling system bias check shall be performed prior to continuation of the test run.

6 POST TEST PERFORMANCE CHECKS

At the end of the sample run, conduct a sampling system bias check for all analyzers. Perform the sampling system bias check by alternately introducing the zero gas and the calibration gas at the probe. During the sampling system check operate the system at the normal sampling rate and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates through the sampling system to the gas analyzer.

6.1 ZERO AND CALIBRATION DRIFT

The test run shall be considered invalid if the difference of zero or calibration gas measured for the post run sampling system bias check and zero or calibration gas

measured for the initial sampling system bias check of the first test run (Section 4.5) exceeds ±3 percent of the range. Use Equation 100-1, below:

$$\text{Drift} = \frac{(C_{fb} - C_{ib})}{r} \qquad \text{Eq. 100 - 1}$$

Where:

C_{fb} = concentration of zero or upscale calibration gas for post run sampling system bias check

C_{ib} = concentration of zero or upscale calibration gas for initial sampling system bias check

r = analyzer range

6.2 SAMPLING SYSTEM BIAS

The test run shall be considered invalid if the difference of zero or calibration gas measured for the post run sampling system bias check and zero or calibration gas measured for the initial analyzer calibration (Section 4.2) exceeds ±5 percent of the range. Calculate bias using Equation 100-2:

$$\text{Bias} = \frac{(C_{fb} - C_a)}{r} \qquad \text{Eq. 100 - 2}$$

Where:

C_{fb} = concentration of zero or upscale calibration gas for post run sampling system bias check

C_a = concentration of zero or upscale calibration gas for initial analyzer calibration

r = analyzer range

7 CALCULATION OF POLLUTANT CONCENTRATION AND MASS EMISSION RATE

7.1 POLLUTANT CONCENTRATION

Determine the average concentration, C_{gas}, of each stack gas constituent using Equation 100-3:

$$C_{gas} = (C_{avg} - C_o) \times \frac{C_{cal}}{(C_{bcal} - C_o)} \qquad \text{Eq. 100 - 3}$$

Where:

C_{gas} = Effluent gas concentration, ppm or % by volume

C_{avg} = Average gas concentration indicated by gas analyzer, ppm or % by volume

C_o = Average of initial (c_{ib}) and final (c_{fb}) system bias responses for zero gas, ppm or % by volume

C_{cal} = Actual concentration of the calibration gas used for the bias check, ppm or % by volume

C_{bcal} = Average of initial (c_{ib}) and final (c_{fb}) sampling system bias responses for the calibration gas, ppm or % by volume

7.2 MASS EMISSION RATE

The emission rate in pounds per hour of pollutant is E in Equation 100-4:

$$E = C_{dgas} \times \frac{M}{385 \times 10^6} \times Q \times 60 \qquad \text{Eq. 100 - 4}$$

Where:

C_{dgas} = effluent gas concentration corrected to dry basis, ppm

M = molecular weight in lb/lb-mole

385 = standard volume in cubic feet of one lb-mole (at 528° R and 1 atmosphere)

Q = Stack flowrate in standard dry cubic feet per minute of stack effluents, determined from ARB Methods 2 and 4, or alternative determinations of flow rate and moisture content

7.3 POLLUTANT CONCENTRATION FOR 12% CO_2 OR 3% O_2

The pollutant concentration C_{dgas} is adjusted for 12% CO_2 in Equation 100-5:

$$C_{12\%\ CO_2} = C_{dgas} \times \frac{12\%}{\%\ CO_2 \text{ during test}} \qquad \text{Eq. 100 - 5}$$

For correction to 3% O_2 (using O_2 in air as 20.9%), use Equation 100-6:

$$C_{3\%\ O_2} = C_{dgas} \times \frac{20.9 - 3.0}{20.9 - \%O_2 \text{ during test}} \qquad \text{Eq. 100 - 6}$$

Table 100.1 (page 1 of 3)
Gas Analyzer Specifications

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Typical Principle of Operation[2]	Ultraviolet or infrared absorption or fluorescence	Chemiluminescence	Infrared absorption	Infrared absorption	Flame ionization or infrared absorption	Paramagnetic or electrochemical cell
Typical Concentration Ranges PPM or % by volume	10 - 2500 ppm	10 - 1000 ppm	10 - 1000 ppm	5 - 20 %	50 ppm - 50%	5 - 25 %
Minimum detection limit, % of full scale for lowest range.	2%	2%	2%	2%	2% as Propane	2%
Noise Level % of range	< ±1%	< ±1%	< ±1%	< ±1%	< ±1%	< ±1%
Response Time to 95% of steady state after a step change in concentration	< 30 secs.	<30 secs.	< 60 secs.	< 60 secs.	< 30 secs.	< 60 secs.

[2] Other types will also be acceptable provided that the criteria listed below are met.

Table 100.1 (page 2 of 3)
Gas Analyzer Specifications

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Repeatability, % of range[3]	1%	1%	1%	1%	1%	1%
Zero Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%
Span Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%
Interference of a component other than the target component measured by the gas analyzer, % of range	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %
Analyzer response to temperature variation[4]	✓	✓	✓	✓	✓	✓

[3] 2% of the analyzer range is the maximum absolute difference between replicate results which may be expected with a probability of 95%.

[4] When sampling zero or span gas, the analyzer response shall not change more than ± 2% of range when the ambient temperature changes ± 10°C from 25°C.

Table 100.1 (page 3 of 3)
Gas Analyzer Specifications

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
A change in ambient temperature of ± 20° C from 25°C shall not cause a permanent change to the zero or span response of analyzer	✓	✓	✓	✓	✓	✓
Linearity [5]	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%

[5] Maximum deviation between a mid-range calibration reading and the reading predicted by a straight line drawn between high-range and zero gas calibration points, as a percent of the range.

State of California
California Environmental Protection Agency
Air Resources Board

Method 425

Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

Adopted: January 22, 1987
Amended: September 12, 1990
Amended: _____

It is proposed that the content of ARB Method 425, Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources, adopted January 22, 1987, be deleted and replaced by the following revised content. For the text of the current test procedure, which is proposed to be replaced, contact Mr. George Lew, Air Resources Board, Monitoring and Laboratory Division, P.O. Box 2815, Sacramento, California 95812, telephone (916) 263-1630.

Method 425

Determination of Total Chromium and Hexavalent Chromium
Emissions from Stationary Sources

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Method 425

Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

1 APPLICABILITY AND PRINCIPLES

1.1 Applicability

This method applies to the determination of hexavalent chromium (Cr6) and total chromium (Cr) emissions from stationary sources. Applicability has been demonstrated for the metal finishing and glass industries. Its applicability has not been demonstrated for sources with high particulate mass emission rates.

The ion chromatographic-colorimetric (IC-C) analytical procedure described is applicable to filter extracts and emission samples collected in impinger solutions of 0.1M sodium hydroxide solution. It is also applicable to samples in water or in the ammonium hydroxide/ammonium sulfate eluent solution described herein. Preconcentration of larger volumes of the sample on an anion guard column prior to injection to increase the sensitivity of the procedure cannot be recommended at this time due to the levels of chromate and interfering compounds found in the commonly available grades of sodium hydroxide and because of the tendency of sodium hydroxide to act as an internal eluent on the preconcentration column.

Any modification of this method shall be subject to approval by the Executive Officer. The term "Executive Officer", as used in this document, shall mean the Executive Officer of the Air Resources Board, or his or her authorized representative.

1.2 Sampling Principle

Particulate emissions are collected from the source in an alkaline medium by use of CARB Method 5, with modifications noted in this method.

1.3 Recovery Principle

The components of the collected sample are each divided into two equal portions with one portion of each component used for total chromium analysis and the other portion used for hexavalent chromium analysis.

1.4 Cr6 Ion Chromatographic-Colorimetric (IC-C) Analytical Principle

This procedure, as described, uses direct sample injection and post column derivatization with a 1,5 diphenylcarbazide colorimetric reagent and photometric detection at 540 nm. Hexavalent chromium is separated from other metallic anions as chromate by a high capacity anion separator column and a colored product having a wide absorption band centered at approximately 540 nm is

formed by reaction with the colorimetric reagent. The colored reaction product is detected photometrically and quantitation as Cr6 is accomplished by linear regression of either peak area or peak height on the concentration of a series of Cr6 calibration standards.

1.5 Cr6 Manual-Colorimetric (M-C) Analytical Principle

For the hexavalent chromium analysis the collected sample component portions are extracted in an alkaline solution and analyzed by the diphenylcarbazide colorimetric method which requires 35mL of sample liquid per analysis.

1.6 Cr Graphite Furnace-Atomic Absorption (GF-AA) Analytical Principle

For the total chromium analysis the collected samples shall be prepared in order to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. Samples are then subjected to an acid digestion procedure. Following the appropriate dissolution and dilution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the chromium concentration.

2 DEFINITIONS

2.1 End User

For the purposes of this method, the regulating agency or its authorized representative shall be considered the end user if a determination of Cr and Cr6 emissions from a stationary source is required as part of a regulatory process. Otherwise the end user shall be the party who defrays the cost of performing this method. The pre-test protocol must identify the end user.

2.2 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). The tester shall ultimately be responsible for performance of this method whether directly or indirectly through co-ordination of the efforts of the sampling and analytical groups.

2.3 Source Target Concentration

This is the target concentration for hexavalent chromium (Cr6) specified by the end user of the test results. The target concentration shall be expressed in units of Cr6 mass per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/m^3 or $\mu g/m^3$).

2.4 Limit of Detection

The limit of detection (LOD) is a limit of the performance of the analytical procedures below which quantitative results must not be reported. The LOD is based on the x-intercept of the calibration plot for absorbance versus concentration adjusted by three times the standard deviation of the absorbance for a mid-point concentration.

2.5 Reporting Limit

The reporting limit (RL) is a limit of the performance of the entire test method below which quantitative mass analyses must not be reported for a given sample run. The RL is based on the minimum analyte mass that must be collected in the sampling train to allow detection by the laboratory according to the requirements of this method. Such mass is the product of the LOD and the liquid volume used to collect the analyte in the sampling train.

2.6 Source Reporting Limit

The source reporting limit (SRL) is a limit of the performance of the entire test method below which quantitative emission results must not be reported.

3 PRE-TEST PROTOCOL

3.1 Responsibilities of the End User and Tester

3.1.1 The End User

Before testing may begin, the end user of the test results must specify the source target concentration to be determined by this method using the guidelines of § 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (§ 3.2) have been met.

3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

The tester shall obtain all relevant data that are required for pre-test calculations of sampling parameters. The tester shall develop and write a pre-test protocol before performing this method to help ensure satisfactory results.

The tester shall be responsible for ensuring that all sampling and analytical reporting requirements are met.

3.2 Pre-Test Protocol

The pre-test protocol should include the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of Cr6 (§ 3.2.1),

(2) preliminary analytical data (§ 3.3) for Cr6, and

(3) planned sampling parameters (§ 3.5).

The protocol must demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. In addition, the pre-test protocol should include information on equipment, logistics, personnel and other resources necessary for an efficient and coordinated test.

At a minimum, the pre-test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be approved by the end user of the results and the tester.

The tester should not proceed with the performance of the remainder of this method unless the pre-test protocol is approved by the tester and the end user.

3.3 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

(1) Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

(2) Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

(3) Interests of the End User, the Tester, and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user may use emissions results from previous tests of the facility or from similar sources. This target concentration is necessary for the calculation of the target sampling parameters required by § 3.5.

3.4 Preliminary Calculations

3.4.1 Determining the Limit of Detection (LOD)

The "Analytical Calibration Procedure" of this test procedure which is appropriate for the target substance shall be used for the analytical calibration and the determination of the limit of detection (LOD) described below. Such analytical calibration shall be performed prior to sampling by the same analytical personnel who perform the analytical calibration subsequent to sampling; this does not exclude the use of documentation for analytical calibration performed for prior tests.

(1) Plotting Absorbance versus Concentration

Plot absorbance as the dependent variable (y-axis) and concentration as the independent variable (x-axis).

(2) Determining the Standard Deviation at the MidPoint

Prepare a standard solution of the target substance with a concentration near the midpoint of the calibration curve.

Analyze four or more aliquots of this solution and plot the results.

Calculate the standard deviation, s_{mid}, of the absorbance.

(3) Calculating the X-Intercept and Slope

Using the least squares method, determine the x-intercept, a, and slope, n, of the line through the data.

Equation 425-1 shall be used to calculate the LOD.

$$LOD = |a| + \left(\frac{3s_{mid}}{n}\right) \qquad 425\text{-}1$$

Where:

LOD	=	limit of detection, ng/mL
$\|a\|$	=	absolute value of x-intercept, ng/mL
$3s_{mid}$	=	three times the standard deviation of the midpoint absorbance, absorbance units
n	=	slope of the calibration line, (absorbance units)/(ng/mL)

3.4.2 **Determining the Reporting Limit (RL)**

To obtain the lowest RL, assume that:

(1) all of the Cr6 in the gas sampled is recovered from the liquid of the probe rinse and the first impinger and

(2) the volume of the liquid of the probe rinse and the first impinger is 220 mL.

Equation 425-2 shall be used to calculate the RL.

$$RL = LOD \times 220 \qquad 425\text{-}2$$

Where:

RL = analytical mass reporting limit, ng
LOD = limit of detection, ng/mL
220 = liquid volume of probe rinse and first impinger, mL

3.5 Sampling Runs, Time, and Volume

3.5.1 **Sampling Runs**

A test shall include at least three sampling runs in series and a blank sampling train.

3.5.2 **Minimum Sample Volume (MSV)**

This is the minimum sample volume that must be collected in the sampling train to provide sufficient Cr6 for analytical quantitation. The MSV must be based on the reporting limit and the source target concentration. The MSV will be adjusted, based on further practical limitations, to yield the planned sample volume (PSV) in subsequent sections.

Equation 425-3 shall be used to calculate the MSV.

$$MSV = RL \times \frac{1}{STC} \qquad 425\text{-}3$$

Where:

MSV = minimum sample volume, dscm
RL = analytical mass reporting limit, ng
STC = source target concentration, ng/dscm

3.5.3 **Minimum Sampling Time (MST)**

This is the minimum time required to collect the minimum sample volume at the expected volumetric sampling rate. The tester should use an average volumetric sampling rate (VSR) appropriate for the source to be tested. If the

VSR cannot be achieved in the field, the sampling time shall be revised using the following equation to achieve the target MSV. The sampling time must be such that the emissions test is conducted during representative operating conditions of the source.

Equation 425-4 shall be used to calculate the MST.

$$MST = \frac{MSV}{VSR} \qquad 425\text{-}4$$

Where:

MST	=	minimum sampling time, hours
MSV	=	minimum sample volume, dscm
VSR	=	volumetric sampling rate, dscm/hour

3.5.4 **Planned Sample Volume (PSV)**

The planned sample volume (PSV) is the volume of emissions that must be sampled to collect for analysis a mass of Cr6 between the RL and the limit of linearity. The PSV is the primary sampling target whenever practically feasible. Calculate the PSV using the largest value for F that will give a practical sample volume.

Equations 425-5 and 425-6 shall be used to calculate the PSV.

$$PSV = MSV \times F \qquad 425\text{-}5$$

$$PSV = PST \times VSR \qquad 425\text{-}6$$

Where:

PSV	=	minimum sampling time, hours
MSV	=	minimum sample volume, dscm
F	=	safety factor for detection ($F \geq 1$)
PST	=	planned sampling time, hours
VSR	=	volumetric sampling rate, dscm/hour

Typically, when the value of F is one or greater, it is safe to assume that Cr6 will be detected at or above the source target concentration (STC). Greater values of F provide greater assurance.

Typically, when the value of F is less than one, it is unsafe to assume that Cr6 will be detected at the source target concentration (STC).

3.5.5 **Planned Sampling Time (PST)**

The planned sampling time (PST) is calculated using Equation 425-7.

$$PST = MST \times F \qquad 425\text{-}7$$

Where:

PST = planned sampling time, hours
MST = minimum sampling time, hours
F = safety factor for detection ($F \geq 1$)

3.5.6 **Pre-Test Calculation of Source Reporting Limit (SRL)**

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for emissions of Cr6 from the source. Notice that the SRL is higher than the STC if F is less than one in which case it is unsafe to assume that Cr6 will be detected at the STC.

Equation 425-4 shall be used to calculate the SRL.

$$SRL = \frac{RL}{PSV} \qquad 425\text{-}8$$

Where:

SRL = source concentration reporting limit, ng/dscm
RL = analytical mass reporting limit, ng
PSV = planned sampling volume, dscm

4 BIASES AND INTERFERENCES

4.1 Sample Instability

Chromium is subject to changes in valence state during the time between sampling and analysis (hold time). Take all reasonable precautions, some of which are required in various sections of this method, to minimize all influences which may change the valence states of chromium in each sample. Factors which influence such changes are hold time, pH, and other chemical species.

4.2 Cr6 IC-C Interferences

A high ionic concentration in the sample may overload the chromatographic column, altering the retention time and/or the shape of the chromate peak. Anionic species such as molybdate or vanadate which will react with the 1,5 diphenylcarbazide post-column reagent to form a colored product absorbing at 520-540 nm may obscure or interfere with the quantitation of the chromate peak by coeluting with or overlapping with it, if the concentration of the interfering compounds is sufficiently high. Some known interferences are:

4.2.1 Molybdenum

Molybdenum as a solution of molybdic acid ($H_2MoO_4 \cdot H_2O$) in water produced a peak which eluted at 3.55 minutes when Cr6 was eluting at 4.25 minutes. The Mo^{6+} peak was resolved from a peak representing 50 ng Cr6/mL up to a concentration of approximately 500 μg Mo^{6+}/mL.

4.2.2 Vanadium

Vanadium as a solution of ammonium vanadate (NH_4VO_3) in water produced a broad peak at 2.80 minutes when Cr6 was eluting at 4.25 minutes. This peak was resolved from a peak representing 50 ng Cr6/mL up to a concentration of approximately 10 μg V^{5+}/mL.

4.3 Cr6 M-C Interferences

Molybdenum, mercury and vanadium react with diphenylcarbazide to form a color; however, approximately 20 mg of elements can be present in a sample without creating a problem. Iron produces a yellow color, but this effect is not measured photometrically at 540 nm.

4.4 Cr GF-AA Interferences

The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters shall be optimized to minimize these effects. If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube shall be cleaned by operating the furnace at higher atomization temperatures.

Nitrogen shall not be used as the purge gas because of a possible CN band interference.

Low concentrations of calcium may cause interferences; at concentrations above 200 mg/L calcium's effect is constant. Calcium nitrate is therefore added to ensure a known constant effect. This step may be omitted if the sample is known to be free of calcium or no analytical interferences are expected.

5 SENSITIVITY

The test method sensitivity is dependent on the parameters chosen during the required pre-test protocol in the "PRE-TEST PROTOCOL" section. In general, the higher the planned sampling volume, the better (lower) the test method sensitivity.

5.1 Cr6 IC-C Sensitivity

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 0.5 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

5.2 Cr6 M-C Sensitivity

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 4.0 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

5.3 Cr GF-AA Sensitivity

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports a value of 1.0 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA sensitivity can be lower than the Cr6 IC-C sensitivity.

6 RANGE

6.1 Cr6 IC-C Range

Using sample loops of 10 uL to 250 uL, the linear range of this procedure without dilution or concentration of the sample is approximately 0.5 ng Cr6/mL to 40 μg Cr6/mL.

6.2 Cr6 M-C Range

A straight line response curve was obtained in the range 0.5 μg Cr6 /50 mL to 3.0 μg Cr6 /50 mL (10 to 60 ng/mL) . For a minimum analytical accuracy of 100 $\pm$ 10 percent, the lower limit of the range is 2 μg/100mL. The upper limit can be extended by appropriate dilution or by using a smaller cell path length after recalibration for the smaller cell.

6.3 Cr GF-AA Range

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports an optimum range of 5 to 100 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA range can be broader than the Cr6 IC-C range.

7 EQUIPMENT

All surfaces which may come in contact with sample shall be glass, quartz, Teflon, or other similarly non-metallic (stainless steel may be a source of chromium contamination) inert material.

Although teflon is not the required material of construction for sampling train components, it can be used to reduce problems with equipment contamination and cleaning.

Any other sampling apparatus which, after review by the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

7.1 Sampling Equipment

Except where otherwise noted in this method, same as CARB Method 5, Section 2.1. Exceptions include a glass nozzle, a glass lined stainless steel probe, 0.1 N NaOH in the first two impingers, a Teflon-coated glass fiber filter, and a silica gel moisture trap after the filter. As shown in Figure 1, sample flow shall be through the probe first, then the impingers, and then the filter.

7.2 Recovery Equipment

Except where otherwise noted in this method, same as CARB Method 5, Section 2.2.

7.3 Analytical Equipment

7.3.1 Cr6 IC-C Analytical Equipment

The following system has been found suitable for hexavalent chromium analysis as described in this procedure. Specifications, analytical ranges, and detection limits were determined using this system. An equivalent system may be used so long as it is demonstrated to be capable of separating and detecting hexavalent chromium, and the sensitivity and precision of the system is determined to be adequate.

7.3.1.1 DIONEX Ion Chromatography System 4000i (or equivalent), including:

Gradient Pump Module

Advanced Chromatography Module

Variable Wavelength Detection Module

Automated Sampler

Eluant Degas Module

Advanced Computer Interface

IBM-AT Compatible Computer, running the DIONEX Autoion 450 (or equivalent) Data System Chromatography Software

Chromatographic Columns

Organic compound guard column: DIONEX MPIC-NG1 (or equivalent) neutral guard column.

Anion guard column (can also used as a preconcentrater column): DIONEX HPIC-AG7 (or equivalent) high-capacity anion guard column.

Separator column: DIONEX HPIC-AS7 or equivalent high-capacity anion separator column.

7.3.1.2 Post-Column Reagent System, including:

Pressurized reagent reservoir.

120 cm Packed Bed Reaction Coil.

7.3.2 Cr6 M-C Analytical Equipment

7.3.2.1 100 mL beakers

7.3.2.2 Filtration Apparatus

Vacuum unit constructed of glass, to accommodate sintered glass funnels. Medium porosity filter paper is optional. Wherever filtering is specified, centrifuging may also be performed at the analyst's option.

7.3.2.3 Volumetric Flasks

100-mL and other appropriate volumes.

7.3.2.4 Hot Plate

7.3.2.5 Pipettes

Assorted sizes, as needed.

7.3.2.6 Spectrophotometer

To measure absorbance at 540nm.

7.3.3 Cr GF-AA Analytical Equipment

7.3.3.1 Philips Beakers

Borosilicate, 125mL, with digestion covers.

7.3.3.2 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

7.3.3.3 Graphite Furnace

Any graphite furnace device with the appropriate temperature and timing controls.

7.3.3.4 Strip Chart Recorder

A recorder is recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

8 PREPARATION OF EQUIPMENT

The following sections specify a recommended cleaning procedure for sampling equipment and extremely stringent cleaning performance criteria. An alternative cleaning procedure is allowed providing that experimental documentation is provided which demonstrates that the alternative cleaning procedure has been established and is at least as effective at achieving the cleaning performance criteria as the recommended procedure.

The chosen cleaning procedure shall be applied to all equipment surfaces (not only the probe surfaces) which can come in contact with the sample.

8.1 Recommended Cleaning Procedure

All surfaces which can come in contact with sample shall be glass, Teflon, or other similarly non-metallic (even stainless steel may be a source of chromium contamination) inert material and shall be prewashed with detergents, soaked in 1:1 HNO_3 for several hours, rinsed with Type II water, and finally rinsed with 0.1 N NaOH batch solution. For awkward objects, such as long glass probes, soaking may be replaced by careful wiping.

Probes are generally the most difficult sampling apparatus to clean. Therefore, before use in sampling, to ensure that sampling equipment is clean and free of chromium contamination, apparatus which may come in contact with sample shall be cleaned and a sample of the final rinse for each probe shall be analyzed for Cr (total chromium). If Cr is detected in the final rinse, each probe shall be re-cleaned until a sample of the final rinse contains no detectable Cr. "Cr GF-AA ANALYTICAL PROCEDURES" shall be followed for this contamination check.

8.2 Alternative Cleaning Procedure

If the specified glass probes are in short supply, the recommended cleaning procedure could double the number of days necessary to complete a series of tests.

Time can be saved by using the following options:

8.2.1 Development, Testing, and Documentation

An alternative cleaning procedure may be used if it is developed, tested, and documented as achieving the objective of no detectable chromium in the last probe cleaning rinse. Testing and documentation shall include: a pre-test visit to the intended site, collection of samples from an intended test point with the highest expected concentration of chromium, trials of other cleaning procedures, and documentation of those alternative cleaning procedures which pass the contamination check of the "Recommended Cleaning Procedure".

8.2.2 Advanced Preparation

The best protection against lost time is to procure enough pre-cleaned equipment before a field trip so that no equipment needs to be re-cleaned and re-used during field sampling. Procure extra pre-cleaned equipment to allow for breakage, etc.

9 REAGENTS

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

9.1 Sampling Reagents

9.1.1 Method 5 Reagents

Except where otherwise noted in this method, same as CARB Method 5, Section 3.1, except Teflon-coated glass fiber filters are used, and 0.1 N NaOH is used in the first two impingers.

9.1.2 Batch of 0.1N NaOH Solution, Analytical Reagent Grade

The most important purpose of this solution is to maintain hexavalent chromium in a high pH solution so that it is not reduced to trivalent chromium. In particular, liquid samples must be taken and transported at a pH of 8.0 or higher.

Any other solution which can meet this and the other performance specifications of this method is also acceptable.

See "PREPARATION OF REAGENTS."

9.2 Recovery Reagents

Except where otherwise noted in this method, same as CARB Method 5, Section 3.2.

9.3 Cr6 IC-C Analytical Reagents

Unless otherwise indicated, all chemicals shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. All reagents shall be analyzed before testing is begun using theIC-C system to be employed in the analysis of the samples, and the Cr6 concentration shall be less than the detection limit.

9.3.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.3.2 Water

All water used in this procedure shall, at minimum, conform to the specifications of American Society for Testing and Materials (ASTM) Type II reagent water as specified in ASTM Test Procedure D 1193. Use of ASTM Type I reagent water.

9.3.3 Eluent

Dissolve 33 g of ammonium sulfate in water in a 1 L Class A volumetric flask. Add 6.5 mL of 29% ammonium hydroxide and make to volume. The concentration of the prepared eluent is 250 mM $(NH_4)_2SO_4$ and 100mM NH_4OH.

9.3.4 Post-Column Reagent

Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of glass distilled HPLC grade methanol. Add to approximately 500 mL of degassed or nitrogen purged or helium purged water containing 28 mL of 96-98% sulfuric acid, and make to 1 L with degassed or nitrogen purged or helium purged water. High purity sulfuric acid such as EM Science Suprapur grade or JT Baker Ultrex grade is recommended. The stability of the post-column reagent is enhanced by preparing it in a nitrogen atmosphere, pressurizing the reagent reservoir with nitrogen, and shielding it from light.

9.3.5 Cr6 Stock Solution

Prepare a standard solution containing 1000 μg Cr6 /mL as a solution of potassium dichromate in water. Use analytical reagent grade $K_2Cr_2O_7$ which has been dried at 105° C for at least one hour. Dissolve 2.8289 g of the dried $K_2Cr_2O_7$ in water in a class A volumetric flask and make to volume with water. Alternatively, obtain a chromate standard solution in water prepared specifically for use in ion chromatography.

9.3.6 Regenerant Solution for the DIONEX MPIC-NG1 Guard Column (or equivalent)

In this application, the DIONEX MPIC-NG1 guard column (or equivalent) is used to trap organic compounds which could adversely affect the anion chromatographic columns. The trapped organic compounds shall be flushed from the column periodically using a 70-90% solution of acetonitrile or methanol in water.

9.4 Cr6 M-C Analytical Reagents

9.4.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.4.2 Type II Water

Type II water is deionized and distilled, meeting American Society for Testing and Materials (ASTM) specification for type reagent - ASTM Test Method D 1193-77. The water shall be monitored for impurities.

9.4.3 Potassium Dichromate Stock Solution

Dissolve 2.829 g of analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) in water, and dilute to 1 liter (1 mL = 1000 μg Cr6).

9.4.4 Potassium Dichromate Standard Solution

Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 100 μg Cr6 with water.

9.4.5 Sulfuric Acid, 6N, Analytical Reagent Grade

Dilute 166 mL sulfuric acid to 1000 mL in water.

9.4.6 Diphenylcarbazide Solution, Analytical Reagent Grade

Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

9.4.7 0.1% Potassium Permanganate Solution

Analytical Reagent Grade

9.4.8 0.01% Potassium Permanganate Solution

Analytical Reagent Grade

9.5 Cr GF-AA Analytical Reagents

9.5.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.5.2 ASTM Type II Water (ASTM D1193)

9.5.3 Concentrated Nitric Acid

Reagent preparation shall use Ultrex (or equivalent) grade HNO_3.

Glassware cleaning shall use ACS reagent grade HNO_3.

9.5.4 Hydrogen Peroxide (30%) (Optional), Analytical Reagent

9.5.5 Matrix Modifier

Follow manufacturer's recommendations, when interferences are suspected.

9.5.6 Total Chromium Standard Stock Solution (1000mg/L)

Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, Fisher Scientific, etc.) and verify by comparison with a second standard, or dissolve 2.829 g of Potassium Dichromate ($K_2Cr_2O_7$, analytical reagent grade) in Type II water and dilute to 1 liter in a volumetric flask.

9.5.7 Total Chromium Working Standards

All total chromium preparations injected for analysis shall be prepared to contain 1.0% (v/v) HNO_3. The zero standard shall be 1.0 % (v/v) HNO_3.

10 PREPARATION OF REAGENTS

10.1 Preparation of Reagents for Sampling

10.1.1 Batch of 0.1N NaOH Solution, Analytical Reagent Grade

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

This is necessary to avoid the use of different 0.1N NaOH solutions with different levels of contamination, especially of Cr6, but also of analytical interferents.

Therefore, sampling and analytical personnel shall coordinate their plans so that all steps in sampling and analysis use the same batch of solution which will be prepared fresh for each source test. Typically, dissolve 4.0 g NaOH in water in a 1 liter volumetric flask and dilute to the mark. Repeat, as necessary, so that a single batch of sufficient volume is prepared to serve all of the needs of sampling and analysis. Store the solution in a tightly capped polyethylene bottle.

The most important purpose of this solution is to maintain hexavalent chromium in a high pH solution so that it is not reduced to trivalent chromium. In particular, liquid samples must be taken and transported at a pH of 8.0 or higher.

Any other solution which can meet this and the other performance specifications of this method is also acceptable.

10.1.2 Removal of Reducing Agents in the Reagents

The 0.1 N NaOH extraction solution and the 6N sulfuric acid solution may contain small amounts of reducing agents that can react with the hexavalent chromium. Potassium permanganate ($KMnO_4$) is added to these reagents in order to neutralize these reducing agents.

Determine the amount of $KMnO_4$ needed as follows:

Pipette 3 mL of the extraction solution into cuvettes A and B. Use cuvette A as a sample cell and cuvette B as a reference cell. Zero the instrument at 528 nm with both cuvettes.

Wait 10 minutes. Add an adequate amount (uL) of 0.01% potassium permanganate solution to cuvette A so that after 10 minutes a slight change in absorbance is observed. This step may have to be repeated a number of times in order to determine the required amount of potassium permangante.

From the change in absorbance, calculate the amount of potassium permanganate per unit volume needed to neutralize the reducing agents found in the reagents.

Determine the amount of higher concentration 0.1% potassium permanganate solution needed to treat the volume of reagent. Pipette this amount of 0.1% $KMnO_4$ into the reagents.

Repeat this procedure with the 6N sulfuric acid solution.

10.2 Preparation of Reagents for Recovery

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

10.3 Preparation of Reagents for Analysis

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

11 CALIBRATION PROCEDURE

11.1 Sampling Calibration Procedure

Perform all of the calibrations described in CARB Method 5, Section 5, with any modifications appropriate for this method.

11.2 Recovery Calibration Procedure

Follow the appropriate analytical calibration procedure.

11.3 Cr6 IC-C Analytical Calibration Procedure

Inject a series of Cr6 calibration standards which brackets the sample concentrations. Typically, 4 to 6 calibration standards will be sufficient to establish the calibration curve. The recommended procedure is to inject one series of calibration standards before the samples, to establish that the system is working properly and has reached equilibrium so that a linear response is attained. A second set of calibration standards is injected at the end of the analytical run to

confirm constancy of response throughout the run. If the peak areas or peak heights of the two sets of calibration standards differs by more than 5% the run shall usually be repeated. If any drift in response which may have occurred is within acceptable limits, use the concentration and response values of the two sets of calibration standards to establish a calibration curve which is used to quantitate the Cr6 concentration in the samples.

11.4 Cr6 M-C Analytical Calibration Procedure

(1) Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials shall be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer shall read correctly within $\pm$5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 540 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

(2) Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 530 and 550 nm using a 50 μg Cr6 standard solution in the sample cell and a reagent blank solution in the reference cell. If a peak does not occur, the spectrophotometer is malfunctioning and shall be repaired. When a peak is obtained within the 530 to 550 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the reagent blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum differences in absorbance between the standard and the reagent blank occurs.

(3) Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance.

(4) Freshly make up each standard for Cr6 in a separate 50mL volumetric flask starting with 35 mL of the same batch of NaOH solution reserved for its sampie set. Then add an appropriate amount of Cr6 to each calibration standard, starting with none for the zero standard. Then add 6N sulfuric acid and diphenylcarbazide solution in the same manner as in sample preparation.

11.5 Cr GF-AA Analytical Calibration Procedure

(1) Calibration standards for total chromium shall start with 1% v/v HNO_3 with no chromium for the reagent blank with appropriate increases in total chromium concentration in the other calibration standards. The calibration standards shall be prepared following the steps outlined for sample preparation in the analytical procedures.

(2) Check standards shall be prepared in the same manner as calibration standards. Check standards shall be prepared separately and independently from the calibration standards and shall serve to protect against errors in the preparation of the calibration standards.

(3) Either (1) run a series of chromium standards and reagent blanks and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

(4) Re-run the lowest calibration standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the standards indicates that the tube shall be replaced.

(5) Duplicates, spiked samples, and check standards shall be routinely analyzed. This requirement is further specified in the quality assurance/quality control procedures.

(6) Calculate Cr concentrations (1) from a calibration curve, or (2) by the method of standard additions, or (3) directly from the instrument's concentration readout. All dilution or concentration factors shall be taken into account. Concentrations reported for multiphased or wet samples shall be appropriately qualified (e.g., 5 μg/g dry weight).

(7) Calibration curves shall be composed of a minimum of a reagent blank and three total chromium standards. A calibration curve shall be made for every batch of samples, unless check standards remain within 10% of the last calibration curve.

(8) Dilute samples with reagent blank solution if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

12 SAMPLING PROCEDURE

At all times during sampling and transport of samples, the pH of the impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

12.1 Method 5 Sampling Procedure and Exceptions

Except where otherwise indicated in this method, all samples are collected from the source by use of CARB Method 5. Exceptions include a glass nozzle, a glass lined stainless steel probe, 0.1 N NaOH in the first two impingers, and a Teflon-coated glass fiber filter. As shown in Figure 1, sample flow shall be through the probe first, then the impingers, and then the filter.

12.2 Sampling Runs

The performance of this test method shall include three or more sampling runs.

The performance criteria documented in the pre-test protocol shall be used by the test crew to maximize, in the test crew's judgement, the degree to which each sampling run occurs during an interval or intervals of time during which the source facility operations are representative of the conditions intended by the pre-test protocol.

A narrative field log shall be kept by the sampling crew to document observations which subsequently can be used by others to evaluate the the degree to which the source facility operations are representative of the conditions intended by the pre-test protocol.

12.3 Field Blank Run

The performance of this test method shall include one or more field blank runs. Every step of the test method shall be followed for each field blank run with the exception that sample gas shall not be withdrawn from the source facility by the field blank train.

13 RECOVERY PROCEDURE

At all times during sampling and transport of samples, the pH of the probe rinse and impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

13.1 Silica Gel Recovery

For stack gas moisture determination, weigh the spent silica gel or silica gel plus impinger to the nearest 0.5 g using a balance. This step may be conducted in the field.

13.2 Probe Recovery

Rinse the probe with at least 100mL of 0.1 N NaOH ; measure and record the probe rinse volume and store the probe rinse in Container 1. Transport the probe rinse to a clean room or to a site with laboratory conditions. Split the probe rinse into two approximately equal volumes; measure and record the volume of each split. Label one split for Cr6 analysis and label the other split for total Cr analysis.

13.3 Impinger and Filter Recovery

This method does not require impinger rinses.

The sampling and analytical personnel shall discuss the expected sample concentrations and the analytical limits of detection for hexavalent and total chromium. The impinger catch and filter shall be handled one of two ways depending on these expectations as directed below in the "Higher Concentrations" and "Lower Concentrations" sections below.

13.3.1 Higher Concentrations

If it is not considered important to minimize the dilution of any sample component, then the contents of both impingers (~200mL total) shall be combined and stored in container 2. (Measure the volume.) As soon as possible, the filter is transported in a filter container to a site with laboratory conditions where it shall be extracted in all of the impinger solution from Container 2. The extraction shall include shaking for a minimum of 30 minutes. The alkaline impinger medium will retard reduction of hexavalent chromium.

Split the extract solution with half saved for hexavalent chromium analysis and half saved for total chromium analysis. Each sample split is ~100 mL. (Measure the volumes.)

13.3.2 Lower Concentrations

If it is considered important to minimize the dilution of any sample component, then the contents of each impinger (~100mL each) may be stored in Containers 2 and 3. (Measure the volumes.) The filter shall be extracted in only one of the impinger contents, whichever is suspected to have the higher concentration. The extraction shall include shaking for a minimum of 30 minutes. The contents of the first impinger are stored in Container 2 and those of the second impinger in Container 3. Whichever impinger contents are not used for extraction shall be handled as a third sample recovery requiring separate analyses.

Split the extract solution with half saved for hexavalent chromium analysis and half saved for total chromium analysis. Each sample split is ~50 mL. (Measure the volumes.)

14 Cr6 IC-C ANALYTICAL PROCEDURES

The ion chromatograph shall be set up and operated according to the instructions of the manufacturer of the instrument. A generalized diagram of the system configuration is shown in Figure 1.

14.1 IC-C Preparation

If any of the samples are suspected to contain particulate material, they shall be filtered through a 0.45 μm or smaller pore size membrane filter prior to analysis.

14.2 IC-C Analysis

14.2.1 Eluent Flow Rate

Adjust the eluent flow rate to 1.5 mL/minute.

14.2.2 Post Column Reagent Flow Rate

Adjust the post column colorimetric reagent flow rate to 0.5 mL/minute. The flow rate from the outlet line of the detector with the post column reagent delivery system on shall be confirmed to be 2.0 mL/minute.

14.3 IC-C Detection

Absorbance of the colored product formed by the reaction of the 1,5 diphenylcarbazide colorimetric reagent with Cr6 has been shown to be maximized at 540 nm for the system described and with the reagents used. The optimum wavelength for detection of the colored Cr6 derivative may vary depending on the source and batch of reagents used, and may be determined experimentally for each system by running a series of Cr6 standards at a range of wavelengths of detection. Alternatively, or in addition, the peak of the absorption band of the colored product can be determined by preparing a Cr6 standard in eluent, adding 1 part of the colorimetric reagent to 3 parts of the Cr6 spiked eluent, and recording a plot of the absorption band using a scanning spectrophotometer. The absorption band of the colored product is relatively broad, and for most applications an adequate response can be attained at wavelengths of 530-540 nm without the necessity of determining the exact wavelength of maximum absorbance.

15 Cr6 M-C ANALYTICAL PROCEDURES

15.1 M-C Preparation

15.1.1 Cr6 Reagent Blank Preparation

For each preparation, transfer 35 mL of solution to a 100mL beaker, adjust the pH to 1.0 $\pm$ 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide

solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes.

15.1.2 Hexavalent Chromium Sample Preparation

For each preparation, transfer 35 mL of solution to a 100mL beaker, adjust the pH to 1.0 $\pm$ 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes. (This leaves at least 15 mL of sample split for further analyses. The total volume of sample split shall be known at this point.)

15.2 M-C Analysis

(1) The analyst shall filter the preparation for clarity at this point. Medium retention filter paper shall be used. The filter paper shall be pre-wetted with a few mL of reagent blank and sample preparation. This will prime the filter so that it won't absorb color complex.

(2) Transfer a portion of the filtered preparation into a 5 cm absorption cell.

(3) Measure the absorbance at the optimum wavelength of 540 nm.

(4) Subtract the sample blank absorbance reading to obtain a net reading.

(5) If the absorbance reading of a sample preparation exceeds the calibration range, dilute with reagent blank or re-measure using less of the sample preparation. (There shall be about 15mL remaining at this point.)

16 Cr GF-AA ANALYTICAL PROCEDURES

16.1 Cr GF-AA Preparation

16.1.1 Cr Reagent Blank Preparation

For total chromium, the reagent blank is an aliquot of 1% HNO_3.

16.1.2 Cr Sample Preparation

In a beaker, add 10ml of concentrated nitric acid to the sample aliquot taken for analysis. Cover the beaker with a digestion coverglass . Place the beaker on a hot plate and reflux the sample down to near dryness. Add another 5mL nitric acid to complete digestion. Reflux the sample volume down to near dryness.

Wash down the beaker walls and digestion cover with distilled water and filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration shall be done only if there is concern that insoluble materials may clog the nebulizer. Adjust the volume to 50 mL or a predetermined value based on the expected Cr concentrations. The final

concentration of HNO_3 in the solution shall be 1 % (v/v). The sample is now ready for analysis. The applicability of a sample preparation technique shall be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

16.2 Cr GF-AA Analysis

16.2.1 Total Chromium Analysis

(1) The 357.9-nm wavelength line shall be used.

(2) Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

(3) Furnace parameters suggested by the manufacturer shall be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters shall be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

(4) Inject a measured uL aliquot of preparation into the furnace and atomize. If the concentration found exceeds the calibration range, the sample shall be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

(5) Subtract a reagent blank reading from a sample reading to obtain a net reading.

17 QUALITY ASSURANCE / QUALITY CONTROL (QA/QC)

17.1 Sampling QA/QC

17.1.1 Pre-Test Protocol

At a minimum, the QA/QC of the pre-test protocol shall include:

(1) target concentration (TC) chosen by consent of interested parties

(2) limit of detection (LOD) based on four or more lab blanks

(3) planned sampling flow rate

(4) planned sampling time

17.1.2 Test Protocol

At a minimum, the QA/QC of the test protocol shall include:

(1) three or more sampling runs

(2) one or more field blanks

17.2 Cr6 IC-C Analytical QA/QC

17.2.1 Check for Matrix Effects on the Cr6 Results

As the analysis for Cr6 by colorimetry is sensitive to the chemical composition of the sample (matrix effects), the analyst shall check at least one sample from each source using the following method: Obtain two equal volume aliquots of the same sample solution. The aliquots shall each contain between 6 and 10 μg of Cr6 (less if not possible). Spike one of the aliquots with an aliquot of standard solution that contains between 6 and 10 μg of Cr6. Now analyze both the spiked and unspiked sample aliquots as described in "Cr6 IC-C ANALYTICAL PROCEDURES" above. Next, calculate the Cr6 mass, in μg, in the aliquot of the unspiked sample solution, Cs, by using Equation 425-9:

$$Cs = Ca \times \left(\frac{As}{At - As} \right) \qquad 425\text{-}9$$

Where:

Cs = Cr6 in the unspiked sample solution, μg.
Ca = Cr6 in the standard solution, μg.
As = absorbance of the unspiked sample solution.
At = Absorbance of the spiked sample solution.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume. If the results of this method used on the single source sample do not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using the method of standard additions procedure.

17.2.2 Blanks

Four or more lab blanks shall be analyzed before any performance of this test procedure.

For each set of three field sampling runs, one or more associated field blank runs shall be analyzed.

17.2.3 Duplicates

For each set of three field sampling runs, one or more samples shall be injected in duplicate.

If the difference between the determined Cr6 concentrations of the sample duplicates exceeds 5% of their mean value, the results for the associated sampling runs shall be considered invalid.

17.3 Cr6 M-C Analytical QA/QC

17.3.1 Check for Matrix Effects on the Cr6 Results

As the analysis for Cr6 by colorimetry is sensitive to the chemical composition of the sample (matrix effects), the analyst shall check at least one sample from each source using the following method: Obtain two equal volume aliquots of the same sample solution. The aliquots shall each contain between 6 and 10 μg of Cr6 (less if not possible). Spike one of the aliquots with an aliquot of standard solution that contains between 6 and 10 μg of Cr6. Now treat both the spiked and unspiked sample aliquots as described in Section 6.4.1 above. Next, calculate the Cr6 mass, in μg, in the aliquot of the unspiked sample solution, Cs, by using Equation 425-10:

$$Cs = Ca \times \left(\frac{As}{At - As} \right) \qquad 425\text{-}10$$

Where:

Cs = Cr6 in the unspiked sample solution, μg.
Ca = Cr6 in the standard solution, μg.
As = absorbance of the unspiked sample solution.
At = Absorbance of the spiked sample solution.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume. If the results of this method used on the single source sample do not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using the method of standard additions procedure.

17.4 Cr GF-AA Analytical QA/QC

(1) Employ a minimum of one matrix-matched sample blank per sample batch to determine if contamination or memory effects are occurring.

(2) Test the system with check standards after approximately every 15 samples.

(3) Run one duplicate sample for every 10 samples, providing there is enough sample for duplicate analysis. A duplicate sample is a sample brought through the whole sample preparation. (See "Cr GF-AA ANALYTICAL PROCEDURES")

(4) Spiked samples or standard reference materials shall be used daily to ensure that correct procedures are being followed and that all equipment is operating properly. This will serve as a check on calibration standards, too.

(5) Whenever sample matrix problems are suspected, the method of standard additions shall be used for the analysis of all extracts, or whenever a new sample matrix is being analyzed.

(6) All quality control data shall be maintained for easy reference or inspection.

18 RECORDING DATA

18.1 Data Records

At a minimum, the tester shall maintain records of field, laboratory, and office data sufficient to support recalculation of reported results by an auditor.

18.2 Narrative Account

At a minimum, the tester shall maintain a narrative account characterizing source and testing operations during the source testing and analysis. In the narrative, include the means by which the values of the source and testing parameters, chosen for the pre-test protocol, were maintained; also include a narrative of unplanned or unexpected events which caused a departure from the chosen values.

19 CALCULATING RESULTS

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

19.1 Total Cr6 in the Sample Train (mCr6)

Calculate and report mCr6, the total μg Cr(VI) in the sample train. This can be obtained from the calibration curve or from the method of standard additions. Note that mCr6 is the sum of the masses of hexavalent chromium analyses performed on all sample portions. Also take into account any dilutions when calculating mCr6.

Calculations shall include only sample portions which have values above the LOD.

Do not subtract the LOD from the sample train values.

19.1.1 Cr6 IC-C Analytical Calculations

Report these calculations based on net values, as determined by the instrument.

If instrument blank values are not automatically taken and subtracted by the instrument, report these calculations based on net values, and report all instrument blank values, too.

See below for determination of net values.

19.1.2 **Cr6 M-C Analytical Calculations**

Report these calculations based on net values using Equation 425-11. Report all instrument blank values, too.

Net Value = Sample Train Component Value - Instrument Blank Value 425-11

19.2 Total Cr in the Sample Train (mCr)

Calculate and report mCr, the total μg of chromium in the sample train. This can be obtained from the calibration curve or from the method of standard additions. Note that mCr is the sum of the masses of total chromium analyses performed on all sample portions. Also take into account the necessary dilutions when calculating out mCr.

Calculations shall include only sample portions which have values above the LOD.

Do not subtract the LOD from the sample train values.

Report these calculations based on net values, and report all instrument blank values, too.

See above for determination of net values.

19.3 Method 5 Testing Parameters

Except where otherwise noted in this method, follow the procedures of ARB Method 5 to determine:

(1) Standard Volume of Gas Sample ≡ (Vsample)

Typical units for Vsample are dry standard cubic meters, dscm.

(2) Isokinetic Variation

(3) Standard Volumetric Flow Rate of Stack Gas ≡ (Qstack)

Typical units for Qstack are dry standard cubic meters per hour, dscm/hour.

19.4 Cr6 Mass Emission Concentration ≡ Cr6 MEC

Calculate and report the Cr6 mass emission concentration in the stack gas, dry basis, corrected to standard conditions, using Equation 425-12:

$$Cr6\ MEC = mCr6 \div Vsample \qquad 425\text{-}12$$

Where:

Cr6 MEC	=	Cr6 concentration in the stack gas, ng/dscm
mCr6	=	Cr6 mass in the sampling train, ng
Vsample	=	stack gas volume sampled, dscm

19.5 Cr6 Mass Emission Rate ≡ Cr6 MER

Calculate and report the Cr6 mass emission rate in the stack gas, dry basis, corrected to standard conditions, using Equation 425-13:

$$Cr6\ MER = Cr6\ MEC \times Qstack \qquad 425\text{-}13$$

Where:

Cr6 MER	=	Cr6 concentration in the stack gas, ng/dscm
mCr6	=	Cr6 mass in the sampling train, ng
Vsample	=	stack gas volume sampled, dscm

19.6 Cr Mass Emission Concentration ≡ Cr MEC

Calculate and report the Cr mass emission concentration in the stack gas, dry basis, corrected to standard conditions, using Equation 425-14:

$$Cr\ MEC = mCr \div Vsample \qquad 425\text{-}14$$

Where:

Cr MEC	=	Cr concentration in the stack gas, ng/dscm
mCr	=	Cr mass in the sampling train, ng
Vsample	=	stack gas volume sampled, dscm

19.7 Cr Mass Emission Rate ≡ Cr MER

Calculate and report the Cr mass emission rate in the stack gas, dry basis, corrected to standard conditions, using Equation 425-15:

$$Cr\ MER = Cr\ MEC \times Qstack \qquad 425\text{-}15$$

Where:

Cr MER	=	Cr concentration in the stack gas, ng/dscm
mCr	=	Cr mass in the sampling train, ng
Vsample	=	stack gas volume sampled, dscm

20 REPORTING RESULTS

20.1 Calculated Results

At a minimum, the tester shall report all calculated results required above. Also, as required by the end user of the test results, the tester shall include specified data records, as described above.

Clearly distinguish sample runs for which Cr6 or Cr were DETECTED above the LOD from sample runs for which Cr6 or Cr were NOT DETECTED above the LOD.

20.2 Narrative Account

At a minimum, the tester shall report a narrative account characterizing source and testing operations during the source testing and analysis. In the narrative, include the means by which the values of the source and testing parameters, chosen for the pre-test protocol, were maintained; also include a narrative of unplanned or unexpected events which caused a departure from the chosen values.

20.3 Final Calculation of Source Reporting Limit (SRL)

Equation 425-14 shall be used to calculate the SRL. This equation is adapted from the pre-test protocol; actual values shall be substituted for the pre-test values.

$$SRL = \frac{ARL}{ASV} \qquad 425\text{-}16$$

Where:

SRL	=	source concentration reporting limit, ng/dscm
ARL	=	actual reporting limit, ng
ASV	=	actual sample volume, dscm

21 ALTERNATIVE TEST METHODS

21.1 Direct Measurement of Gas Volumes through Pipes and Small Ducts

Air Resources Board Method 2A may be used, where applicable, as an alternative to pitot tube methods specified in Method 5, as referenced herein.

21.2 Other Impinger Solutions (Instead of NaOH)

0.1 N KOH may be substituted for 0.1 N NaOH in the impinger solution. Other substitutions, e.g. $NaHCO_3$, may be made provided that at all times during sampling and transport of samples, the pH of the impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

21.3 Total Chromium Determination by Flame Atomic Absorption Spectroscopy

For high total chromium concentrations which are within the detection range of flame atomic absorption spectroscopy, this analytical method may be used instead of the furnace type method specified in these pages. This option applies only to the analysis of total chromium. The remainder of the test method shall be performed as specified.

21.4 Other Methods

Alternative test methods may be used provided that they are equivalent to Method 425 and approved in writing by the Executive Officer of the California Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

22 REFERENCES

(1) US. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Method 7191 SW-846 (1986), Third Edition.

(2) EPA Method 5, Determination of Particulate Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

(3) (Draft) Laboratory and Field Evaluations of Methodology for Determining Hexavalent Chromium Emissions from Stationary Sources; Prepared by: Anna C. Carver, Entropy Environmentalists, Inc., Research Triangle Park, NC 27709; EPA Contract No. 68-02-4550; Prepared for: Dr. Joseph E. Knoll, United States Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, North Carolina 27711, UNDATED.

23 FIGURES

The following figures summarize features of this method:

Figure 1.
Sample Collection and Recovery for Hexavalent and Total Chromium

Figure 2.
Hexavalent Chromium Analysis

Figure 3.
Total Chromium Analysis

Figure 1.
Sample Collection and Recovery for Hexavalent and Total Chromium

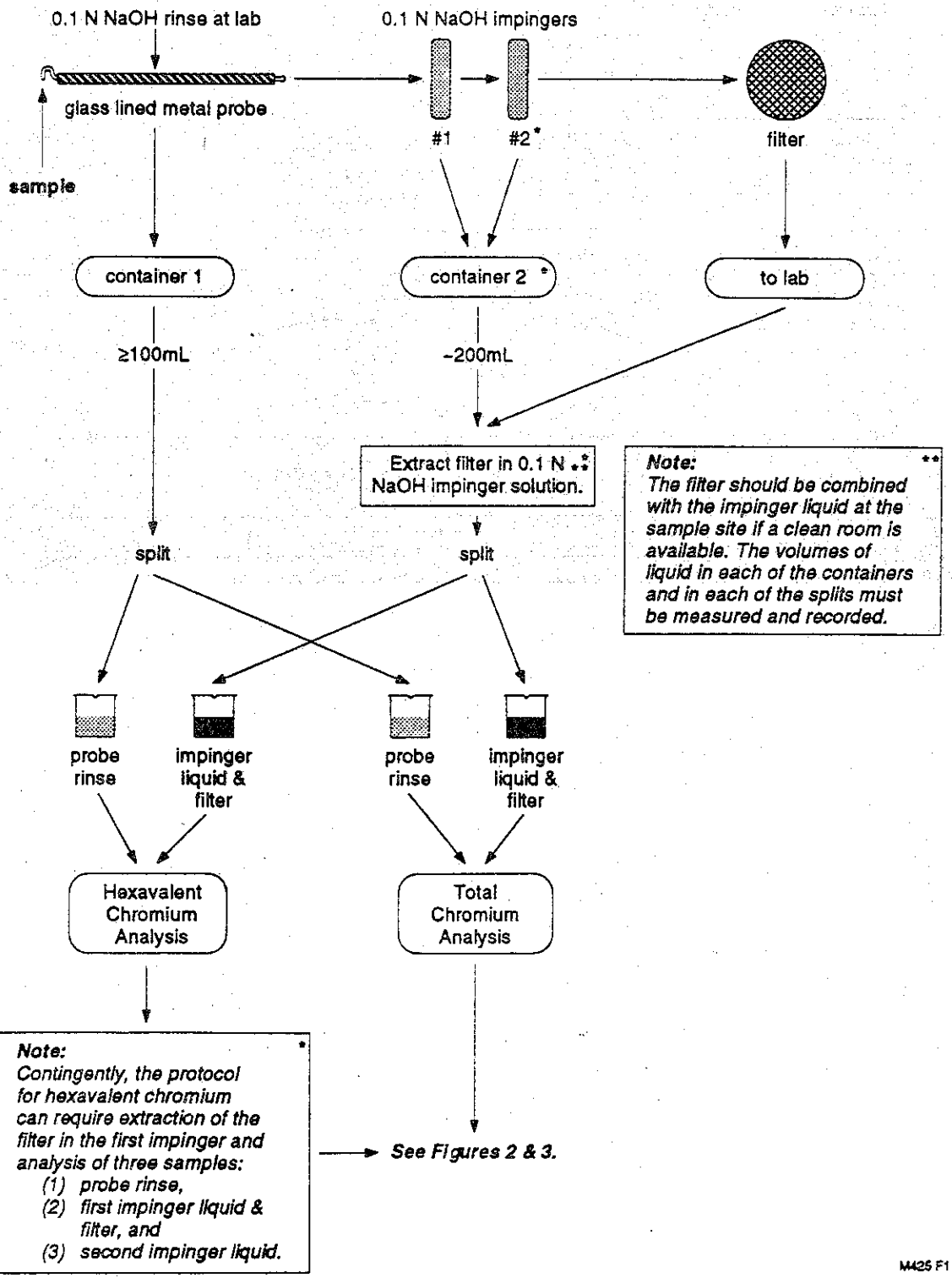


Figure 2.
Hexavalent Chromium Analysis

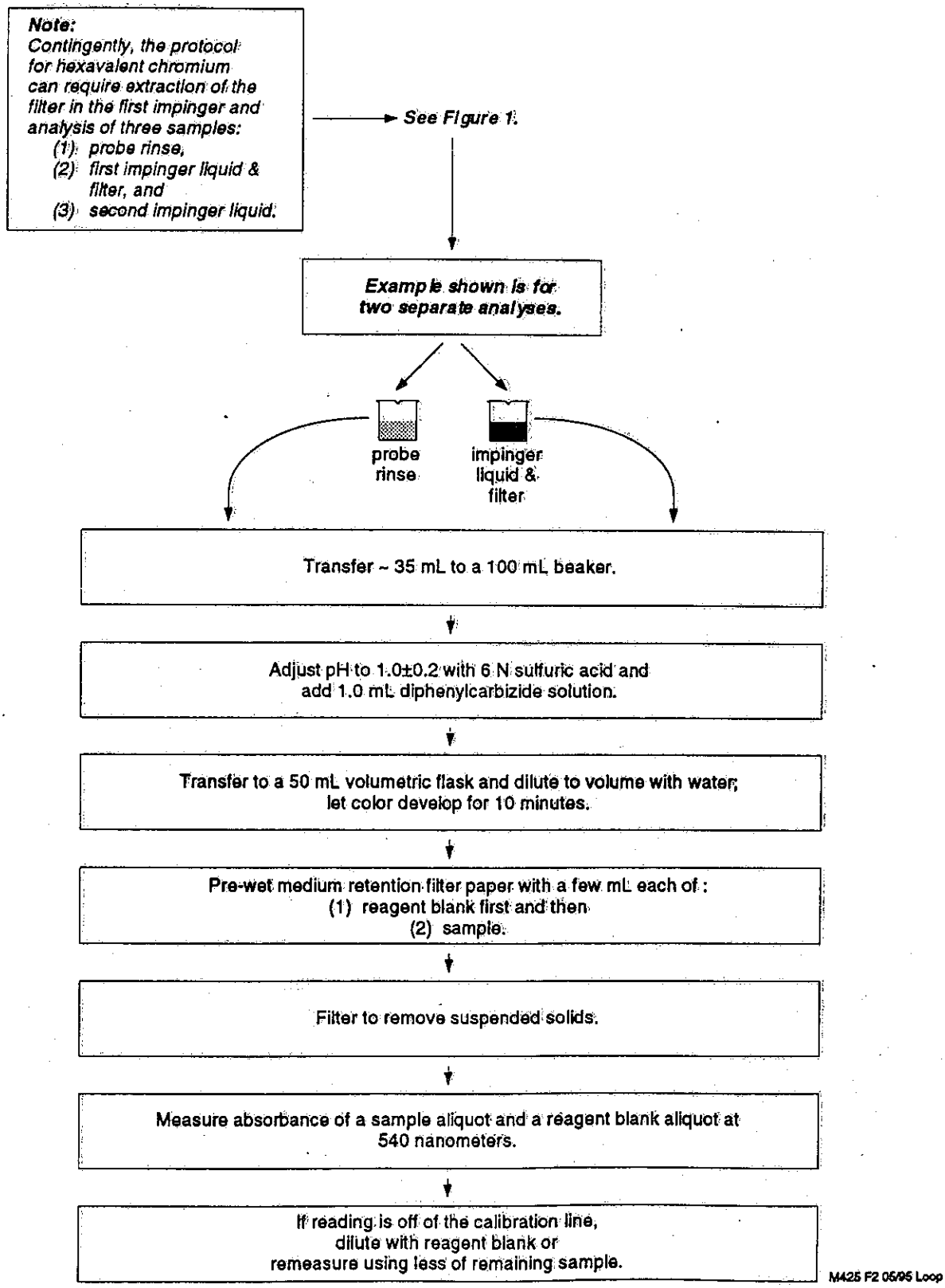
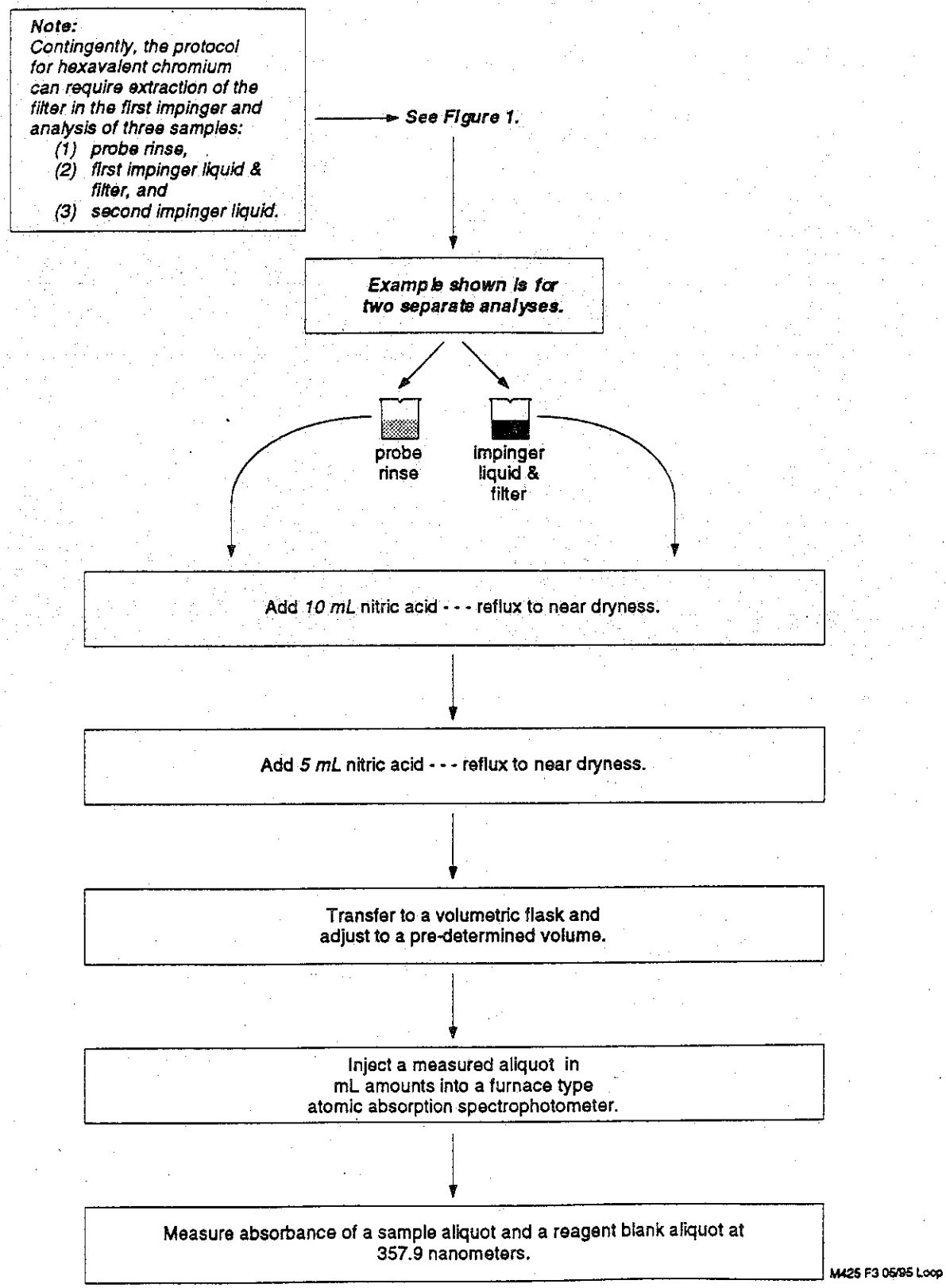


Figure 3.
Total Chromium Analysis



ERRATA

State of California
California Environmental Protection Agency
Air Resources Board

Method 429

Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources

Adopted: September 12, 1989
Amended: [insert date of amendment]

It is proposed that the content of ARB Method 429, Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources, adopted September 12, 1989, be deleted and replaced by the following revised content. For the text of the current test procedure, which is proposed to be replaced, contact Mr. George Lew, Air Resources Board, Monitoring and Laboratory Division, P.O. Box 2815, Sacramento, California 95812, telephone (916) 263-1630.

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APPENDIX A

Method 429

Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions From Stationary Sources

1. INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of nineteen polycyclic aromatic hydrocarbons (PAH) in emissions from stationary sources. These are listed in Table 1. The sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample as well as the original sample size and instrument sensitivity.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to approval by the Executive Officer of the California Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

Particulate and gaseous phase PAH are extracted isokinetically from the stack and collected on XAD-2 resin, in impingers, or in upstream sampling train components (filter, probe, nozzle). Only the total amounts of each PAH in the stack emissions can be determined with this method. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH.

The required analytical method is isotope dilution mass spectrometry combined with high resolution gas chromatography. This entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts and analysis of the processed extract for PAH using high-resolution capillary column gas chromatography coupled with either low resolution mass spectrometry (HRGC/LRMS), or high resolution mass spectrometry (HRGC/HRMS). To ensure comparable results, the same MS method must be used for samples collected at all tested locations at those sources where more than one location is tested.

Minimum performance criteria are specified herein which must be satisfied to ensure the quality of the sampling and analytical data.

1.3 DEFINITIONS AND ABBREVIATIONS

1.3.1 Internal Standard

An internal standard is a ^{2}H-labelled PAH which is added to all field samples, blanks and other quality control samples before extraction. It is also present in the calibration solutions. Internal standards are used to measure the

concentration of the analyte and surrogate compounds. There is one internal standard assigned to each of the target analytes and surrogates.

1.3.2 Surrogate Standard

A surrogate standard is a labelled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before the gaseous emissions are sampled. The surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of the how effectively the sampling train retains PAH collected on the XAD-2 resin. The recovery of the surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

1.3.3 Alternate Standard

An alternate standard is a ^{2}H-labelled PAH compound which is added to the impinger contents prior to extraction to estimate the extraction efficiency for PAHs in the impinger sample.

1.3.4 Recovery Standard

A recovery standard is a ^{2}H-labelled PAH compound which is added to the extracts of all field samples, blanks, and quality control samples before HRGC/MS analysis. It is also present in the calibration solution. The response of the internal standards relative to the recovery standard is used to estimate the recovery of the internal standards. The internal standard recovery is an indicator of the overall performance of the analysis.

1.3.5 Relative Response Factor

The relative response factor is the response of the mass spectrometer to a known amount of an analyte or labelled compound (internal standard or surrogate standard) relative to a known amount of an internal standard or another labelled compound (recovery standard or internal standard).

1.3.6 Performance Standard

A performance standard is a mixture of known amounts of selected standard compounds. It is used to demonstrate continued acceptable performance of the GC/MS system. These checks include system performance checks, calibration checks, quality checks, matrix recovery, and surrogate recoveries.

1.3.7 Performance Evaluation Sample

A performance evaluation sample is one prepared by EPA or other laboratories that contains known concentrations of method analytes, and has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a

competent analyst. Concentrations must be in the same range as typical field samples. Analyte concentrations are not known by the analyst.

1.3.8 Laboratory Control Sample

A laboratory control sample is one that contains known concentrations of method analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze field samples containing the same analytes. Analyte concentrations are known by the analyst. The laboratory must prepare the control sample from stock standards prepared independently from those used for calibration.

1.3.9 End User

The regulating agency shall be considered the end user if this test method is conducted for regulatory purposes, or the regulating agency shall designate the end user for the purposes of this method. Otherwise the end user shall be the party who defrays the cost of performing this test method. In any case, the pre-test protocol (Section 2) must identify the end user.

1.3.10 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). In some cases, the tester may be part of the regulating agency. The tester shall be the party ultimately responsible for the performance of this test method whether directly or indirectly through the co-ordination of the efforts of the analytical group and the efforts of the sampling group.

1.3.11 Analyst

This term refers to the analytical group that performs the analytical procedures to generate the required analytical data.

1.3.12 Source Target Concentration

This is the target concentration for each emitted PAH of interest specified by the end user of the test results. The target concentration shall be expressed in units of mass of target substance per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/dscm or μg/dscm)

1.3.13 The Method Detection Limit

The method detection limit (MDL) is based on the precision of detection of the analyte concentration near the detection limit. It is the product of the standard deviation of seven replicate analyses of resin samples spiked with low concentrations of the analyte and Student's t value for 6 degrees of freedom at a confidence level of 99 %.

1.3.14 The Practical Quantitation Limit

The practical quantitation limit (PQL) is a limit for each compound at or below which data must not be reported. It is the minimum sample mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision limits established by the MDL determination. The PQLs will be estimated at 5 times the MDL for those PAH that are not contaminants of the resin. The PQL for the remainder will be estimated at 5 times the blank XAD-2 resin level.

2. THE SOURCE TEST PROTOCOL

Every performance of this test method shall have an identified operator of the source to be tested, an identified end user of the test method results, and an identified tester who performs this test method. Figure 1 is a summary of the responsibilities of the parties involved in the coordination and performance of the source test. The protocol for the entire test procedure should be understood and agreed upon by the responsible parties prior to the start of the test.

2.1 RESPONSIBILITIES OF THE END USER AND THE TESTER

2.1.1 The End User

Before testing may begin, the end user of the test results (1.3.9) shall specify a source target concentration for each of the PAH to be determined by this method using the guidelines of Section 2.2.1.

The end user shall approve the source test protocol only after reviewing the document and determining that the minimum pre-test requirements (Sections 2.2 to 2.5) have been met.

2.1.2 The Tester

The tester (1.3.10) shall have the primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the analytical group and the efforts of the sampling group.

The tester shall be responsible for the selection of an analyst with documented experience in the satisfactory performance of the method. The tester shall obtain from the analyst all of the analytical data (Section 2.3) that are required for pre-test calculations of sampling parameters.

Before performing the rest of this method, the tester shall develop and write a source test protocol (Section 2.2) to help ensure that useful test method results are obtained. The tester shall plan the test based on the information provided by the end user, the results of pre-test surveys of the source, and the tester's calculations of target source testing parameters (Section 2,2).

The tester shall be responsible for ensuring that all of the sampling and analytical reporting requirements (Section 10) are met.

2.1.3 The Analyst

The analyst shall be responsible for performing all of the required analytical procedures described in this test method and reporting the results as required by Sections 2.3, 4.2.1, 4.2.2, 10.1.1, 10.1.2, 10.1.3, and 10.2).

2.2 PRE-TEST REQUIREMENTS

The source test protocol shall specify the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of each emitted PAH of interest (2.2.1),

(2) preliminary analytical data (2.3) for each target PAH, and

(3) planned sampling parameters (2.5.4, 2.5.5, and 2.5.6).

The protocol must demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. The source test protocol shall describe the procedures for all aspects of the source test including information on supplies, logistics, personnel and other resources necessary for an efficient and coordinated test.

The source test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be signed by the end user of the results and the tester.

The tester shall not proceed with the performance of the remainder of this method unless the source test protocol is signed by the tester and the end user.

2.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. This will be the primary reporting objective of the emissions test. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

2.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

2.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

Note that some risk assessment methodologies will assume that a PAH is present at the detection limit or one half of the detection limit even when the compound is not detected. This is inappropriate for planning for the performance of the test method because by definition a substance cannot be detected at one half of its detection limit. In such cases, the target sampling parameter must be the maximum practical sample volume.

2.2.1.3 **Interests of the End User, the Tester and the Stationary Source**

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user may use emissions results from previous tests of the facility or from similar facilities.

If estimates of the emissions are not availble, the tester must conduct a preliminary test at each emissions point of interest. This target concentration is necessary for the calculation of the target sampling parameters required by Section 2.5. Therefore, the emissions measured during the preliminary test must be representative of source operation. The tester must document operating conditions, and know from historical data, the extent to which the results of this preliminary run are representative of emissions from the source. This will require documentation of operating conditions during the preliminary test, and a knowledge of the potential variability in emissions with differences in source operation.

As an alternative to conducting a preliminary test, the end user may specify, as a sampling target, the longest practical sampling time so as to obtain the lowest practically achievable source reporting limit (Section 2.5.6).

2.3 REQUIRED PRELIMINARY ANALYTICAL DATA

2.3.1 Results of Blank Contamination Checks

The tester must obtain from the analyst the results of the PAH contamination checks. The analytical report must satisfy the reporting requirements of Sections 10 and 10.1.

The analyst shall use the procedures described in Sections 4.2.1 and 4.2.2 to clean the sampling media (filters and XAD-2 resin) and check for PAH contamination.

Table 3 shows the results of analyses of different lots of re-cleaned XAD-2 resin. The purpose of this table is to show typical variability. Actual results may vary from one test to another.

2.3.2 The Method Detection Limit

The method detection limit (MDL) must be determined by the same analyst (1.3.11) that will perform the analyses subsequent to sampling. Before estimating the method detection limit (MDL), the analyst shall identify those PAH that are contaminants of the XAD-2 resin using the procedures described in Sections 4.2.2.1 to 4.2.2.4. The analyst shall determine the MDL as described in Section 8.3 and Appendix A.

2.3.3 The Practical Quantitation Limit

The analyst shall calculate the practical quantitation limits (PQLs) for the target PAH. This value will be 5 times the MDL or 5 times the XAD-2 background level for those compounds that have been identified by the analyst as contaminants.

Table 2 lists practical quantitation limits obtained during ARB's development of this method. The values for the PQLs will vary with the performance of individual laboratories. Therefore, the tester must obtain PQL values for all of the target analytes from the analyst .

2.4 EXPECTED RANGE IN TARGET CONCENTRATIONS OF INDIVIDUAL PAHs

The PAH compounds in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration PAH could contain levels of other PAHs that exceed the upper limit of the method.

In some cases the solution is two GC/MS injections - first with the undiluted extract, and then again after appropriate dilution of the extract. At other times the required minimum dilution might be so large as to result in the reduction of the internal standard response below the minimum required by the method. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained. All major modifications must be approved by the Executive Officer.

2.5 SAMPLING RUNS, TIME, AND VOLUME

2.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

2.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable mass of PAH for quantitation. It must be based on a) the practical quantitation limit (2.3.3), b) the source target concentration (2.2.1), and c) sampling limitations. Use Equation 429-1 to calculate the target MSV for each PAH analyte.

$$MSV(dscm) = PQL \times \frac{1}{STC} \qquad 429\text{-}1$$

Where:

PQL = The practical quantitation limit, ng/sample (Section 2.3.3)
STC = The source target concentration, ng/dscm (Section 2.2.1)

2.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected average volumetric sampling rate (VSR). Use Equation 429-2 to calculate the minimum sampling time (MST) required to collect the minimum sample volume calculated in Section 2.5.2. The tester must use an average volumetric sampling rate (VSR) appropriate for the source to be tested.

$$MST(hours) = \frac{MSV}{VSR} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad 429\text{-}2$$

Where:

VSR = Expected average volumetric sampling rate, dscfm
60 = Factor to convert minutes to hours
0.028317 = Factor to convert dscf to dscm

The end user must decide whether the MSTs are all practically feasible and whether they can be increased to allow for any deviation from the sampling and analytical conditions assumed by the test plan. Based on this decision, the tester must use either Section 2.5.4 (a) or 2.5.4 (b) to calculate a planned sample volume (PSV).

2.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the PQL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either 2.5.4 (a) or 2.5.4 (b).

(a) If the end user has decided that the MSTs can be increased, the tester must use Equation 429-3 to calculate the PSV using the largest of the 19 MSV values calculated in Section 2.5.2. and the largest value for F that will give a practically achievable sample volume that provides the target analytes at levels between the PQL and the limit of linearity. Use this PSV to calculate the planned sampling time (Section 2.5.5 a) and Equation 429-6.

(b) If the MSTs are not all practically achievable, the tester and the end user must agree on a maximum practical sampling time (Section 2.5.5b). This value must then be used for the PST in Equation 429-4 to calculate the PSV. The tester must identify in the

source test protocol the target analytes for which the PSV is lower than the MSV. The primary reporting objective of the test cannot be achieved for those analytes. If the primary reporting objective cannot be achieved for all of the target analytes, it must be discussed in the protocol and the alternative reporting objective (Section 2.5.6) must be approved by the end user of the results.

The volume of sample that is actually collected will be determined by practical sampling limitations, the intended use of the data and the level of uncertainty that the end user can tolerate in the measurement of the target concentrations. This uncertainty will decrease as the value of F (Equation 429-5) increases.

$$PSV(dscm) = MSV \times F \qquad 429\text{-}3$$

$$PSV(dscm) = PST \times VSR \qquad 429\text{-}4$$

$$F = \frac{PSV}{MSV} \qquad 429\text{-}5$$

Where:

PST = Planned sampling time from Section 2.5.5
F = A safety factor (>1) that allows for deviation from ideal sampling and analytical conditions

2.5.5 Planned Sampling Time (PST)

Two options are available for calculating the planned sampling time depending on whether the primary objective can be achieved for all of the target analytes.

(a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target analytes and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field (Section 4.4.4.1), the sampling time must be recalculated using the actual VSR and the target PSV in equation 429-6.

(b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$PST(hours) = \frac{PSV}{VSR} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad 429\text{-}6$$

2.5.6 Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the source reporting limit for each target PAH. The SRL shall be calculated using Equation 429-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$SRL(ng/dscm) = \frac{PQL}{PSV} \qquad 429\text{-}7$$

Where:

SRL = Preliminary estimate of source reporting limit, ng/dscm
PQL = Practical quantitation limit, ng
PSV = Planned sample volume, dscm

2.5.7 Example Calculations

Figure 9 B is an example of the minimum required calculations of sampling parameters for the source test protocol.

3. INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, sorbents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 6.1.1.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Transformation of PAH and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAH such as benzo[a]pyrene, benzo[a]anthracene, and fluoranthene when trapped on filters can readily react with stack gases. These PAH are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.

PAH degradation may be of even greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water they are converted into sulfuric acid and nitric acid respectively. There is evidence that under such conditions certain PAH will be degraded. It is recommended that the PAH levels in the impingers be used as a qualitative tool to determine if breakthrough has occurred in the resin.

4. SAMPLING APPARATUS, MATERIALS AND REAGENTS

4.1 SAMPLING APPARATUS

The sampling train components listed below are required. The tester may use an alternative to the required sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 2. The train consists of nozzle, probe, heated particulate filter, condenser, and sorbent module followed by three impingers and a silica gel drying cartridge. An in-stack filter may not be used because at the in-stack temperatures the filter material must be of a material other than the Teflon required by the method. A cyclone or similar device in the heated filter box may be used for sources emitting a large amount of particulate matter.

For sources with a high moisture content, a water trap may be placed between the heated filter and the sorbent module. Additional impingers may also be placed after the sorbent module. If any of these options are used, details must be provided in the test report. The train may be constructed by adaptation of an ARB Method 5 train. Descriptions of the train components are contained in the following sections.

4.1.1 Probe Nozzle

Quartz, or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1 of ARB method 5.

4.1.2 Probe

The probe should be lined or made of Teflon, quartz, or borosilicate glass. The liner or probe is to provide an inert surface for the PAH in the stack gas. The liner or probe extends past the retaining nut into the stack. A temperature-controlled jacket provides protection of the liner or probe. The liner shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without the use of sealing greases.

4.1.3 **Preseparator**

A cyclone, a high capacity impactor or other device may be used if necessary to remove the majority of the particles before the gas stream is filtered. This catch must be used for any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other materials may be used subject to approval by the Executive Officer.

4.1.4 **Filter Holder**

The filter holder shall be constructed of borosilicate glass, with a Teflon frit or Teflon coated wire support and glass-to-glass seal or Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe, cyclone, or nozzle depending on the configuration used. Other holder and gasket materials may be used subject to approval by the Executive Officer.

4.1.5 **Sample Transfer Line**

The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings that are capable of forming leak-free, vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6 **Condenser**

The condenser shall be constructed of borosilicate glass and shall be designed to allow the cooling of the gas stream to at least 20°C before it enters the sorbent module. Design for the normal range of stack gas conditions is shown in Figure 3.

4.1.7 **Sorbent Module**

The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum tight seals without the use of sealant greases (Figure 3). The vertical resin trap is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must have been cooled to 20 °C (68°F) or less. The gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

4.1.8 **Impinger Train**

Connect three or more impingers in series with ground glass fittings able to form leak-free, vacuum tight seals without sealant greases. All impingers shall be of the Greenburg-Smith design modified by replacing the tip with a

1.3 cm (1/2 in.) I.D. glass tube extending to 1.3 cm (1/2 in.)from the bottom of the flask.

The first impinger may be oversized for sampling high moisture streams. The first and second impingers shall contain 100 mL of 3 mM sodium bicarbonate ($NaHCO_3$) and 2.4 mM sodium carbonate Na_2CO_3) (Section 4.2.5). This is intended to neutralize any acids that might form in the impingers. The third impinger shall be empty. Silica gel shall be added to the fourth impinger. A thermometer which measures temperatures to within 1°C (2°F), shall be placed at the outlet of the third impinger.

4.1.9 Silica Gel Cartridge

This may be used instead of a fourth impinger. It shall be sized to hold 200 to 300 gm of silica gel.

4.1.10 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs with other sampling components as part of an assembly, the arrangements must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free arrangements are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

Source-sampling assemblies that do not meet these minimum spacing requirements (or the equivalent of these requirements) may be used only if the pitot tube coefficients of such assemblies have been determined by calibration procedures approved by the Executive Officer.

4.1.11 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure readings.

4.1.12 Metering System

Vacuum gauge, leak-free pump, thermometers accurate to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 2. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.13 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall

be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.14 Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred configuration and alternative arrangements of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.15 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder during sampling of (120 ± 14°C) (248 ± 25°F). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

4.1.16 Balance

To weigh the impingers and silica gel cartridge to within 0.5 g.

4.2 SAMPLING MATERIALS AND REAGENTS

4.2.1 Filters

The filters shall be Teflon coated glass fiber filters without organic binders, or Teflon membrane filters, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard Method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose. Record the manufacturer's lot number.

4.2.1.1 Contamination Check of Filter

The tester must have the filters cleaned by the analyst and checked for contamination prior to use in the field. The contamination check must confirm that there are no PAH contaminants present that will interfere with the analysis of the sample PAHs of interest at the target reporting limits. The analyst must record the date the filter was cleaned.

The filters shall be cleaned in batches not to exceed 50 filters. To clean the filters, shake for one hour in methylene chloride in a glass dish that has been cleaned according to Section 6.2. After extraction, remove the filters and dry them under a clean N_2 stream. Analyze one filter using the same extraction, clean-up and analysis procedures to be used for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

$$\text{Blank value per filter} = \frac{\text{Total mass (ng) of analyte}}{\text{No. filters extracted}} \qquad 429\text{-}8$$

The acceptance criteria for filter cleanliness depends on 1) the method reporting limit, 2) the expected field sample volume and 3) the desired reporting limit for the sampled emissions stream. Filters with PAH levels equal to or greater than the target reporting limit for the analyte(s) of concern shall be rejected for field use.

If the filter does not pass the contamination check, re-extract the batch and analyze a clean filter from the re-extracted batch. Repeat the re-extraction and analysis until an acceptably low background level is achieved. Store the remainder tightly wrapped in clean hexane-rinsed aluminum foil as described in Section 4.3.3.

Record the date of the last cleaning of the filters and the date of the PAH analysis, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain this laboratory report with the date of cleaning of the filters, and the date of the filter contamination check from the analyst, and report them in the source test protocol and the test report as required by Sections 10.1 and 10.3.

4.2.2 Amberlite XAD-2 Resin

The XAD-2 resin must be purchased precleaned and then cleaned again as described below before use in the sampling train.

4.2.2.1 Cleaning XAD-2 Resin

This procedure must be carried out in a giant Soxhlet extractor which will hold enough XAD-2 for several sorbent traps, method blanks and QC samples. Use an all glass thimble containing an extra coarse frit for extraction of the XAD-2. The frit is recessed 10 to 15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen to prevent floating on the methylene chloride.

Clean the resin by two sequential 24 hour Soxhlet extractions with methylene chloride. Replace with fresh methylene chloride after the first 24 hour period.

4.2.2.2 Drying Cleaned XAD-2 Resin

The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. A 10.2 cm ID Pyrex pipe 0.6 m long with suitable retainers as shown in Figure 4 will serve as a satisfactory column. Connect the liquid nitrogen

cylinder to the column by a length of cleaned 0.95 cm ID copper tubing, coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C.

Continue the flow of nitrogen through the adsorbent until all the residual solvent is removed. The rate of flow should be high enough that the particles are gently agitated but not so high as to cause the particles to break up.

4.2.2.3 **Residual Methylene Chloride Check.**

Extraction: Weigh a 1.0 g sample of dried resin into a small vial, add 3 mL of hexane, cap the vial and shake it well.

Analysis: Inject a 2 μL sample of the extract into a gas chromatograph operated under the following conditions:

Column:	6 ft x 1/8 in stainless steel containing 10% OV-101 on 100/120 Supelcoport.
Carrier Gas:	Helium at a rate of 30 mL/min.
Detector:	Flame ionization detector operated at a sensitivity of 4 X 10^{-11} A/mV.
Injection Port Temperature:	250 °C.
Detector Temperature:	305 °C.
Oven Temperature:	30 °C for 4 min; programmed to rise at 40 °C per min until it reaches 250 °C; return to 30 °C after 1000 seconds.

Compare the results of the analysis to the results from a reference solution prepared by adding 2.5 μL of methylene chloride into 100 mL of hexane. This corresponds to 100 μg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the methylene chloride in the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

4.2.2.4 **Contamination Check of XAD-2 Resin**

The cleaned, dried XAD-2 resin must be checked for PAH contamination. Analyze a sample of the resin equivalent in size to the amount required to charge one sorbent cartridge for a sampling train. The extraction, concentration, cleanup and GC/MS analytical procedures shall be the

same for this sample as for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

The acceptance limit will depend on the PQL, the expected concentration in the sampled gas stream, and the planned sample volume. The contamination level must be less than the PQL or no more than 20 percent of the expected sample level.

If the cleaned resin yields a value for a target analyte which is not acceptable for the end user's intended application of the test results, repeat the extraction unless the analyst has historical data that demonstrate that re-extraction cannot reasonably be expected to further reduce the contamination levels. The tester must obtain these data from the analyst and include them in both the source test protocol and the emissions test report.

The contamination check shall be repeated if the analyst does not have such historical data. The analyst shall reclean and dry the resin (4.2.2.1, 4.2.2.2, and 4.2.2.3) and repeat the PAH analysis of the re-cleaned resin. If the repeat analysis yields a similar result to the first, record the contamination level for both the initial cleaning and the re-cleaning.

The analyst shall record the dates of the cleaning and extraction of the resin, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain the dates of cleaning and the laboratory report of the results of the contamination check from the analyst, and report them in both the source test protocol and the emissions test report as required by Sections 10.1 and 10.3.

The tester shall identify the analytes for which the PQLs will be based on a blank contamination value, and calculate the PQLs as required by Section 2.3.3.

4.2.2.5 Storage of XAD-2 Resin

After cleaning, the resin may be stored in a wide mouth amber glass container with a Teflon-lined cap, or placed in one of the glass adsorbent modules wrapped in aluminum foil and capped or tightly sealed with Teflon film at each end. The containers and modules shall then be stored away from light at temperatures 4 ^{o}C or lower until the resin is used in the sampling train.

The adsorbent must be used within twenty one (21) days of cleaning. If the adsorbent is not used within 21 days, it must be re-checked for contamination before use.

4.2.3 **Silica Gel**

Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other desiccants (equivalent or better) may be used, subject to approval by the Executive Officer.

4.2.4 **Reagent Water**

Deionized, then glass-distilled, and stored in hexane- and methylene chloride-rinsed glass containers with TFE-lined screw caps.

4.2.5 **Impinger Solution**

Sodium bicarbonate 3 mM, and sodium carbonate 2.4 mM. Dissolve 1.0081 g sodium bicarbonate ($NaHCO_3$) and 1.0176 g of sodium carbonate (Na_2CO_3) in reagent water (4.2.4), and dilute to 4 liters.

4.2.6 **Crushed Ice**

Place crushed ice in the water bath around the impingers.

4.2.7 **Glass Wool**

Cleaned by sequential rinsing in three aliquots of hexane, dried in a 110 °C oven, and stored in a hexane-washed glass jar with TFE-lined screw cap.

4.2.8 **Chromic Acid Cleaning Solution**

Dissolve 200 g of sodium dichromate in 15 mL of reagent water, and then carefully add 400 mL of concentrated sulfuric acid.

4.3 **PRE-TEST PREPARATION**

The positive identification and quantitation of PAH in an emissions test of stationary sources are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Sections 4.3.7 and 8 are to be used to monitor the performance of the sampling methods, identify problems, and take corrective action.

4.3.1 **Calibration**

All sampling train components shall be maintained and calibrated according to the procedure described in APTD-0576 (Section 11.7), unless otherwise specified herein. The tester shall maintain a record of all calibration data.

4.3.1.1 **Probe Nozzle**

Probe nozzles shall be calibrated according to the procedure described in ARB Method 5.

4.3.1.2 **Pitot Tube**

Calibrate the Type S pitot tube assembly according to the procedure described in Section 4 of ARB Method 2.

4.3.1.3 **Metering System**

Calibrate the metering system before and after use according to the requirements of Section 5.3 of ARB Method 5.

4.3.1.4 **Temperature Gauges**

Use the procedure in Section 4.3 of ARB Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as those used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

4.3.1.5 **Leak Check of Metering System Shown in Figure 1**

The tester shall use the procedure described in Section 5.6 of ARB Method 5

4.3.1.6 **Barometer**

Calibrate against a mercury barometer.

4.3.2 **Cleaning Glassware for Sampling and Recovery**

All glass parts of the train upstream of and including the sorbent module and the first impingers shall be cleaned as described in Section 3A of the 1974 issue of Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples (Reference 11.4). Take special care to remove residual silicone grease sealants on ground glass connections of used glassware. These greasy residues shall be removed by soaking several hours in a chromic acid cleaning solution (4.2.8) prior to routine cleaning as described above. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are stated in Section 8.2.

Rinse all glassware with acetone, hexane, and methylene chloride prior to use in the PAH sampling train.

Glassware used in sample recovery procedures must be rinsed as soon as possible after use with the last solvent used in it. This must be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are stated in Section 8.2.

4.3.3 **Preparation of Filter**

The clean dry filter (4.2.1) must be kept tightly wrapped in hexane-rinsed aluminum foil and stored at 0 to 4°C in a container away from light until

sampling. Before inserting the filter in the sampling train, check visually against light for irregularities and flaws or pinhole leaks.

4.3.4 **Preparation of Sorbent Cartridge, Method Blank, and Laboratory Control Samples**

Sorbent Cartridge

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned resin to completely fill the glass sorbent cartridge which has been thoroughly cleaned as prescribed (4.2.2).

Add the required surrogate standards (Table 7) to the sorbent cartridges for all of the sampling and blank trains for each series of test runs. Follow the resin with hexane-rinsed glass wool, cap both ends, and wrap the cartridge in aluminum foil. Store the prepared cartridges as required by Section 4.3.5.

The sorbent cartridges must be loaded, and the surrogate standards must be added to the resin in a clean area in the laboratory. There must be no turnaround of a used cartridge in the field.

The analyst shall record the date that the surrogate standards were added to the resin and the amount of each compound. The tester shall obtain these data from the analyst and report them in the source test protocol and the test report.

The appropriate levels for the surrogate standards are given in Table 7 which shows the spiking plan for surrogate standards, internal standards, alternate standards, and recovery standards. All of these required compounds are generally available. Additional labelled PAH may also be used if available. The labelled compounds used as surrogate standards must be different from the internal standards used for quantitation, and from the alternate and recovery standards. If the spiking scheme (Table 7) is modified, the tester must demonstrate that the proposed modification will generate data of satisfactory quality. Table 7A shows an approved modification that has been used in ARB's method development. All modifications must be approved by the Executive Officer before the emissions test is performed.

Laboratory Method Blank

Take a sample of XAD-2 resin from the same batch used to prepare the sampling cartridge. This will serve as the laboratory method blank (Section 8.1.1). The mass of this sample must be the same as that used in the sampling train. Spike with the same surrogate standards at the same levels used in the sampling cartridges.

Laboratory Control Sample

Set aside two samples of XAD-2 resin from the same batch used to prepare the sampling cartridge. These will serve as the laboratory control samples. (Section 8.1.3). The mass of each sample must be the same as that used in the sampling train.

4.3.5 Storage of Prepared Cartridges, Method Blank and Laboratory Control Sample

Store the aluminum foil wrapped sorbent cartridges away from light at 4 °C or lower until they are fitted into the sampling trains. Do not remove the caps before the setup of the sampling train.

The maximum storage time from cleaning of the resin to sampling with the spiked resin cartridge must not exceed 21 days (4.2.2.5).

Store the laboratory method blank and laboratory control samples in amber glass jars with Teflon lined lids at temperatures no higher than 4 °C.

4.4 SAMPLE COLLECTION

Because of the complexity of this method, testers must be experienced with the test procedures in order to ensure reliable results.

4.4.1 Preliminary Field Determinations

Select the sampling site and the minimum number of sampling points according to ARB Method 1 or as specified by the Executive Officer.

Determine the stack pressure, temperature, and the range of velocity heads using ARB Method 2. Conduct a leak-check of the pitot lines according to ARB Method 2, Section 3.1.

Determine the moisture content using ARB Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings.

Determine the stack gas dry molecular weight, as described in ARB Method 2, Section 3.6. If integrated sampling (ARB Method 3) is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. Do not change the nozzle size during the run. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of ARB Method 2).

Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

The target sample volume and sampling time must already have been calculated for the source test protocol and approved by the end user as required by Sections 2.2 and 2.5. The total sampling time must be such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Executive Officer), and (2) the total gas sample volume collected (corrected to standard conditions) will not be less than the target value calculated for the source test protocol (Section 2.5.5).

To avoid timekeeping errors, the number of minutes sampled at each point should be an integer or an integer plus one-half minute.

4.4.2 Preparation of Collection Train

Keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Caution: Do not use sealant greases in assembling the sampling train.

Record the performance of the setup procedures for the sampling train. Figure 10 is an example of a form for recording the sampling train setup data. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

Place 100 ml of the impinger solution (4.2.5) in the first impinger and weigh. Record the total weight. Repeat the procedure for the second impinger. Leave the third impinger empty. Weigh the empty third impinger and record the weight.

Weigh 200 to 300 g of silica gel to the nearest 0.5 g directly into a tared impinger or silica gel cartridge just prior to assembly of the sampling train. The tester may optionally measure and record in advance of test time the weights of several portions of silica gel in air-tight containers. One portion of the preweighed silica gel must then be transferred from its container to the silica gel cartridge or fourth impinger. Place the container in a clean place for later use in the sample recovery.

Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly of the filter holder is completed.

Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 2. Place crushed ice around the impingers.

4.4.3 Leak Check Procedures

4.4.3.1 Pretest Leak Check

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize. Leak-check the train at the sampling site by plugging the nozzle with a TFE plug and pulling a vacuum of at least 380 mm Hg (15 in. Hg).

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

The following leak-check instructions for the sampling train are described in Section 4.1.4.1 of ARB Method 5. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse the direction of the by-pass valve. This will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as described below and start over.

Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable. Repeat the leak check procedure until an acceptable leakage rate is obtained. Record the leakage rate on the field data sheet (Figure 5).

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.4.3.2 **Leak Checks During Sample Run**

If, during the sampling run, it becomes necessary to change a component (e.g., filter assembly or impinger), a leak check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure described in Section 4.4.3.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either (1) record the leakage rate and correct the volume of gas sampled since the last leak check as shown in Section 4.4.3.4 below, or (2) void the sampling run. Record the leakage rate.

Immediately after component changes, leak-checks must be conducted according to the procedure outlined in Section 4.4.3.1 above. Record the leakage rate on the field data sheet (Figure 5).

4.4.3.3 **Post Test Leak Check**

A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.4.3.1 except that it shall be conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. Record the leakage rate on the field data sheet (Figure 5). If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester

shall either, (1) record the leakage rate and correct the sample volume as shown in Section 4.4.3.4 below, or (2) void the sampling run.

4.4.3.4 **Correcting for Excessive Leakage Rates**

If the leakage rate observed during any leak-check after the start of a test exceeds the maximum leakage rate L_a (see definition below), replace V_m in Equation 429-9 with the following expression.

$$V_m - \sum_{i=1}^{n} (L_i - L_a)\theta_i - (L_p - L_a)\theta_p \qquad 429\text{-}9$$

Where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak-check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak-check performed prior to the "ith" leakcheck (i = 1,2,3...n), m^3/min (ft^3/min).

θ_i = Sampling time interval between two successive leak-checks beginning with the interval between the first and second leak-checks, min.

θ_p = Sampling time interval between the last (n^{th}) leak-check and the end of the test, min.

Substitute only for those leakage rates (L_i or L_p) which exceed L_a.

4.4.4 **Train Operation**

4.4.4.1 **Sampling Train**

During the sampling run maintain a sampling rate within 10 percent of true isokinetic, unless otherwise specified or approved by the Executive Officer. The actual sampling rate must be at or above the VSR (Equation 429-4) to collect the target sample mass in the estimated sampling time. If the target sampling rate cannot be achieved, adjust the planned sampling time to achieve the target sample volume (PSV).

For each run, record the data required on the sample data sheet shown in Figure 5. The operator must record the dry gas meter reading at the beginning of the test, at the beginning and end of each sampling time

increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

Record other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate.

Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream.

Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) (M_d) is equal to 29 ± 4. APTD-0576 (Reference 11.7) details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 11.8) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Turn on the recirculating pump for the adsorbent module and the condenser, and begin monitoring the temperature of the gas entering the adsorbent trap. Ensure that the temperature of the gas is 20 ^{o}C or lower before sampling is started.

Traverse the stack cross section, as required by ARB Method 1 or as specified by the Executive Officer, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes. This minimizes the chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain the temperature at the condenser outlet below 20^{o}C (68^{o}F). Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced during a sample run. Another complete filter assembly must be used rather than changing the filter itself. Before a new filter assembly is installed, conduct a leak-check as outlined in Section 4.4.3.2. The total PAH analysis shall include the combined catches of all filter assemblies.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to approval by the Executive Officer.

Note that when two or more trains are used, a separate analysis of each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.4.3.3. Also, leak-check the pitot lines as described in ARB Method 2; the lines must pass this leak-check, in order to validate the velocity head data. Record leakage rates.

Record any unusual events during the sampling period.

4.4.4.2 Blank Train

There shall be at least one blank train for each series of three or fewer test runs. For those sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three or fewer runs.

Prepare and set up the blank train in a manner identical to that described above for the sampling trains. The blank train shall be taken through all of the sampling train preparation steps including the leak check without actual sampling of the gas stream. Recover the blank train as described in Section 5.3. Follow all subsequent steps specified for the sampling train including extraction, analysis, and data reporting.

4.4.5 Calculation of Percent Isokinetic

Calculate percent isokinetic (Section 4.5.7) to determine whether the run should be repeated. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Executive Officer for possible variance on the isokinetic rates.

4.5 CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

4.5.1 Nomenclature

A = Cross-sectional area of stack, ft^2.

A_n = Cross-sectional area of nozzle, ft^2.

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_s = Concentration of PAH in stack gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

G_s = Total mass of PAH in stack gas sample, ng.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

I = Percent isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "ith" component change (i = 1, 2, 3, ...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

M_d = Molecular weight of stack gas, dry basis, lb/lb-mole (g/g-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, lb/lb-mole (g/g-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscf/min (dscm/min).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

R = Ideal gas constant 0.06236 mm Hg-m^3/°K-g-mole (21.85 in Hg-ft^3/R-lb-mole).

T_m = Absolute average dry gas meter temperature, °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{1c} = Total volume of liquid collected in impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf).

v_s = Stack gas velocity, calculated by ARB Method 2, Equation 2-9, ft/sec (m/sec).

Y = Dry gas meter calibration factor.

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

φ_w = Sampling time interval, from the final (n^{th}) component change until

13.6 = Specific gravity of mercury.

60 = Conversion factor, sec/min.

100 = Conversion to percent.

4.5.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See sampling run record (Figure 5).

4.5.3 Dry Gas Volume

Use Equation 429-10 to correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg).

$$V_{m(std)} = V_m \, Y \, \frac{T_{std}}{T_m} \, \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{P_{std}} = K_1 \, V_m \, Y \, \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m} \qquad 429\text{-}10$$

Where:

$K_1 = \frac{T_{std}}{P_{std}}$ = 0.3858 °K/mm Hg for metric units

= 17.65 °R/in Hg for English units

NOTE: Equation 429-10 may be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, V_m in Equation 429-10 must be modified as described in Section 4.4.3.4.

4.5.4 Average Stack Gas Velocity

Calculate the average stack gas velocity, v_s, as specified in ARB Method 2, Section 5.2.

4.5.5 Volume of Water Vapor

Calculate the volume of water vapor using Equation 429-11 and the weight of the liquid collected during sampling (Sections 5.3.6 and 5.3.8).

$$V_{w(std)} = V_{1c} \, \frac{\rho_w}{M_w} \, \frac{RT_{std}}{P_{std}} = K_2 \, V_{1c} \qquad 429\text{-}11$$

Where:

K_2 = 0.001333 m_3/mL for metric units, or

= 0.04707 ft_3/mL for English units.

4.5.6 Moisture Content

Calculate the moisture content of the gas, B_{ws}.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad 429\text{-}12$$

NOTE: In saturated or water-droplet laden streams, the procedure for determining the moisture content is given in the note to Section 1.2 of Method 4. For the purpose of this method, the average stack-gas temperature from Figure 5 may be used for this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F)

4.5.7 Isokinetic Variation

4.5.7.1 Calculation from Raw Data

$$I = \frac{100 T_s \left[K_3 V_{1c} + \frac{V_m Y}{T_m} \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60 \theta v_s P_s A_n} \qquad 429\text{-}13$$

Where:

K_3 = 0.003454 mm Hg-m^3/mL-^oK for metric units

= 0.002669 in Hg-ft^3/mL-^oR for English units

4.5.7.2 Calculation from Intermediate Values

$$I = \frac{100 T_s V_{m(std)} P_{std}}{T_{std} v_s \theta A_n P_s 60 (1 - B_{ws})} \qquad 429\text{-}14$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s v_s \theta A_n (1 - B_{ws})}$$

Where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

4.5.8 Average stack gas dry volumetric flow rate

Use Equation 429-15 to calculate the average dry volumetric flow rate of the gas.

$$Q_{std} = 60 K_1 (1 - B_{ws}) v_s A \left(\frac{P_s}{T_s} \right) \qquad 429\text{-}15$$

Where:

$K_1 = \frac{T_{std}}{P_{std}}$ = 0.3858 ^oK/mm Hg for metric units

= 17.65 ^oR/in Hg for English units

4.6 ISOKINETIC CRITERIA

If 90 percent < I < 110 percent, the isokinetic results are acceptable. If there is a bias to the results because I < 90 percent or I > 110 percent, then the results must be rejected and the test repeated, unless the test results are accepted by the Executive Officer.

5 SAMPLE RECOVERY

5.1 SAMPLE RECOVERY APPARATUS

5.1.1 Probe Nozzle Brush

Inert bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

5.1.2 Wash Bottles

Teflon wash bottles are required; Teflon FEP®.

5.1.3 Glass Sample Storage Containers

Precleaned narrow mouth amber glass bottles, 500 mL or 1000 mL. Screw cap liners shall be Teflon.

5.1.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with Teflon lined screw caps.

5.1.5 Balance

To measure condensed water to within 0.5 g.

5.1.6 Silica Gel Storage Containers

Air tight metal containers to store silica gel.

5.1.7 Funnel and Rubber Policeman

To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.1.8 Funnel

To aid in sample recovery. Glass or Teflon® must be used.

5.1.9 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the aluminum foil.

5.1.10 Aluminum Foil

Heavy-duty, precleaned with methylene chloride.

5.2 SAMPLE RECOVERY REAGENTS

5.2.1 Reagent Water

Deionized (DI), then glass distilled, and stored in hexane and methylene chloride-rinsed glass containers with TFE-lined screw caps.

5.2.2 Acetone

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.3 Hexane

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.4 Methylene Chloride

Nanograde quality or equivalent. A blank must be screened by the analytical detection method.

5.3 SAMPLE RECOVERY PROCEDURE

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period and a post test leak check has been performed (4.4.3.3). Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Conduct the post test leak check as described in Section 4.4.3.3. Remove the probe from the train and close off both ends of the probe with precleaned aluminum foil (5.1.10). Seal off the inlet to the train with a ground glass cup or precleaned aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area must be clean, and enclosed so that the chances of contaminating the sample will be minimized.

No smoking is allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, broken filters, color of the impinger liquid, etc. Figure 6 summarizes the recovery procedure described in Sections 5.3.1 to 5.3.8.

Figure 11 is an example of a form for recording the performance of the sample recovery procedure. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

5.3.1 **Sample Container No. 1 (front half rinses)**

Quantitatively recover material deposited in the nozzle, probe, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone, hexane, and methylene chloride three times each. Place all these rinses in Container No.1. Mark the liquid level.

5.3.2 **Cyclone Catch**

If the optional cyclone is used, quantitatively recover the particulate matter by sequentially rinsing the cyclone with acetone, hexane, and methylene chloride. Store in a clean sample container and cap.

5.3.3 **Sample Container No. 2 (filter)**

Carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. Do not wrap the filter in aluminum foil. If it is necessary to fold the filter, make sure that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

5.3.4 **Sorbent Module**

Remove the sorbent module from the train and cap it.

5.3.5 **Sample Container No. 3 (back half rinses)**

Rinse the back half of the filter holder, the transfer line between the filter and the condenser, and the condenser (if using the separate condenser-sorbent trap) three times each with acetone, hexane and methylene chloride, and collect all rinses in Container No. 3. If using the combined condenser/sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2 portion. If the optional water knockout trap has been employed, the contents and rinses shall be placed in Container No. 3. Rinse it three times each with acetone, hexane, and methylene chloride. Mark the liquid level.

The back half rinses may also be combined in a single container with the front half rinses (Section 5.3.1).

5.3.6 **Sample Container No. 4 (impinger contents)**

Wipe off the outside of each of the first three impingers to remove excess water and other material. Weigh the impingers and contents to the nearest ±0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the silica gel (Section 5.3.8) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). Pour the impinger catch directly into Container No. 4. Mark the liquid level.

5.3.7 Sample Container No. 5 (Impinger rinses)

Rinse each impinger sequentially three times with acetone, hexane, and methylene chloride and pour rinses into Container No. 5. Mark the liquid level. These rinses may be combined with the previously weighed impinger contents in Container No. 4.

5.3.8 Weighing Silica Gel

Weigh the spent silica gel to the nearest 0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the impingers (Section 5.3.6) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). .

5.4 SAMPLE PRESERVATION AND HANDLING

From the time of collection to extraction, maintain all samples (Sections 5.3.1 to 5.3.7) at 4°C or lower and protect from light. All samples must be extracted as soon as practically feasible, but within 21 days of collection; and all extracts must be analyzed as soon as practically feasible, but within 40 days of extraction. Success in meeting the holding time requirement will depend on pre-test planning by the tester and the laboratory.

6 ANALYTICAL PREPARATION

This method is restricted to use only by or under the supervision of analysts experienced in the use of capillary column gas chromatography/mass spectrometry and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedures described in Sections 7.3, 8.2.6, and 8.3.1.

6.1 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Reference 11.9 describes procedures for handling hazardous chemicals in laboratories.

The following method analytes have been classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene and dibenzo-(a,h,)anthracene. A guideline for the safe handling of carcinogens can be found in Section 5209 of Title 8 of the California Administrative Code.

6.2 CLEANING OF LABORATORY GLASSWARE

Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) must be cleaned as soon as possible after use by rinsing with the last solvent used in it. This must be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are given in Section 8.2.

Clean aluminum foil with acetone followed by hexane and methylene chloride.

6.3 APPARATUS

6.3.1 Grab Sample Bottle

Amber glass, 125-mL and 250-mL, fitted with screw caps lined with Teflon. The bottle and cap liner must be acid washed and solvent rinsed with acetone and methylene chloride, and dried before use.

6.3.2 Concentrator Tube, Kuderna-Danish

10-mL, graduated (Kontes-K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper must be used to prevent evaporation of extracts.

6.3.3 Evaporation Flask, Kuderna-Danish

500-mL (Kontes K-570001-0500 or equivalent). (Attached to concentrator tube with springs).

6.3.4 Snyder Column, Kuderna-Danish

Three-ball macro (Kontes K-569001-0121 or equivalent).

6.3.5 Snyder Column, Kuderna-Danish

Two-ball micro (Kontes K-569001-0219 or equivalent).

6.3.6 Minivials

1.0 mL vials; cone-shaped to facilitate removal of very small samples; heavy wall borosilicate glass; with Teflon-faced rubber septa and screw caps.

6.3.7 Soxhlet Apparatus

1 liter receiver, 1 heating mantle, condenser, Soxhlet extractor.

6.3.8 Rotary Evaporator

Rotovap R (or equivalent), Brinkmann Instruments, Westbury, NY.

6.3.9 **Nitrogen Blowdown Apparatus**

N-Evap Analytical Evaporator Model 111 (or equivalent), Organomation Associates Inc., Northborough, MA.

6.3.10 **Analytical Balance**

Analytical. Capable of accurately weighing to the nearest 0.0001 g.

6.3.11 **Disposable Pipet**

5 3/4 inch x 7.0 mm OD.,

6.4 **SAMPLE PREPARATION REAGENTS**

6.4.1 **Reagent water**

Same as 5.2.1.

6.4.2 **Acetone**

Same as 5.2.2.

6.4.3 **Hexane**

Same as 5.2.3.

6.4.4 **Methylene Chloride**

Same as 5.2.4.

6.4.5 **Sulfuric Acid**

ACS. Reagent grade. Concentrated, sp. gr. 1.84.

6.4.6 **Sodium Sulfate**

ACS. Reagent grade. Granular, anhydrous. Purify prior to use by extracting with methylene chloride and oven drying for 4 or more hours in a shallow tray. Place the cleaned material in a glass container with a Teflon lined screw cap, and store in a desiccator.

6.4.7 **Silica Gel**

For column chromatography, type 60, EM reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate by heating in a foil covered glass container for longer than 16 hours at 130 ^{o}C, then store in a desiccator. The storage period shall not exceed two days.

NOTE: The performance of silica gel in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that satisfies the performance criteria of Section 6.6.1.

6.4.8 **Alumina: Acidic**

Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190 °C.

NOTE: The performance of alumina in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that meets the performance criteria of Section 6.6.1.

6.4.9 **Nitrogen**

Obtained from bleed from liquid nitrogen tank.

6.5 **SAMPLE EXTRACTION**

WARNING: Stack sampling will yield both liquid and solid samples for PAH analysis. Samples must not be split prior to extraction even when they appear homogeneous as in the case of single liquid phase samples. Solid samples such as the resin are not homogeneous and particulate matter may not be uniformly distributed on the filter. In addition, filter samples are generally so small that the desired detection limit might not be achieved if the sample were split.

The recovered samples may be combined as follows:

1) Particulate filter and particulate matter collected on the filter (Section 5.3.3), cyclone catch (Section 5.3.2) and sample container No. 1 (Section 5.3.1).

2) Sample container No. 3 (Section 5.3.5), resin (Section 5.3.4) and rinse of resin cartridge.

3) Sample container No.4 (Section 5.3.6) and sample container No.5 (Section 5.3.7)

Two schemes for sample preparation are described in Sections 6.5.1 and 6.5.2 below. One of these must be used.

Section 6.5.1 describes sample preparation procedures for separate GC/MS analyses of impingers and the remainder of the sampling train. Figure 7 is a flowchart of the extraction and cleanup procedures.

Section 6.5.2 describes sample preparation procedures for GC/MS analysis of a single composite extract from each sampling train. The recovered samples are combined as shown in Figure 8.

6.5.1 **Separate Analysis of Impingers**

A separate analysis of the impingers can be used to determine whether there has been breakthrough of PAHs past the resin.

6.5.1.1 **Extraction of Liquid Samples**

A. Sample Container No. 1 (Front half rinses)

Concentrate the contents of sample container No. 1 (Section 5.3.1) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. This residue will likely contain particulate matter which was removed in the rinses of the probe and nozzle. Transfer the residue (along with three rinses of the final sample vessel) to the Soxhlet apparatus with the filter and particulate catch and proceed as described under Section 6.5.1.2 below.

B. Sample Container No. 3 (Back half rinses)

Concentrate the contents of sample container No. 3 (Section 5.3.5) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. Combine this residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the resin sample, and proceed as described under Section 6.5.1.2 below.

C. Containers No. 4 and No. 5 (Impinger contents and rinses)

Place the contents of Sample Containers No. 4 and No. 5 (Sections 5.4.6 and 5.4.7) in a separatory funnel. Add the appropriate amount of ^{2}H-labelled alternate standard solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A. The amounts required by Section 7.2.4 are based on a final volume of 500 μL for analysis (450 μL of sample extract and 50 μL of recovery standard solution). Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions. Divide the extract in two - one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4°C away from light.

Pour the remaining extract through Na_2SO_4 into a round bottom flask. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or less if the methylene chloride can be removed with less hexane. Add the appropriate amount of alternate standard (Section 7.2.7) to achieve the final extract concentrations shown in Table 6 or 6A. This standard must be used to monitor the efficiency of the cleanup procedure.

Concentrate the remaining sample to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer the extract to a 8-mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.1.2 **Extraction of Solid Samples**

Filter, Particulate matter, and Resin

The Soxhlet apparatus must be large enough to allow extraction of the sample in a single batch. Clean the Soxhlet apparatus by a 4 to 8-hr Soxhlet with methylene chloride at a cycling rate of 3 cycles per hour. Discard the solvent. Add 20 g Na_2SO_4 to the thimble. Combine the filter, resin, glass wool, and concentrated front and back half rinses (6.5.1.1A and 6.5.1.1B) and place on top of the Na_2SO_4. Add the appropriate amount of internal standard (Section 7.2.4 and Table 7) to achieve the final extract concentrations indicated in Table 8.

Place the thimble in the Soxhlet apparatus, and add about 700 mL of methylene chloride to the receiver. Assemble the Soxhlet, turn on the heating controls and cooling water, and allow to reflux for 16 hours at a rate of 3 cycles per hour. After extraction, allow the Soxhlet to cool. Divide the sample in two - one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4°C away from light.

Exchange the remaining extract to hexane. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or as necessary to remove the methylene chloride. Add the appropriate amount of alternate standard (Section 7.2.7 and Table 7 or 7A) to achieve the final extract concentrations shown in Table 8 or 8A. This alternate standard must be used to monitor the efficiency of the cleanup procedure when the impingers are analyzed separately from the remainder of the sampling train.

Concentrate the remaining sample to about 2 mL with a Kuderna-Danish concentrator or rotoevaporator, then transfer the extract to a 8-mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.2 **Single Composite Extract For Analysis**

6.5.2.1 **Extraction of Aqueous Samples**

Containers No. 4 and No. 5 (Impinger contents and rinses)

Pour the contents of Sample Containers No. 4 and No. 5 (Sections 5.3.6 and 5.3.7) into an appropriate size separatory funnel. Do not add internal standards. Instead, add the appropriate amount of alternate standard spiking solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A.

Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions with the solid samples and concentrated rinses (6.5.2.2) in a Soxhlet extractor.

6.5.2.2 Extraction of Solid Samples

Concentrate the front and back half rinses as described in Sections 6.5.1.1A and 6.5.1.1B. Clean the Soxhlet apparatus as in Section 6.5.1.2. Place the filter and resin in the Soxhlet apparatus along with the concentrated front and back half rinses and the impinger extract. Add the internal standards, extract the sample, and concentrate the extract as described in Section 6.5.1.2. Divide the extract into two equal portions. Store one of these, the archive sample, at 4 °C away from light. The remaining extract must be exchanged to hexane as described in Section 6.5.1.2. Do not add the alternate standard to this composite extract. It has already been added to the impinger sample (6.5.2.1).

Concentrate the extract to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer to a 8-mL test tube with hexane or equivalent non-polar solvent such as isooctane. Proceed with sample cleanup procedures below (Section 6.6)

6.6 COLUMN CLEANUP

Several column chromatographic cleanup options are available. Either of the two described below may be sufficient. Before using a procedure for the cleanup of sample extracts, the analyst must demonstrate that the requirements of Sections 8.1.3.1 and 8.2.6 can be met using the cleanup procedure. Acceptable alternative cleanup procedures may also be used provided that the analyst can demonstrate that the performance requirements of Sections 8.1.3.1 and 8.2.6 can be met. Compliance with the requirements of Sections 8.1.1.1 and 8.2.6 must also be demonstrated whenever there is a change in the column cleanup procedure used for the initial demonstration.

The sample extract obtained as described in Sections 6.5.1C and 6.5.1.2 or 6.5.2.2 is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively with hexane rinsings to at least one of the columns described below.

6.6.1 Column Preparation

A. Silica Gel Column

Pack a glass gravity column (250 mm x 10 mm) in the following manner:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column and add 10 grams of activated silica gel (Section 6.4.7) in methylene chloride. Tap the column to settle the silica gel, and then add a 1 cm layer of anhydrous sodium sulfate (Section 6.4.6)

Variations among batches of silica gel may affect the elution volume of the various PAH. Therefore, the volume of solvent required to completely elute all of the PAH must be verified by the analyst. The weight of the silica gel can then be adjusted accordingly. Satisfactory

recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the silica gel columns.

B. Acid Alumina Column

Pack a 250 mm x 10 mm glass gravity column as follows:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column. Add 6 g of acid alumina prepared as described in Section 6.4.8. Tap the column gently to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

Satisfactory recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the acid alumina columns.

6.6.2 Column Chromatography Procedure

A. Silica Gel Column

Elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL sample extract onto the column using two additional 2 mL rinses of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, begin elution of the column with 25 mL of hexane followed by 25 mL of methylene chloride/hexane (2:3)(v/v). Collect the entire eluate. Concentrate the collected fraction to about 5 mL using the K-D apparatus or a rotary evaporator. Do not allow the extract to go to dryness.

Transfer to a minivial using a hexane rinse and concentrate to 450 μL using a gentle stream of nitrogen. Store the extracts in a refrigerator at 4 ^{o}C or lower away from light until GC/MS analysis (Section 7).

B. Alumina Column

Elute the column with 50 mL of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow.

Transfer 1 mL of the sample extract onto the column. Rinse out extract vial with two 1 mL rinses of hexane and add it to the top of the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column.

Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 2 mL of hexane was used as a rinse, then 12 mL of additional hexane should be used. Collect the effluent and concentrate to about 2 mL using the K-D apparatus or a rotary evaporator.

Transfer to a minivial using a hexane rinse and concentrate to 450 μL using a gentle stream of nitrogen. Store the extracts at 4°C or lower away from light until GC/MS analysis.

7 GC/MS ANALYSIS

7.1 APPARATUS

7.1.1 Gas Chromatograph

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The GC injection port must be designed for capillary columns. Splitless injection is recommended.

7.1.2 Column

Fused silica columns are required.

A. 30 M long x 0.32 mm ID fused silica capillary column coated with a crosslinked phenyl methyl silicone such as DB-5.

B. Any column equivalent to the DB-5 column may be used as long as it has the same separation capabilities as the DB-5.

7.1.3 Mass Spectrometer

7.1.3.1 Low Resolution

A low resolution mass spectrometer (LRMS) equipped with a 70 eV (nominal) ion source operated in the electron impact ionization mode, and capable of monitoring all of the ions in each Selected Ion Monitoring (SIM) group (Table 13) with a total cycle time of 1 second or less.

7.1.3.2 High Resolution

The high resolution mass spectrometer (HRMS) must be capable of operation in the SIM mode at a resolving power of 8,000. Electron impact ionization must be used. The mass spectrometer must be capable of monitoring all of the ions listed in each of the three SIM descriptors (Table 14) with a total cycle time of 1 second or less.

7.1.4 GC/MS Interface

Any gas chromatograph to mass spectrometer interface may be used as long as it gives acceptable calibration response for each analyte of interest at the desired concentration and achieves the required tuning performance criteria (Sections 7.3.5 and 7.3.6). All components of the interface must be glass or glass-lined materials. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the mass spectrometer ion source without being exposed to the ionizing electron beam.

7.1.5 Data Acquisition System

A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and plot a Selected Ion Current Profile or SICP (a plot of the abundances of the selected ions versus time or scan number). Software must also be able to integrate, in any SICP, the abundance between specified time or scan-number limits.

The data system must provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals.

The data system must also be able to provide hard copies of a summary report of the results of the GC/MS runs. Figures 14A to 14C show the minimum data that the system must be available to provide.

7.2 REAGENTS

7.2.1 Stock Standard Solution (1.00 µg/µL)

Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.2.2 Preparation of Stock Solutions

A. Calibration standards. Prepare stock calibration standard solutions of each of the PAH analytes by accurately weighing the required amount of pure material. Dissolve the material in isooctane and dilute to volume. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

   Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

B. Internal standards. Prepare stock solutions in isooctane of the fourteen internal standards listed in Table 4 or 4A at concentrations of 1000 ng/µL.

C. Recovery standards. Prepare stock solutions in isooctane of the three recovery standards listed in Table 4 or 4A at concentrations of 1000 ng/µL.

D. Alternate standard. Prepare a stock solution in isooctane of the alternate standard listed in Table 4 or 4A at a concentration of 1000 ng/µL.

E. Surrogate standards. Prepare stock solutions in isooctane of the surrogate standards listed in Table 4 or 4A at a concentration of 1000 ng/μL.

Store stock standard solutions in Teflon®-sealed screw-cap bottles at 4°C and protect from light. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just before using them to prepare calibration standard solutions or spiking solutions.

Replace stock standard solutions every 12 months or more frequently if comparison with quality control check samples according to Section 7.4.1 indicates a problem.

7.2.3 Calibration Standards

Prepare calibration standards at a minimum of five concentration levels. One of the calibration standards should be at a concentration near, but above, the method detection limit. The others should include the range of concentrations found in real samples but should not exceed the linear range of the GC/MS system.

Prepare calibration working standard solutions by combining appropriate volumes of individual or mixed calibration standards with internal standard, recovery standards, and alternate standard spiking solution and making up to volume with hexane to obtain the solution concentrations given in Tables 5, 6, and 6A. The suggested ranges are 0.25 ng/μL to 5.0 ng/μL for LRMS and 10 pg/μL to 500 pg/μL for HRMS.

All standards must be stored at 4°C or lower and must be freshly prepared if the check according to Section 7.4.1 indicates a problem.

7.2.4 Internal Standard (IS) Spiking Solution

The concentration of internal standard in the IS spiking solution must be such that the amount of solution added to the calibration standard solution and the sample is at least 2 mL.

Prepare the internal standard spiking solution by using appropriate volumes of stock solutions of Section 7.2.2B to give the concentrations shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the internal standards that must be added to the sample (Table 7 or 7A) before extraction to achieve, in a final volume of 500 μL, the sample extract concentrations shown in Table 8 for LRMS and Table 8 or 8A for HRMS analysis. The target concentrations in Tables 8 and 8A are based on a final volume of 500 μL and 100 percent recovery of the internal standards added to the sample.

7.2.5 Recovery Standard Spiking Solution

The concentration of recovery standard in this spiking solution must be such that the amount of solution added to the concentrated sample extract is 50 μL to give a final extract volume of 500 μL.

Use an appropriate volume of stock solution of Section 7.2.2C to prepare a recovery standard spiking solution with the concentrations shown in Table 4or 4A. Store at 4 °C or lower.

A volume of 50 µL of the recovery standard spiking solution shown in Table 4 or 4A will provide the amount of each recovery standard required by Table 7 or 7A to achieve the target sample concentration of Table 8 or 8A. Final volumes, may be adjusted depending on the target detection limit.

7.2.6 Surrogate Standard Spiking Solution

The concentration of surrogate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sorbent module is at least 2 mL.

Prepare the surrogate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2E to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the surrogate standards that must be added to the sample (Table 7 or 7A) before sampling to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.7 Alternate Standard Spiking Solution

The concentration of alternate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sample extracts is at least 2 mL.

Prepare the alternate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2D to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the alternate standard that must be added to the sample (Table 7 or 7A) before extraction to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.8 Calibration Check Standard

The calibration check standard shall be used for column performance checks, and for continuing calibration checks. Solution #3 from Table 5 shall be the calibration check standard for LRMS, while Solution #3 from Table 6 or 6A shall be the calibration check standard for HRMS.

7.3 INITIAL CALIBRATION

An acceptable initial calibration (7.3.8) is required before any samples are analyzed, and then intermittently throughout sample analyses as dictated by results of the continuing calibration procedures described in Section 7.4. The GC/MS system must be properly calibrated and the performance documented during the initial calibration.

7.3.1 Retention Time Windows

Before sample analysis, determine the retention time windows during which the selected ions will be monitored. Determine Relative Retention Time (RRTs) for each analyte by using the corresponding ^{2}H - labelled standard.

7.3.2 GC Operating Conditions

The GC column performance (Section 7.3.5) must be documented during the initial calibration. Table 10 summarizes GC operating conditions known to produce acceptable results with the column listed. The GC conditions must be established by each analyst for the particular instrumentation by injecting aliquots of the calibration check standard (7.2.8). It may be necessary to adjust the operating conditions slightly based on observations from analysis of these solutions. Other columns and/or conditions may be used as long as column performance criteria of Section 7.3.5 are satisfied.

Thereafter the calibration check standard must be analyzed daily to verify the performance of the system (Section 7.4).

7.3.3 GC/MS Tuning Criteria

A. Low Resolution Mass Spectrometry

Use a compound such perfluorotributylamine (PFTBA) to verify that the intensity of the peaks is acceptable. If PFTBA is used, mass spectral peak profiles for m/z 69, 219 and 264 must be recorded, plotted, and reported. The scan should include a minimum of +/- two peaks (i.e, m/z 67-71 for the m/z 69 profile).

B. High Resolution Mass Spectrometry

Tune the instrument to meet the minimum required resolving power of 8,000 at 192.9888 or any other PFK reference signal close to 128.0626 (naphthalene). Use peak matching and the chosen PFK reference peak to verify that the exact mass of m/z 242.9856 is within 5 ppm of the required value. The selection of the low and high mass ions must be such that they provide the largest voltage jump performed in any of the three mass descriptors.

7.3.4 MS Operating Conditions

A. Low Resolution Mass Spectrometry

Analyze standards and samples with the mass spectrometer operating in the Selected Ion Monitoring (SIM) mode with a total cycle time of 1 second or less.

B. **High Resolution Mass Spectrometry**

Analyze standards and samples with the mass spectrometer operating in the SIM mode with a total cycle time (including the voltage reset time) of one second or less.

A reference compound such as Perfluorokerosene (PFK) must be used to calibrate the SIM mass range. One PFK ion per mass descriptor is used as a lock-mass ion to correct for mass drifts that occur during the analysis. In addition to the lock-mass ion, several ions characteristic of PFK are monitored as QC check ions (Table 13).

7.3.5 **GC Column Performance Criteria**

A. The height of the valley between anthracene and phenanthrene at m/z 178 or the ^{2}H-analogs at m/z 188 shall not exceed 50 percent of the taller of the two peaks.

B. The height of the valley between benzo(b)fluoranthene and benzo(k)fluoranthene shall not exceed 60 percent of the taller of the two peaks.

If these criteria are not met and normal column maintenance procedures are not successful, the column must be replaced and the initial calibration repeated.

7.3.6 **Mass Spectrometer Performance**

A. **Low Resolution Mass Spectrometry**

Verify acceptable sensitivity during initial calibration. Demonstrate that the instrument will achieve a minimum signal-to-noise ratio of 10:1 for the quantitation and confirmation ions when the calibration standard with the lowest concentration is injected into the GC/MS system.

B. **High Resolution Mass Spectrometry**

Record the peak profile of the high mass reference signal (m/z 242.9856) obtained during peak matching by using the low-mass PFK ion at m/z 192.9888 (or lower in mass) as a reference. The minimum resolving power of 8,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity.

The format of the peak profile representation must allow manual determination of the resolution, that is, the horizontal axis must be a calibrated mass scale (amu or ppm per division).

The peak width of the high mass ion at 5 percent of the peak height must not exceed 125 ppm in mass.

7.3.7 Calibration Procedure

Using stock standards, prepare at least five calibration standard solutions, using the same solvent that was used in the final sample extract. Keep the recovery standards and the internal standards at fixed concentrations. Adjust the concentrations recommended in Tables 5 and 6, if necessary, to ensure that the sample analyte concentration falls within the calibration range. The calibration curve must be described within the linear range of the method. Calibrate the mass spectrometer response using a 2 μL aliquot of each calibration solution. Analyze each solution once.

Calculate:

A. the relative response factors (RRFs) for each analyte as described in Sections 7.7.1.1, 7.7.1.2, and 7.7.1.3.

B. the mean RRFs as required by Section 7.7.1.4.

C. the standard deviation (SD) and relative standard deviation (RSD) as required by Section 7.7.2.

Report all results as required by Section 10.2.

7.3.8 Criteria for Acceptable Initial Calibration

An acceptable initial calibration must satisfy the following performance criteria:

A. The requirements of Sections 7.3.5 and 7.4.6 must be met.

B. The signal to noise ratio (S/N) for the GC signals present in every selected ion current profile (SICP) must be > 10:1 for the labelled standards and unlabelled analytes.

C. The percent relative standard deviation for the mean relative response factors must be no greater than 30 percent for both the unlabelled analytes and internal standards (Section 7.7.2). Otherwise, take corrective action as required by Section 7.7.2.

7.4 CONTINUING CALIBRATION

The continuing calibration consists of an analysis of the calibration check standard (Section 7.2.8) once during each 12-hour shift as described in Section 7.4.1.

The criteria for acceptable continuing calibration are given in Section 7.4.2. These must be satisfied or else corrective action must be taken as required by Section 7.4.2.

7.4.1 Calibration Check

The calibration check standard (Section 7.2.8) must be analyzed at the beginning and end of each analysis period, or at the beginning of every 12-hour shift if the laboratory operates during consecutive 12 hour shifts.

Inject a 2-μL aliquot of the calibration check standard (Section 7.2.8) into the GC/MS. Use the same data acquisition parameters as those used during the initial calibration.

Check the retention time windows for each of the compounds. They must satisfy the criterion of Section 7.4.2C

Check for GC resolution and peak shape. Document acceptable column performance as described in Section 7.3.5. If these criteria are not met, and normal column maintenance procedures are unsuccessful, the column must be replaced and the calibration repeated.

Calculate the continuing RRF and ΔRRF, the relative percent difference (RPD) between the daily RRF and the initial calibration mean RRF as described in Section 7.7.1.5.

Report the results as required by Section 10.2.

7.4.2 Continuing Calibration Performance Criteria

An acceptable continuing calibration must satisfy the following performance criteria:

A. The signal to noise ratio (S/N) for the GC signals present in the selected ion current profile (SICP) for all labelled and unlabelled standards must be $\geq$ 10:1.

B. The measured RRFs of all analytes (labelled and unlabelled) must be within 30 percent of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

C. The retention time for any internal standard must not change by more than 30 seconds from the most recent calibration check. Otherwise, inspect the chromatographic system for malfunctions and make the necessary corrections. Document acceptable performance with a new initial calibration curve.

7.5 GC/MS ANALYSIS

The laboratory may proceed with the analysis of samples and blanks only after demonstrating acceptable performance as specified in Sections 7.3 and 7.4.

Analyze standards, field samples and QA samples (Section 8.1) with the gas chromatograph and mass spectrometer operating under the conditions recommended in Sections 7.3.2 and 7.3.4.

Approximately I hr before HRGC/LRMS or HRGC/HRMS analysis, adjust the sample extract volume to approximately 500 μL. This is done by adding 50 μL of the recovery standard spike solution (Section 7.2.5, and Table 4 or 4A) to the 450 μL final volume (Section 6.6.2) of the concentrated sample extract give the sample extract concentration required by Table 8 or 8A. If the sample volume must be changed to achieve a desired detection limit, the recovery spike solution concentration must be adjusted accordingly to achieve the target concentrations of Table 8 or 8A.

Inject a 2 μL aliquot of the sample extract (Section 6.6.2) on to the DB-5 column. Use the same volume as that used during calibration. Recommended GC/MS operating conditions are described in Section 7.3.

The presence of a given PAH is qualitatively confirmed if the criteria of Section 7.6.1 are satisfied.

The response for any quantitation or confirmation ion in the sample extract must not exceed the response of the highest concentration calibration standard.

Collect, record, and store the data for the calculations required by Sections 9.1.7, 9.1.8, 9.1.9, and 9.1.10. Report the results as required by Section 10.2.

7.6 QUALITATIVE ANALYSIS

7.6.1 Identification Criteria

7.6.1.1 Ion Criteria

For LRMS analysis, all quantitation and confirmation ions (Table 13) must be present.

7.6.1.2 Relative Retention Time (RRT) Criteria

The relative retention time (RRT) of the analyte compared to the RRT for the ^{2}H-standards must be within $\pm$0.008 RRT units of the relative retention times obtained from the continuing calibration (or initial calibration if this applies).

7.6.1.3 Signal to Noise Ratio

The signal to mean noise ratio must be 10:1 for the internal standards. This ratio for the unlabelled compounds must be greater than 2.5 to 1 for the quantitation ions for HRMS and for both quantitation and confirmation ions for LRMS.

If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst must employ additional cleanup on the archive sample and reanalyze.

7.7 QUANTITATIVE ANALYSIS

7.7.1 Relative Response Factors (RRFs)

7.7.1.1 RRF for Unlabelled PAH and Surrogate Standards from Initial Calibration Data

Use the results of the calibration and Equation 429-13 to calculate the relative response factors (RRFs) for each calibration compound and surrogate standard in each calibration solution (Tables 5 or 5A). Table 11 shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5. Table 11A shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.2 RRF for Determining Internal Standard Recovery

Use the results of the calibration in Equation 429-18 to calculate the relative response factor for each internal standard relative to an appropriate recovery standard. Table 11 shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5. Table 11A shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.3 RRF for Determining Alternate Standard Recovery

Use the calibration results and Equation 429-19 to calculate the response factor for the alternate standard relative to the appropriate recovery standard. Table 11 shows the assignment of the recovery standards for calculating alternate standard recovery for the calibration solution shown in Table 5. for the calibration solution shown in Table 5. Report the results as required by Section 10.2.

7.7.1.4 Mean Relative Response Factor

Use Equation 429-20 to calculate the mean RRF for each compound (unlabelled calibration standards, surrogate standards, internal standards and alternate standard). This is the average of the five RRFs calculated for each compound (one RRF calculated for each calibration solution). The mean RRF may be used if the linearity criterion of Section 7.7.2 is satisfied.
Report the results as required by Section 10.2.

7.7.1.5 RRF from Continuing Calibration Data

Analyze one or more calibration standards (one must be the medium level standard) on each work shift of 12 hours or less. Use Equations 429-17, 429-18, and 429-19 to calculate the RRFs for each analyte. Use Equation 429-22 to calculate ΔRRF, the relative percent difference

between the daily RRF and the mean RRF calculated during initial calibration. Check whether the performance criterion of Section 7.4.2B is satisfied. Report the results as required by Section 10.2.

7.7.2 Relative Standard Deviation of Relative Response Factors

For each analyte, calculate the sample standard deviation (SD) of the RRFs used to calculate the mean RRF. Use Equation 429-21 to calculate the percent relative standard deviation (%RSD) for each analyte. The analyst may use the mean RRF if the percent relative standard deviation of the RRFs is 30% or less. If the RSD requirement is not satisfied, analyze additional aliquots of appropriate calibration solutions to obtain an acceptable RSD of RRFs over the entire concentration range, or take action to improve GC/MS performance. Otherwise, use the complete five point calibration curve for that compound.

8 QUALITY ASSURANCE/QUALITY CONTROL

Each laboratory that uses this method is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability (according to Sections 7.3 and 8.1.3.1), and periodic analysis of blanks and spiked samples as required in Sections 8.1.1 and 8.1.3.2 as a continuing check on performance.

The laboratory must maintain performance records to document the quality of data that are generated. The results of the data quality checks must be compared with the method performance criteria to determine if the analytical results meet the performance requirements of the method. The laboratory must generate accuracy statements as described in Section 8.4.1.

8.1 QA SAMPLES

8.1.1 Laboratory Method Blank

The analyst must run a laboratory method blank with each set of 15 or fewer samples. The method blank must be a resin sample from the same batch used to prepare the sampling cartridge and the laboratory control samples. The method blank must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

The analyst shall perform all of the same procedures on the method blank as are performed on the solid samples (Section 6.5.2.1) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

8.1.2 Performance Evaluation Samples

The laboratory should analyze performance evaluation samples quarterly when these samples become available. These samples must be prepared and analyzed by the same methods used for the field samples. Performance for the most recent quarter should be reported with the results of the sample analysis.

8.1.3 Laboratory Control Sample (LCS)

8.1.3.1 Initial Demonstration of Laboratory Capability

Before performing sample analyses for the first time, the analyst shall demonstrate the ability to generate results of acceptable precision and accuracy by using the following procedures.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike at least four resin samples cleaned as described in Section 4.2.2 with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure.

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A) percent recoveries for the internal standards and alternate standard,
(B) the mass of each target analyte in μg/sample or ng/sample,
(C) the average of the results for the four analyses in μg/sample or ng/sample,
(D) the average recovery (R) as a percentage of the amount added, and
(E) the relative standard deviation S_R.

Report the results as required by Section 10.2.4.

If all the acceptance criteria of Section 8.2.6 are satisfied for all of the target PAH, the analyst may begin analysis of blanks and samples. Otherwise, corrective action must be taken as required by Section 8.2.6.

8.1.3.2 Ongoing Analysis of LCS

The analyst must run two laboratory control samples with each set of 15 or fewer samples. The resin for the LCS must be taken from the same batch used to prepare the sampling cartridge and the laboratory method blank. The LCS resin must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike each resin sample with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure.

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A) percent recoveries for the internal standards and alternate standard,
(B) the mass of each target analyte in μg/sample or ng/sample,
(C) the average of the results for the two analyses in μg/sample or ng/sample,
(D) the average recovery as a percentage of the amount added, and
(E) the relative percent difference for the two analyses.

Report the results as required by Section 10.2.

Add the results which satisfy the performance requirements of Section 8.2.6 to the results of the initial LCS analyses (8.1.3.1) and previous ongoing data for each compound in the LCS sample.

Update the charts as described in Section 8.4.1.

8.2 ACCEPTANCE CRITERIA

8.2.1 Blank Trains

The levels of any unlabelled analyte quantified in the blank train must not exceed 20 percent of the level of that analyte in the sampling train. If this criterion cannot be met, calculate a reporting limit that is five times the blank value (Equations 429-32 and 429-33). Do not subtract the blank value from the sample value.

8.2.2 Surrogate Standard Recovery

Acceptable surrogate (field spike) recoveries should range from 50 to 150 percent. If field spike recoveries are not within the acceptable range, this must be clearly indicated in the laboratory report. The affected sampling run must be identified in the report of the calculated emissions data.

8.2.3 Internal Standard Recovery

Recoveries for each of the internal standards must be greater than 50 percent and less than 150 percent of the known value.

If internal standard recoveries are outside of the acceptable limits, the signal to noise ratio of the internal standard must be greater than 10. Otherwise the analytical procedure must be repeated on the stored portion of the extract.

NOTE: This criterion is used to assess method performance. As this is an isotope dilution technique, it is, when properly applied, independent of internal standard recovery. Lower recoveries do not necessarily

invalidate the analytical results for PAH, but they may result in higher detection limits than are desired.

If low internal standard recoveries result in detection limits that are unacceptable, the cleanup and GC/MS analysis must be repeated with the stored portion of the extract. If the analysis of the archive sample gives low recoveries and high detection limits, the results of both analyses must be reported.

8.2.4 Laboratory Method Blank

The laboratory method blank must not contain any of the target analytes listed in Table 1 at levels exceeding the PQL or 5 percent of the analyte concentration in the field sample.

If the method blank is contaminated, check solvents, reagents, standard solutions apparatus and glassware to locate and eliminate the source of contamination before any more samples are analyzed. Table 3 shows those compounds that commonly occur as contaminants in the method blank, and the ranges of concentrations that have been reported.

If field samples were processed with a laboratory method blank that showed PAH levels greater than 5 percent of the field sample, they must be re-analyzed using the archived portion of the sample extract.

Recoveries of the internal standards must satisfy the requirements of 8.2.3. If the internal standard recoveries are less than 50%, the S/N ratio must be greater than 10 for the internal standard.

8.2.5 Performance Evaluation Sample

The following will be a requirement when performance evaluation samples become available, and performance criteria have been established:

Performance for the most recent quarter must be reported with the results of the sample analysis. If the performance criteria (to be established) are not achieved, corrective action must be taken and acceptable performance demonstrated before sample analysis can be resumed.

8.2.6 Laboratory Control Samples

8.2.6.1 Initial and Ongoing Analysis

The signal of each analyte in the initial and ongoing laboratory control samples must be at least 10 times that of the background.

Acceptable accuracy is a percent recovery between 50 and 150 percent.
Acceptable precision for the initial LCS samples is a relative standard deviation (RSD) of 30 percent or less.
Acceptable precision for the ongoing analysis of duplicate samples is a relative percent difference of 50 percent or less.

If the RSD for the initial demonstration exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.
If the RPD for any ongoing duplicate analyses exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

Beginning with Section 8.1.3.1, repeat the test for those analytes that failed to meet the performance criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.1.3.1 for the initial analysis and Section 8.3.1.2 for the ongoing analysis.

8.3 ESTIMATION OF THE METHOD DETECTION LIMIT (MDL) AND PRACTICAL QUANTITATION LIMIT (PQL)

8.3.1 Initial Estimate of MDL and PQL

The analyst shall prepare a batch of XAD-2 resin as described in Sections 4.2.2.1 to 4.2.2.3, then check for contamination as required by Section 4.2.2.4. Identify those PAH analytes present at background levels that are too high for the MDL determination. Use the procedure of Appendix A to calculate MDLs for the remaining target PAH compounds. A suggested initial spike level for the MDL determination is 5 times a theoretical method quantitation limit (TMQL) estimated according to Equation 429-16.

$$TMQL = C \times \frac{V}{P} \times 100 \times 2 \qquad 429\text{-}16$$

Where:

C = the concentration of the PAH in the lowest concentration calibration standard used in the initial calibration, (ng/μL)

V = the final extract volume, (μL)

P = the assumed percent recovery (50%) of the internal standard

2 = a factor to account for the fact that the final extract volume (V) contains one half of the analyte in the sample. The other half is archived.

8.3.2 Ongoing Estimation of MDL and PQL

Once every quarter in which this method is used, the analytical laboratory must analyze one spiked resin sample as described in Appendix A. Include all initial and quarterly results in the calculation of the standard deviation and MDL for each analyte that has not been identified as a common contaminant of the XAD-2 resin.

If the MDL for any analyte exceeds the MDL established during the initial determination, take corrective action as necessary, and repeat the monthly analysis. If any MDL still exceeds the initial MDL, then the initial standard deviation estimation procedure (Appendix A) must be repeated.

8.4 LABORATORY PERFORMANCE

The analyst must have documented standard operating procedures (SOPs) that contain specific stepwise instructions for carrying out this method. The SOPs must be readily available and followed by all personnel conducting the work. The SOP must be made available for review upon request by the Executive Officer, the tester or reviewer of the analytical results. The analyst may impose restrictions on the dissemination of the information in the SOP.

The analyst must have documented precision and accuracy statements (Section 8.4.1) readily available.

The analyst must have results of the initial and ongoing estimates of the MDL (Sections 8.3.1 and 8.3.2) readily available.

8.4.1 Precision and Accuracy Statement

The precision and accuracy statements for the analytical procedure shall be based on the results of the initial and ongoing LCS analyses. The frequency of analysis is stated in Section 8.1.3.

Prepare a table of the recoveries and the relative percent difference for each ongoing analysis of the LCS and LCS duplicate. Figure 15A is an example of such a table. This must be included in the analytical data package submitted for each set of sample analyses.

Prepare a quality control chart for each target analyte that provides a graphic representation of continued laboratory performance for that target analyte. Figure 15B is an example QC chart for benzo(a)pyrene.

9. CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

9.1 ANALYST'S CALCULATIONS

The analyst shall carry out the calculations described in Sections 9.1.1 to 9.1.11.

9.1.1 Relative Response Factors (RRF) for Unlabelled PAH and Surrogate Standards

Calculate the RRF for each target unlabelled PAH analyte and surrogate standard in each calibration solution . Use Equation 429-17 and the data obtained during initial calibration (7.3.7) or continuing calibration (7.4.1).

$$RRF_s = \frac{A_s \times Q_{is}}{A_{is} \times Q_s} \qquad 429\text{-}17$$

Where:

A_s = Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 11 or 11A, 13, and 14).

A_{is} = Area of the response for characteristic ions of the appropriate internal standard (Tables 11 or 11A, 13, and 14).

Q_s = Amount of the unlabelled PAH calibration analyte or surrogate standard injected on to GC column, ng.

Q_{is} = Amount of the appropriate internal standard injected on to GC column, ng.

9.1.2 RRF for Determination of Internal Standard Recovery

Calculate RRF_{is} according to Equation 429-18, using data obtained from the analysis of the calibration standards.

$$RRF_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times Q_{is}} \qquad 429\text{-}18$$

Where:

A_{rs} = Area of the response for characteristic ions of the appropriate recovery standard (Tables 11 or 11A, 13, and 14).

Q_{rs} = Amount of the appropriate recovery standard injected on to GC column, ng.

9.1.3 RRF for Determination of Alternate Standard Recovery

Calculate RRF_{as} according to Equation 429-19, using data obtained from the analysis of the calibration standards.

$$RRF_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times Q_{as}} \qquad 429\text{-}19$$

Where:

A_{as} = Area of the response for characteristic ions of the alternate standard (Tables 13 and 14).

Q_{as} = Amount of alternate standard injected on to the GC column, ng.

9.1.4 Mean Relative Response Factors ($\overline{RRF}$)

Calculate the mean RRF for each target unlabelled PAH, surrogate standard, internal standard and alternate standard using Equation 429-20 and the RRFs calculated according to Sections 9.1.1, 9.1.2, and 9.1.3.

$$\overline{RRF} = \frac{1}{n} \sum_{i=1}^{n} (RRF)_i \qquad 429\text{-}20$$

Where:

RRF_i = RRF calculated for calibration solution "i" using one of Equations 429-17, 429-18 or 429-19.

n = The number of data points derived from the calibration. The minimum requirement is a five-point calibration (Section 7.2.3, Tables 5 and 6 or 6A)

9.1.5 Percent Relative Standard Deviation (%RSD) of Relative Response Factors

Use Equation 429-21 to calculate the relative standard deviation of the Relative Response Factors for each analyte.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100\% \qquad 429\text{-}21$$

Where:

$\overline{RRF}$ = Mean relative response factor of a given analyte as defined in Sections 7.7.1.4 and 9.1.4.

SD = The sample standard deviation of the relative response factors used to calculate the mean RRF.

9.1.6 Continuing Calibration ΔRRF

Use Equation 429-22 to calculate ΔRRF, the relative percent difference (RPD) between the daily RRF and the mean RRF calculated during initial calibration.

$$\Delta RRF = \frac{RRF_c - \overline{RRF}}{\overline{RRF}} \times 100\% \qquad 429\text{-}22$$

Where:

RRF_c = The RRF of a given analyte obtained from the continuing calibration (Section 7.4).

9.1.7 Percent Recovery of Internal Standard, R_{is}

Calculate the percent recovery, R_{is} for each internal standard in the sample extract, using Equation 429-23.

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times \overline{RRF_{is}} \times Q_{is}} \times 100\% \qquad 429\text{-}23$$

Where:

$\overline{RRF_{is}}$ = Mean relative response factor for internal standard (Equations 429-18 and 429-20).

9.1.8 Percent Recovery of Surrogate Standard, R_{ss}

Calculate the percent recovery, R_{ss} for each surrogate standard in the sample extract, using Equation 429-24.

$$R_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times \overline{RRF_s} \times Q_{ss}} \times 100\% \qquad 429\text{-}24$$

Where:

A_{ss} = Area of the response for characteristic ions of the surrogate standard (Tables 13 and 14).

Q_{ss} = Amount of the surrogate standard added to resin cartridge before sampling, ng.

$\overline{RRF_s}$ = Mean relative response factor for surrogate standard (Equations 429-17 and 429-20).

9.1.9 Percent Recovery of Alternate Standard, R_{as}

Calculate the percent recovery, R_{as} for the alternate standard in the sample extract, using Equation 429-25.

$$R_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times \overline{RRF_{as}} \times Q_{as}} \times 100\% \qquad 429\text{-}25$$

Where:

$\overline{RRF_{as}}$ = Mean relative response factor for alternate standard (Equations 429-19 and 429-20).

9.1.10 Mass of the Target Analytes and Surrogate Standards in Emissions Sample or Blank Train

Use Equation 429-26 to determine the total mass of each PAH compound or surrogate standard in the sample:

Report the PQL (9.1.11) for those analytes that were not present at levels higher than the PQL provided to the tester prior to testing (2.3.3).

$$M = \frac{Q_{is} \times A_s}{A_{is} \times \overline{RRF}} \qquad 429\text{-}26$$

Where:

M = Mass (ng) of surrogate standard (M_s) or target analyte (M_t) detected in the sample.

Q_{is} = Amount of internal standard or surrogate standard added to each sample.

A_s = Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 13 and 14).

A_{is} = Area of the response for characteristic ions of the appropriate internal standard (Tables 13, and 14).

$\overline{RRF}$ = Mean relative response factor of a given analyte calculated as required by Sections 7.7.1.4 and 9.1.4.

9.1.11 Analytical Reporting Limit

The analyst shall report the PQL (Section 2.3.3) for those analytes that were not present in the emissions sample or blank train at levels higher than the pre-test estimate of the PQL.

9.2 TESTER'S CALCULATIONS

9.2.1 Sample/Blank Train PAH Mass Ratio

Use Equation 429-27 to calculate the sample/blank train mass ratio for each PAH detected at levels above the MDL in both the field sample and the blank train.

$$RATIO = \frac{M_t}{M_{BT}} \qquad 429\text{-}27$$

Where:

M_t = Mass of target PAH analyte detected in the sampling train (Equation 429-26).

M_{BT} = Mass of the same PAH analyte detected in the blank train.

If the sample to blank train PAH mass ratio is less than five, calculate the reporting limit for the tested source as required by Section 9.2.4.2. Do not calculate M_c (Section 9.2.2) or M_e (Section 9.2.3) for the emissions report.

9.2.2 PAH Concentration in Emissions

Use Equation 429-28 to calculate the concentration in the emissions of 1) the PAH analytes detected in the sampling train but not in the blank train, and 2) the PAH analytes that satisfy the minimum sample to blank train mass ratio required by Section 9.2.1.

$$M_c = \frac{M_t}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}28$$

Where:

M_c = Concentration of PAH in the gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

M_t = Mass of PAH compound in gas sample, ng (Equation 429-26)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscf (Equation 429-10)

0.028317 = Factor for converting dscf to dscm.

9.2.3 PAH Mass Emission Rate

Use Equation 429-29 to calculate the mass emission rate for each PAH compound that satisfies the minimum sample/blank train PAH mass ratio (Section 9.2.1).

$$M_e = \frac{M_s}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}29$$

Where:

M_e = Mass emission rate for PAH analyte, ng/second

M_t = Mass of PAH compound in the gas sample, ng (Equation 429-26)

Q_{std} = Average stack gas dry volumetric flow rate corrected to standard conditions, dscf/min.

60 = Factor for converting minutes to seconds

9.2.4 Source Reporting Limit

9.2.4.1 PAH Not Detected in Either Sampling or Blank Train

Use Equation 429-30 or 429-31 to calculate the reporting limit for those analytes that were not detected at levels above the PQL in either the sampling or blank train.

$$RL_{cs} = \frac{PQL}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}30$$

$$RL_{es} = \frac{PQL}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}31$$

Where:

RL_{cs} = Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

RL_{es} = Reporting limit for the tested source, (ng/sec.).

0.028317 = Factor for converting dscf to dscm.

60 = Factor for converting minutes to seconds.

9.2.4.2 PAH Detected in Blank Train and Sample/Blank Train Ratio < 5

If the sample to blank train PAH mass ratio is less than five, then Equation 429-32 or 429-33 shall be used to calculate the reporting limit for that PAH.

$$RL_{cb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}32$$

$$RL_{eb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}33$$

Where:

RL_{cb} = Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

RL_{eb} = Reporting limit for the tested source, (ng/sec.).

M_{BT} = The total mass of that PAH analyte in the field blank train.

10. REPORTING REQUIREMENTS

The source test protocol must contain all the sampling and analytical data required by Sections 2.2 to 2.5, 4.2.1.1, and 4.2.2.4, as well as the information listed in Sections 10.1 and 10.2 that pertain to identification and quantitation of the samples.

The emissions test report must contain all of the sampling and analytical data necessary to calculate emissions values for the target analytes or to demonstrate satisfactory performance of the method.

The end user or reviewer should be able to obtain from the source test report all information necessary to recalculate all reported test method results or to verify that all required procedures were performed.

Any deviations from the procedures described in this method must be documented in the analytical and sampling report.

10.1 SOURCE TEST PROTOCOL

At a minimum, the source test protocol must include all of the data required by Section 2.2 and the information listed in Sections 10.1.1 through 10.1.4.

10.1.1 Preparation of Filters

A. Manufacturer's lot number for the batch of filters to be used in the test.

B. Contamination check of filter (Section 4.2.1.1)

(i) Date of cleaning.
(ii) Date of PAH analysis.
(iii) Table of results of PAH analysis required by Section 4.2.1. The analytical report must include all of the data listed in Section 10.2.

C. Storage conditions prior to the test (4.3.3)

10.1.2 Preparation of XAD-2 resin

A. ID for the batch to be used in the test. The same batch must be used for the sampling train and the laboratory QC samples.

B. Contamination check of resin (Sections 4.2.2.1 to 4.2.2.4)

(i) Date of cleaning.
(ii) Date of PAH analysis.
(iii) Table of results of PAH analysis required by Secton 4.2.2.4. The analytical report must include all of the data listed in Section 10.2.

C. Addition of surrogate standards to the resin cartridge.

(i) Amount of each compound.
(ii) Date of spiking.

D. Storage conditions prior to the test (Section 4.3.3)

10.1.3 Method Detection Limits and Practical Quantitation Limits

The MDL and PQL for each target analyte determined as required by Sections 2.3.2 and 2.3.3.

10.1.4 Target Sampling Parameters

A. Source target concentration of each emitted PAH of interest.

B. Results of calculations required by Sections 2.5.2 to 2.5.5.

Figure 9 shows the minimum required calculations of target sampling parameters.

10.2 LABORATORY REPORT

The analyst must generate a laboratory report for each pre-test analysis of the sampling media (Sections 2.3, 4.2.2.1, and 4.2.2.4) and each post-test analysis of the sampling trains and laboratory QC samples.

A minimum of 7 post-test analyses are required to determine the emissions from the source and to document the quality of the emissions data. These are the analyses of three sampling runs, one blank train, one laboratory method blank and two laboratory control samples.

At a minimum, any report (data package) from the analyst to the tester shall contain the information listed in Sections 10.2.1 to 10.2.6 pertaining to identification and PAH quantitation of all samples.

10.2.1 Five-point Initial Calibration

The report of the results of the initial five-point calibration must include the data listed in A, B, and C below:

A. Mass chromatograms for each initial calibration solution that show at a minimum:

(i) Instrument ID,
(ii) laboratory sample ID on each chromatogram.
(iii) date and time of GC/MS analysis,
(iv) mass of monitored ions for each compound in the calibration solution - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
(v) retention time for each compound in the calibration solution, and
(vi) either peak height or area of the signals observed for the monitored ion masses.

B. A summary table of the data obtained for each initial calibration solution that shows at a minimum:

(i) Instrument ID,
(ii) laboratory sample ID,
(iii) date and time of GC/MS analysis,
(iv) retention time for each compound - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
(v) relative retention time for each unlabelled PAH,
(vi) either peak height or area of the signals observed for the monitored ion masses,
(vii) the relative response factors for each unlabelled PAH, internal standard, surrogate standard, and alternate standard, and
(viii) analyst's signature

Figure 14A is an example of a summary table that contains the minimum required information for the analysis of a single calibration solution.

C. A summary table that shows at a minimum:

(i) Instrument ID,
(ii) the date and time of the GC/MS analysis,
(iii) the relative response factor (RRF) calculated for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in each calibration solution,
(iv) the average relative response factor ($\overline{RRF}$) calculated for the five point calibration,
(v) the relative standard deviation of the relative response factors, and
(vi) the recovery of each internal standard in percent.

Figure 14B is an example of a report that contains the minimum required information for a five point calibration summary.

10.2.2 Continuing Calibration

The report of the results of a continuing calibration must include the data listed in 10.2.2 A, B, and C below:

A. Mass chromatogram that shows at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data obtained for the continuing calibration that shows at a minimum, the information listed in 10.2.1 B.

C. A summary table that shows at a minimum:

(i) the relative response factor (RRF) for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,
(ii) the average relative response factor ($\overline{RRF}$) for each compound calculated for the five point calibration,

(iii) ΔRRF for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,
(iv) the recovery of each internal standard in percent.

Figure 14C is an example of a summary report that contains the minimum information required by Section 10.2.2C for the analysis of the continuing calibration solution.

10.2.3 Laboratory Method Blank

The laboratory report of the results of the analysis of the method blank must include at a minimum the data listed in 10.2.3 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the data obtained for each method blank that shows at a minimum, the information listed in 10.2.5 B.

C. A summary table that reports the same data as listed in 10.2.5 C below.

10.2.4 Laboratory Control Samples

The report of the results of the analysis of the LCS samples must include at a minimum the data listed in 10.2.4 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data for each sample that shows at a minimum, the information listed in 10.2.1 B, and in addition:

(i) Client's sample ID
(ii) mass of each analyte,
(iii) the recovery of each internal standard, and alternate standard,

Figure 16A is an example of a summary table that contains the minimum information required by 10.2.4 B.

C. A summary table that reports for the two LCS analyses:

(i) client's sample ID,
(ii) sample matrix description,
(iii) date of cleaning of the XAD-2 resin,
(iv) lot number for the resin (resin for all field samples and QA samples must come from the same lot),
(v) date of extraction of LCS samples,

Figure 15A is an example of a summary table that contains the minimum information required by 10.2.4 C.

10.2.5 Emissions Samples

The report of the results of the analyses of the three sampling trains and the blabk train must include the data listed in 10.2.5 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A, and in addition,

(i) client's sample ID

B. A summary table of the data for the analysis of each sample that shows at a minimum, the information listed in 10.2.1 B, and in addition,

(i) client's sample ID
(ii) Date of five point initial calibration (ICAL)
(iii) ICAL ID,
(iv) mass of each analyte,
(v) the recovery of each internal standard, alternate standard and surrogate standards in percent.

Figure 16A is an example of a summary table that contains the minimum information required by 10.2.5 B.

C. A summary table that reports:

(i) client's sample ID (from a chain of custody record submitted by the tester),
(ii) sample matrix description,
(iii) date of cleaning of the XAD-2 resin,
(iv) lot number for the resin (resin for all field samples and QA samples must come from the same lot),
(ii) date of submittal of the tester's samples
(v) date of extraction of samples,
(vi) Initial calibration Run ID,
(vii) Continuing calibration ID

Figure 16B is an example of a summary table that contains the minimum information required by 10.2.5C.

10.2.6 Data Flags

The laboratory report must include an explanation of any qualifiers that are used to indicate specific qualities of the data.

10.3 EMISSIONS TEST REPORT

The emissions test report should include narrative that describes how the test was done. The tester's report must also include all the appropriate sections used in a report from a Method 5 test such as a description of the plant process, sampling port locations, control equipment, fuel being used, general plant load

conditions during the test (description of plant production equipment problems, etc.), and anything else necessary to characterize the condition being tested.

The tester's report must also include all of the information listed in Sections 10.3.1 to 10.3.4.

10.3.1 Tester's Summary of Analytical Results

The tester must summarize the results of the minimum seven analyses required for each source test. At a minimum, the summary must contain the information listed in Figure 17A including all data flags.

The tester must obtain the detailed analytical results (Section 10.2) from the laboratory and include them in the appendices as required below.

10.3.2 Field Data Summary

The report from the tester to the end user must contain a field data summary. This summary must include at a minimum a table of the results of the calculations required by Section 4.5. as well as the values which were used to calculate the reported results. Figure 17B is an example of a field data summary that contains the minimum required information.

10.3.3 PAH Emissions Results

Figure 17C show the calculations of the concentrations and mass emission rates of the target PAH. The reviewer should be able to use the data in Figures 17A and 17B to check the calculations in Figure 17C. The reviewer should also be able to check the appendix to the report to determine the accuracy and the quality of the data summarized by the tester in Figures 17A and 17B.

10.3.4 Appendix to the Emissions Test Report

At a minimum, the following raw data or signed copies must be included in an appendix to the emissions test report.

A. Record of data for sample site selection and minimum number of traverse points.

B. Moisture determination for isokinetic settings.

C. Velocity traverse data.

D. Gas analysis for determination of molecular weight.

E. Calibration records.

F. Method 429 sampling run sheets.

G. PAH laboratory reports listed in Section 10.2

The information listed above is to be considered as the minimum that should be included to characterize a given operating condition. The end user or the executive officer may require additional information for any given project.

11. BIBLIOGRAPHY

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11.2 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3611A. Alumina Column Cleanup and Separation of Petroleum Wastes. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

11.3 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3630B. Silica Gel Cleanup. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

11.4 Thomason, J.R., ed., Cleaning of Laboratory Glassware. Section 3, A, pp 1-7 in "Analysis of Pesticide Residues in Human and Environmental Samples", Environmental Protection Agency, Research Triangle Park, N.C. (1974).

11.5 ARB Method 428. Determination of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Emissions From Stationary Sources. September, 1990.

11.6 U. S. Environmental Protection Agency, Method 1625 Revision B - Semivolatile Organic Compounds by Isotope Dilution. 40 CFR Ch.1 (7-1-95 Edition) Pt. 136, App. A.

11.7 Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March, 1972.

11.8 Shigehara, R.T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News, 2: 4-11. October, 1974

11.9 "Prudent Practices in the Laboratory. Handling and Disposal of Chemicals," National Academy Press. Washington D.C. 1995.

TABLE 1

METHOD 429 TARGET ANALYTES

Naphthalene
2-Methylnaphthalene
Acenaphthene
Acenaphthylene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene
Benzo(ghi)perylene

TABLE 2

PRACTICAL QUANTITATION LIMITS FOR TARGET PAHs

	LRMS (μg/sample)	HRMS (ng/sample)	
Naphthalene	244	480	370
2-Methylnaphthalene	1.25	66	19
Acenaphthene	0.210	5.0	5.0
Acenaphthylene	0.104	5.0	5.0
Fluorene	0.207	16.5	5.5
Phenanthrene	0.85	22	14
Anthracene	0.146	5.0	5.0
Fluoranthene	0.346	5.0	5.0
Pyrene	0.191	5.0	5.0
Benzo(a)anthracene	0.167	5.0	5.0
Chrysene	0.272	5.0	5.0
Benzo(b)fluoranthene	1.119	5.0	5.0
Benzo(k)fluoranthene	0.738	5.0	5.0
Benzo(e)pyrene	0.146	5.0	5.0
Benzo(a)pyrene	0.191	5.0	5.0
Perylene	0.143	5.0	5.0
Indeno(1,2,3-cd)pyrene	0.798	5.0	5.0
Dibenz(a,h)anthracene	0.465	5.0	5.0
Benzo(ghi)perylene	0.305	5.0	5.0

TABLE 3

PAH ANALYSIS BY HRMS OF DIFFERENT LOTS OF CLEANED RESIN

PAH ANALYTES	CONCENTRATION (ng/sample)												
	SAMPLE IDENTIFICATION												
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13
Naphthalene	480	220	198	120	350	340	320	360	370	380	340	520	220
2-Methylnaphthalene	65	32	38	15.6	32	15.6	32	26	19	45	15	32	48
Acenaphthylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Acenaphthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Fluorene	16.5	9.8	13	< 5.0	5.7	5.4	7.4	5.8	5.5	10	5.5	6.8	5.0
Phenanthrene	22	16	32	<12.5*	14	14.8	16	12	14	24	13	<13.0*	14
Anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Chrysene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(b)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(k)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(e)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Indeno(1,2,3-cd)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Dibenzo(a,h)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(g,h,i)perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0

* 5 x the concentration of the lowest calibration standard

TABLE 4

COMPOSITION OF THE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration ng/µl LRMS	Concentration pg/µl HRMS
1.	**Surrogate Standards**		
	d_{10}-Fluorene	1.0	250
	d_{14}-Terphenyl	1.0	250
2.	**Internal Standards**		
	d_8-Naphthalene	1.0	100
	d_{10}-2-Methylnaphthalene	1.0	100
	d_8-Acenaphthylene	1.0	100
	d_{10}-Phenanthrene	1.0	100
	d_{10}-Fluoranthene	1.0	100
	d_{12}-Benzo(a)anthracene	1.0	100
	d_{12}-Chrysene	1.0	100
	d_{12}-Benzo(b)fluoranthene	1.0	200
	d_{12}-Benzo(k)fluoranthene	1.0	200
	d_{12}-Benzo(a)pyrene	1.0	200
	d_{12}-Perylene	1.0	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	200
	d_{14}-Dibenz(a,h)anthracene	1.0	200
	d_{12}-Benzo(ghi)perylene	1.0	200
3.	**Alternate Standard**		
	d_{10}-Anthracene	1.0	100
4.	**Recovery Standards**		
	d_{10}-Acenaphthene	20.0	2000
	d_{10}-Pyrene	20.0	2000
	d_{12}-benzo(e)pyrene	20.0	2000

TABLE 4A

COMPOSITION OF ALTERNATIVE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration pg/μl HRMS
1A.	**Surrogate Standards**	
	d_{12}-Benzo(e)pyrene	250
	d_{14}-Terphenyl	250
2A.	**Internal Standards**	
	d_8-Naphthalene	100
	d_8-Acenaphthylene	100
	d_{10}-Acenaphthene	100
	d_{10}-Fluorene	100
	d_{10}-Phenanthrene	100
	d_{10}-Fluoranthene	100
	d_{12}-Benzo(a)anthracene	100
	d_{12}-Chrysene	100
	d_{12}-Benzo(b)fluoranthene	200
	d_{12}-Benzo(k)fluoranthene	200
	d_{12}-Benzo(a)pyrene	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	200
	d_{14}-Dibenz(a,h)anthracene	200
	d_{12}-Benzo(ghi)perylene	200
3A.	**Alternate Standard**	
	d_{10}-Anthracene	100
4A.	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	2000
	d_{10}-Pyrene	2000
	d_{12}-Perylene	2000

TABLE 5

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (ng/μL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	0.25	0.5	1.0	2.5	5.0
2-Methylnaphthalene	0.25	0.5	1.0	2.5	5.0
Acenaphthene	0.25	0.5	1.0	2.5	5.0
Acenaphthylene	0.25	0.5	1.0	2.5	5.0
Fluorene	0.25	0.5	1.0	2.5	5.0
Phenanthrene	0.25	0.5	1.0	2.5	5.0
Anthracene	0.25	0.5	1.0	2.5	5.0
Fluoranthene	0.25	0.5	1.0	2.5	5.0
Pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)anthracene	0.25	0.5	1.0	2.5	5.0
Chrysene	0.25	0.5	1.0	2.5	5.0
Benzo(b)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(k)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(e)pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)pyrene	0.25	0.5	1.0	2.5	5.0
Perylene	0.25	0.5	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.25	0.5	1.0	2.5	5.0
Dibenz(a,h)anthracene	0.25	0.5	1.0	2.5	5.0
Benzo(ghi)perylene	0.25	0.5	1.0	2.5	5.0
Internal Standards					
d_8-Naphthalene	1.0	1.0	1.0	1.0	1.0
d_{10}-2-Methylnaphthalene	1.0	1.0	1.0	1.0	1.0
d_8-Acenaphthylene	1.0	1.0	1.0	1.0	1.0
d_{10}-Phenanthrene	1.0	1.0	1.0	1.0	1.0
d_{10}-Fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Chrysene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(b)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(k)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-Perylene	1.0	1.0	1.0	1.0	1.0
d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	1.0	1.0	1.0	1.0
d_{14}-Dibenz(a,h)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(ghi)perylene	1.0	1.0	1.0	1.0	1.0

TABLE 5 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (ng/μL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	1.0	1.0	1.0	1.0	1.0
d_{14}-Terphenyl	1.0	1.0	1.0	1.0	1.0
Alternate Standard					
d_{10}-Anthracene	1.0	1.0	1.0	1.0	1.0
Recovery Standards					
d_{10}-Acenaphthene	1.0	1.0	1.0	1.0	1.0
d_{10}-Pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0

TABLE 6

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/μL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500
Internal Standards					
d_8-Naphthalene	100	100	100	100	100
d_8Methylnaphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

TABLE 6 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/μL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-Acenaphthene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-benzo(e)pyrene	200	200	200	200	200

TABLE 6A

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/μL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500
Internal Standards					
d_8-Naphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Acenaphthene	100	100	100	100	100
d_{10}-Fluorene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

TABLE 6A (CONT)

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/μL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{12}-benzo(e)pyrene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-2-Methylnaphthalene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200

TABLE 7

SPIKE LEVELS FOR LABELLED STANDARDS

Time of Addition	Analyte	LRMS (μg/sample)	HRMS (ng/sample)
Before sampling	**Surrogate Standards**		
	d_{10}-Fluorene	2.0	500
	d_{14}-Terphenyl	2.0	500
Before extraction	**Internal Standards**		
	d_8-Naphthalene	2.0	200
	d_{10}-2-Methylnaphthalene	2.0	200
	d_8-Acenaphthylene	2.0	200
	d_{10}-Phenanthrene	2.0	200
	d_{10}-Fluoranthene	2.0	200
	d_{12}-Benzo(a)anthracene	2.0	200
	d_{12}-Chrysene	2.0	200
	d_{12}-Benzo(b)fluoranthene	2.0	400
	d_{12}-Benzo(d)fluoranthene	2.0	400
	d_{12}-Benzo(a)pyrene	2.0	400
	d_{12}-Perylene	2.0	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
	d_{14}-Dibenz(a,h)anthracene	2.0	400
	d_{12}-Benzo(ghi)perylene	2.0	400
Before extraction	**Alternate Standard**		
	d_{10}-Anthracene	2.0	200
Before GC/MS	**Recovery Standards**		
	d_{10}-Acenaphthene	1.0	100
	d_{10}-Pyrene	1.0	100
	d_{12}-benzo(e)pyrene	1.0	100

TABLE 7A

SPIKE LEVELS FOR LABELLED STANDARDS FOR ALTERNATIVE HRMS SPIKING SCHEME

Time of Addition	Analyte	HRMS (ng/sample)
Before sampling	**Surrogate Standards**	
	d_{12}-benzo(e)pyrene	500
	d_{14}-Terphenyl	500
Before extraction	**Internal Standards**	
	d_8-Naphthalene	200
	d_8-Acenaphthylene	200
	d_{10}-Acenaphthene	200
	d_{10}-Fluorene	200
	d_{10}-Phenanthrene	200
	d_{10}-Fluoranthene	200
	d_{12}-Benzo(a)anthracene	200
	d_{12}-Chrysene	200
	d_{12}-Benzo(b)fluoranthene	400
	d_{12}-Benzo(d)fluoranthene	400
	d_{12}-Benzo(a)pyrene	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	400
	d_{14}-Dibenz(a,h)anthracene	400
	d_{12}-Benzo(ghi)perylene	400
Before extraction	**Alternate Standard**	
	d_{10}-Anthracene	200
Before GC/MS	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	100
	d_{10}-Pyrene	100
	d_{12}-Perylene	100

TABLE 8

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT[1]

	ng/μl LRMS	pg/μl HRMS
Surrogate Standards		
d_{10}-Fluorene	2.0	500
d_{14}-Terphenyl	2.0	500
Internal Standards		
d_8-Naphthalene	2.0	200
d_{10}-2-Methylnaphthalene	2.0	200
d_8-Acenaphthylene	2.0	200
d_{10}-Phenanthrene	2.0	200
d_{10}-Fluoranthene	2.0	200
d_{12}-Benzo(a)anthracene	2.0	200
d_{12}-Chrysene	2.0	200
d_{12}-Benzo(b)fluoranthene	2.0	400
d_{12}-Benzo(k)fluoranthene	2.0	400
d_{12}-Benzo(a)pyrene	2.0	400
d_{12}-Perylene	2.0	400
d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
d_{14}-Dibenz(a,h)anthracene	2.0	400
d_{12}-Benzo(ghi)perylene	2.0	400
Alternate Standard		
d_{10}-Anthracene	1.0	200
Recovery Standards		
d_{10}-Acenaphthene	1.0	200
d_{10}-Pyrene	1.0	200
d_{12}-benzo(e)pyrene	1.0	200

[1] Assuming 100 percent recovery.

TABLE 8A

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT OBTAINED WITH ALTERNATIVE HRMS SPIKING SCHEME[1]

	pg/μl HRMS
Surrogate Standards	
d_{12}-benzo(e)pyrene	500
d_{14}-Terphenyl	500
Internal Standards	
d_8-Naphthalene	200
d_8-Acenaphthylene	200
d_{10}-Acenaphthene	200
d_{10}-Fluorene	200
d_{10}-Phenanthrene	200
d_{10}-Fluoranthene	200
d_{12}-Benzo(a)anthracene	200
d_{12}-Chrysene	200
d_{12}-Benzo(b)fluoranthene	400
d_{12}-Benzo(k)fluoranthene	400
d_{12}-Benzo(a)pyrene	400
d_{12}-Indeno(1,2,3,c-d)pyrene	400
d_{14}-Dibenz(a,h)anthracene	400
d_{12}-Benzo(ghi)perylene	400
Alternate Standard	
d_{10}-Anthracene	200
Recovery Standards	
d_{10}-2-Methylnaphthalene	200
d_{10}-Pyrene	200
d_{12}-Perylene	200

[1] Assuming 100 percent recovery.

TABLE 9

CONCENTRATIONS OF COMPOUNDS IN LABORATORY CONTROL SPIKE SAMPLE

	ng/sample	
	LRMS	HRMS
Unlabelled Compounds		
Naphthalene	2.0	1000
2-Methylnaphthalene	2.0	200
Acenaphthylene	2.0	200
Acenaphthene	2.0	200
Fluorene	2.0	200
Phenanthrene	2.0	500
Anthracene	2.0	200
Fluoranthene	2.0	200
Pyrene	2.0	200
Benzo(a)anthracene	2.0	200
Chrysene	2.0	200
Benzo(b)fluoranthene	2.0	200
Benzo(k)fluoranthene	2.0	200
Benzo(e)pyrene	2.0	200
Benzo(a)pyrene	2.0	200
Perylene	2.0	200
Indeno(1,2,3,c-d)pyrene	2.0	200
Dibenz(a,h)anthracene	2.0	200
Benzo(ghi)perylene	2.0	200
Alternate Standard		
d_{10}-Anthracene	2.0	200

TABLE 10

RECOMMENDED GAS CHROMATOGRAPHIC OPERATING CONDITIONS FOR PAH ANALYSIS

Column Type	DB-5
Length (m)	30
ID (mm)	0.25
Film Thickness (μm)	0.32
Helium Linear Velocity (cm/sec)	30
Injection mode	Splitless
Splitless Time (sec)	30
Initial Temperature (^{0}C)	45
Initial Time (min)	4
Program Rate (^{0}C/min)	8
Final Temperature (^{0}C)	300
Final Hold Time	until benzo(ghi) perylene has eluted
Injector Temperature (^{0}C)	320

TABLE 11

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION OF RRFs AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_8-Acenaphthylene
Fluorene	d_{10}-Phenanthrene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Perylene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{10}-Fluorene	d_{10}-Phenanthrene
d_{14}-Terphenyl	d_{10}-Fluoranthene

TABLE 11A

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION OF RRFs AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-Acenaphthene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_{10}-Acenaphthene
Fluorene	d_{10}-Fluorene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{14}-Terphenyl	d_{10}-Fluoranthene
d_{12}-Benzo(e)pyrene	d_{12}-Benzo(a)pyrene

TABLE 12

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-Acenaphthene
d_{10} -2-Methylnaphthalene	d_{10}-Acenaphthene
d_8-Acenaphthylene	d_{10}-Acenaphthene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(k)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(a)pyrene	d_{12}-Benzo(e)pyrene
d_{12}-Perylene	d_{12}-Benzo(e)pyrene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Benzo(e)pyrene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(ghi)perylene	d_{12}-Benzo(e)pyrene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 12A

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-2-Methylnaphthalene
d_{10} -2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
d_8-Acenaphthylene	d_{10}-2-Methylnaphthalene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(k)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(a)pyrene	d_{12}-Perylene
d_{12}-Perylene	d_{12}-Perylene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Perylene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Perylene
d_{12}-Benzo(ghi)perylene	d_{12}-Perylene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 13

QUANTITATION AND CONFIRMATION IONS FOR SELECTED ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Naphthalene	128	127	10
d_8-Naphthalene	136	68	80
2-Methylnaphthalene	142	141	80
d_{10}-2-Methylnaphthalene	152		
Acenaphthylene	152	153	15
d_8-Acenaphthylene	160		
Acenaphthene	154	153	86
d_{10}-Acenaphthene	164		
Fluorene	166	165	80
d_{10}-Fluorene	176		
Phenanthrene	178	176	15
d_{10}-Phenanthrene	188	94	
Anthracene	178	176	15
d_{10}-Anthracene	188	94	
Fluoranthene	202	101	15
d_{10}-Fluoranthene	212	106	
Pyrene	202	101	15
d_{10}-Pyrene	212	106	
Benzo(a)anthracene	228	114	15
d_{12}-Benzo(a)anthracene	240	120	
Chrysene	228	114	15
d_{12}-Chrysene	240	120	
d_{14}-Terphenyl	244	122	15

TABLE 13 (CONT)

QUANTITATION AND CONFIRMATION IONS FOR SELECTED ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Benzo(b)fluoranthene	252	126	25
d_{12}-Benzo(b)fluoranthene	264	132	
Benzo(k)fluoranthene	252	126	25
d_{12}-Benzo(k)fluoranthene	264	132	
Benzo(e)pyrene	252	126	25
d_{12}-Benzo(e)pyrene	264	132	
Benzo(a)pyrene	252	126	25
d_{12}-Benzo(a)pyrene	264	132	
Perylene	252	126	26
d_{12}-Perylene	264	132	
Indeno(1,2,3-cd)pyrene	276	138	28
d_{12}-Indeno(1,2,3-cd)pyrene	288		
Dibenz(ah)anthracene	278	139	24
d_{14}-Dibenz(ah)anthracene	292		
Benzo(ghi)perylene	276	138	37
d_{12}-Benzo(ghi)perylene	288		

TABLE 14

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte	Ion Type	Accurate m/z
1	Naphthalene	M	128.0626
	PFK	LOCK	130.9920
	d_8-Naphthalene	IS	136.1128
	2-Methylnaphthalene	M	142.0782
	d_{10}-2-Methylnaphthalene	IS	152.1410
	Acenaphthylene	M	152.0626
	d_8-Acenaphthylene	IS	160.1128
	Acenaphthene	M	154.0782
	d_{10}-Acenaphthene	RS	164.1410
	PFK	QC	169.9888
2	Fluorene	M	166.0782
	d_{10}-Fluorene	SS	176.1410
	Phenanthrene	M	178.0782
	d_{10}-Phenanthrene	IS	188.1410
	Anthracene	M	178.0782
	d_{10}-Anthracene	AS	188.1410
	Fluoranthene	M	202.0782
	d_{10}-Fluoranthene	IS	212.1410
	Pyrene	M	202.0782
	PFK	QC	204.9888
	d_{10}-Pyrene	RS	212.1410
	Benzo(a)anthracene	M	228.0939
	d_{12}-Benzo-a-Anthracene	IS	240.1692
	Chrysene	M	228.0939
	d_{12}-Chrysene	IS	240.1692
	PFK	LOCK	230.9856
	d_{14}-Terphenyl	SS	244.1974

IS = Internal Standard
SS = Surrogate Standard
AS = Alternate Standard
RS = Recovery Standard
LOCK = Lock-Mass Ion
QC = Quality Control Check Ion

TABLE 14 (CONT)

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte	Ion Type	Accurate m/z
3	Perylene	M	252.0939
	d_{12}-Perylene	IS	264.1692
	PFK	QC	268.9824
	Benzo(b)fluoranthene	M	252.0939
	d_{12}-Benzo(b)fluoranthene	IS	264.1692
	Benzo(k)fluoranthene	M	252.0939
	d_{12}-Benzo-k-fluoranthene	IS	264.1692
	Benzo(e)pyrene	M	252.0939
	d_{12}-Benzo(e)pyrene	RS	264.1692
	Benzo(a)pyrene	M	252.0939
	d_{12}-Benzo(a)pyrene	IS	264.1692
	Benzo(ghi)perylene	M	276.0939
	d_{12}-Benzo(ghi)perylene	IS	288.1692
	Indeno(1,2,3-cd)pyrene	M	276.0939
	d_{12}-Indeno(1,2,3-cd)pyrene	IS	288.1692
	Dibenzo(ah)anthracene	M	278.1096
	PFK	LOCK	280.9824
	d_{14}-Dibenzo(ah)anthracene	IS	292.1974

The following nuclidic masses were used:

H = 1.007825 ^{2}H = 2.014102 C = 12.000000

IS = Internal Standard
SS = Surrogate Standard
AS = Alternate Standard
RS = Recovery Standard
LOCK = Lock-Mass Ion
QC = Quality Control Check Ion

FIGURE 1

METHOD 429 FLOWCHART

1

§1.3.9 *The end user is identified*
§1.3.10 *The tester is designated*

2

The end user chooses:
§2.1.1 • source target concentration

3

§2.1.2 *The tester selects analyst with documented*
§8.4 *experience in satisfactory performance of analytical*
§8.4.1 *procedures*

4

Tester and laboratory coordinate:
§4.3.2 • pre-test cleaning of glassware
§4.2 • pre-test cleaning, contamination checks, and
§4.3.3 storage of sampling materials and reagents
§4.3.4 • preparation of filter, sorbent cartridges, method blanks, and LCS

5

Tester requests pre-test analytical results from laboratory:
§10.1.1 • contamination check of filters
§10.1.2 • contamination check of XAD-2 resin
§10.1.3 • Method detection limits (MDLs) and Practical quantitation limits (PQLs)

6

Tester calculates and plans:
§2.5 • ≥3 sampling runs and ≥1 blank sampling train
• sample volume
• sampling time
• source reporting limit
• chain of custody

7

Tester performs:
§4.3.1 • calibration of equipment

8

Tester writes:
§2.2 • pre-test protocol

9

Tester performs:
§4.4.1 • preliminary field sampling determinations
§4.4.2 • sampling train preparation
§4.4.3 • leak checks
§4.4.4 • sampling procedure
• ≥3 sampling runs
• ≥1 blank sampling train
§5 • recovery of all runs and blank sampling train

10

Tester delivers:
§5.3 • recovered sampling runs and blank train(s)
§5.4 • chain of custody record

11

Laboratory performs:
§6 • extraction of field samples
§7 • analyses
§8 • QA/QC procedures
§9 • chain of custody
§10.2 • reporting requirements

12

Tester performs:
§4.3.1 • post-test calibrations
§9.2 • calculations
§10.3 • data recording and chain of custody
• reporting requirements

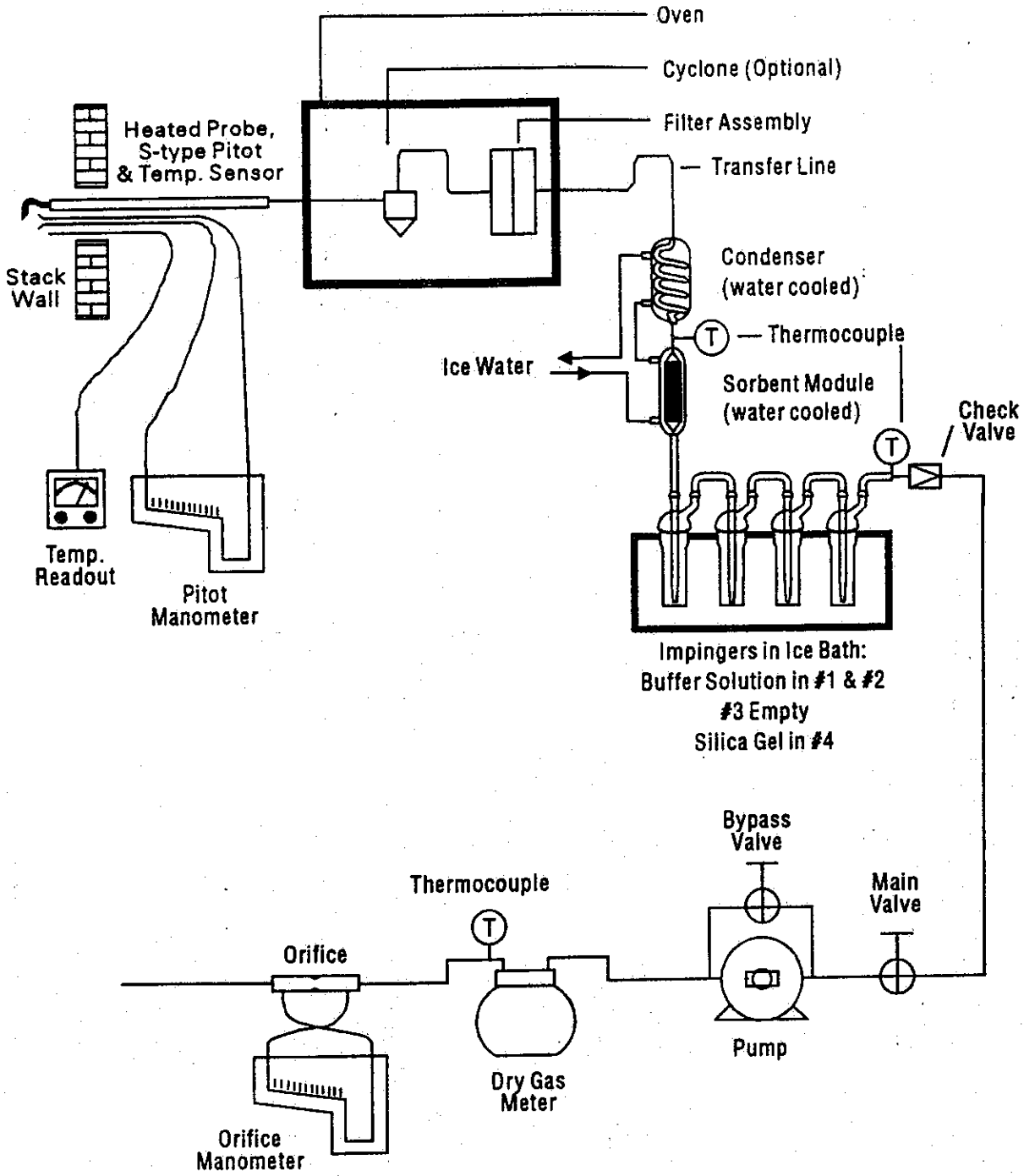

Figure 2
PAH Sampling Train

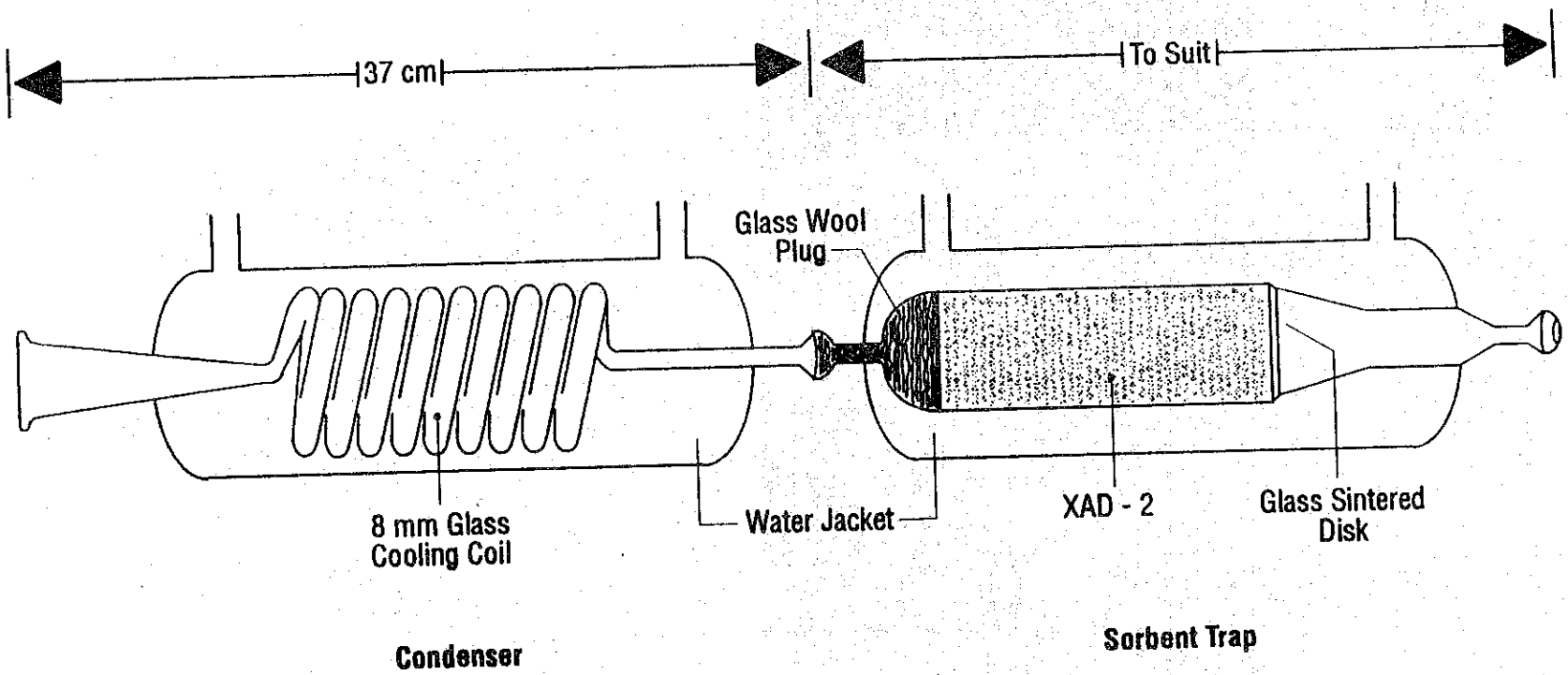

Figure 3

Condenser and Sorbent Trap for Collection of Gaseous PAHs

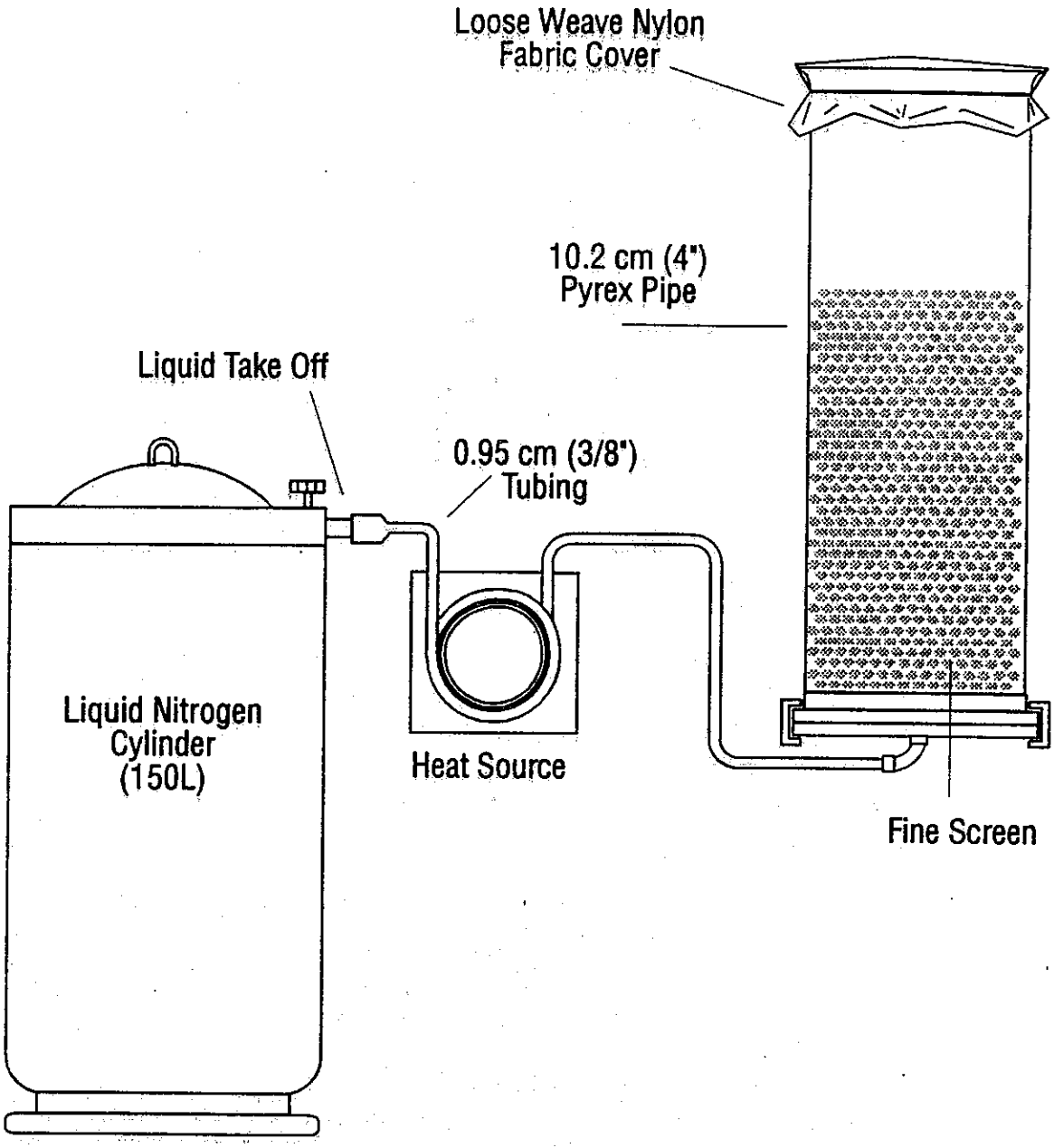

Figure 4

XAD-2 Fluidized Bed Drying Apparatus

FIGURE 5

METHOD 429 FIELD DATA RECORD

Run No. _____
Location _____
Date _____
Operator _____
Meter Box No. _____
Local Time
Start/Stop _____
ΔH@ _____
Stack Diameter _____
Meter Box Calibration
Factor (Y) _____

Pitot Tube Factor _____
Probe Tip Dia, in. _____
Probe Length _____
Sampling Train Leak Test Leak Rate
Before _____ in. Hg _____ cu.ft/min
After _____ in. Hg _____ cu.ft/min
Leak Check Volume _____ cu. ft.
Pitot Tube Leak Check
Before _____ After _____

Project No. _____
Plant Name _____
Ambient Temp °F _____
Meter Temp °F _____
Bar. Press, "Hg _____
Stack Press, "H_2O _____
Assumed Moisture, % _____
Heater Box Setting, °F _____
Probe Heater Setting, °F _____
Assumed M.W. (wet%) _____
Assumed M.W. (dry%) _____

Sampling Point	Clock Time	Dry Gas Meter, cu, ft.	Pitot ΔP in. H_2O	Orifice ΔH "H_2O		Temperature (°F)			Pump Vacuum in. Hg
				Desired	Actual	Impinger	Filter box	Stack	
Start									

Figure 6
Recovery of PAH Sampling Train

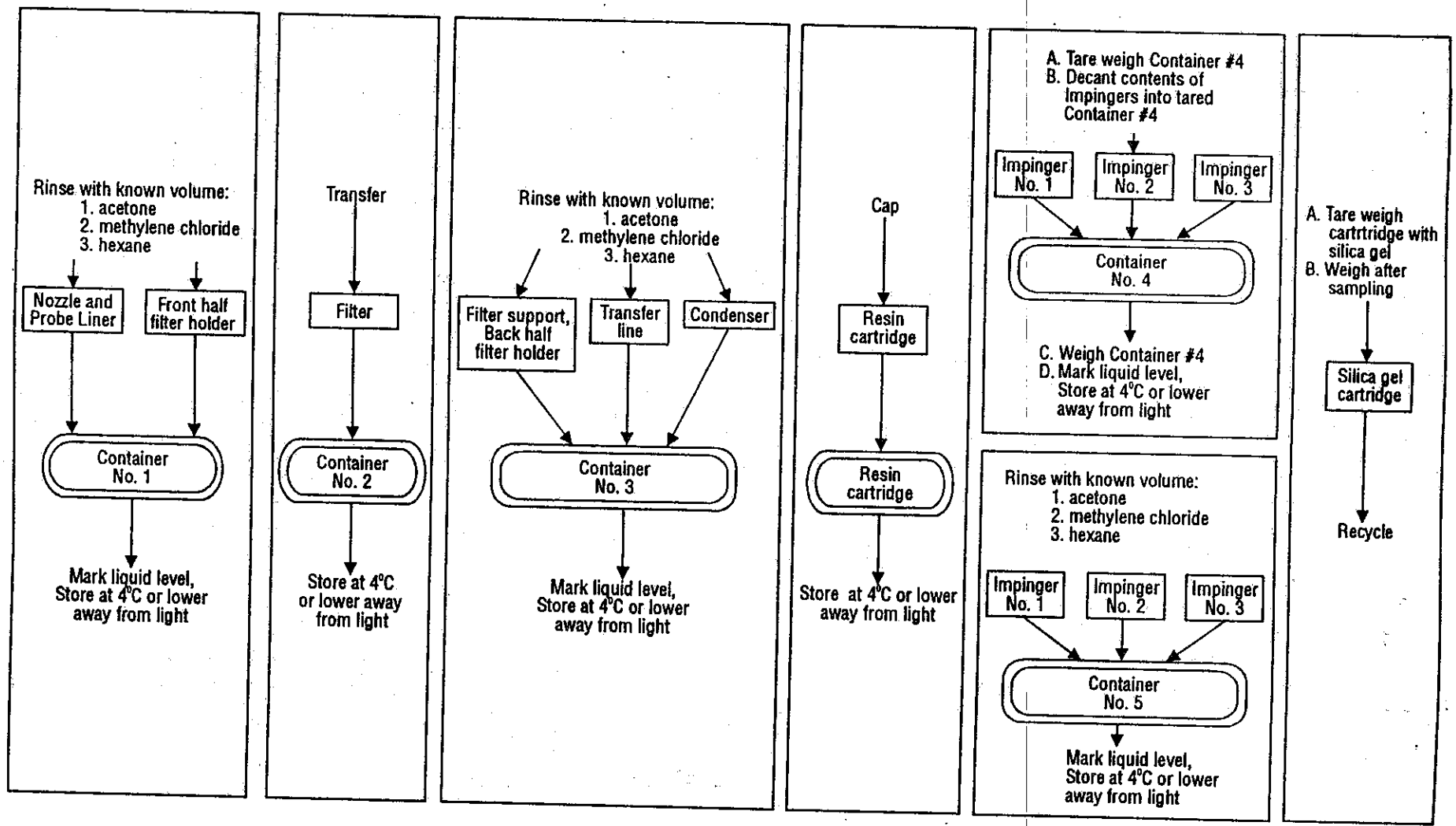

Figure 7

Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Split Sample

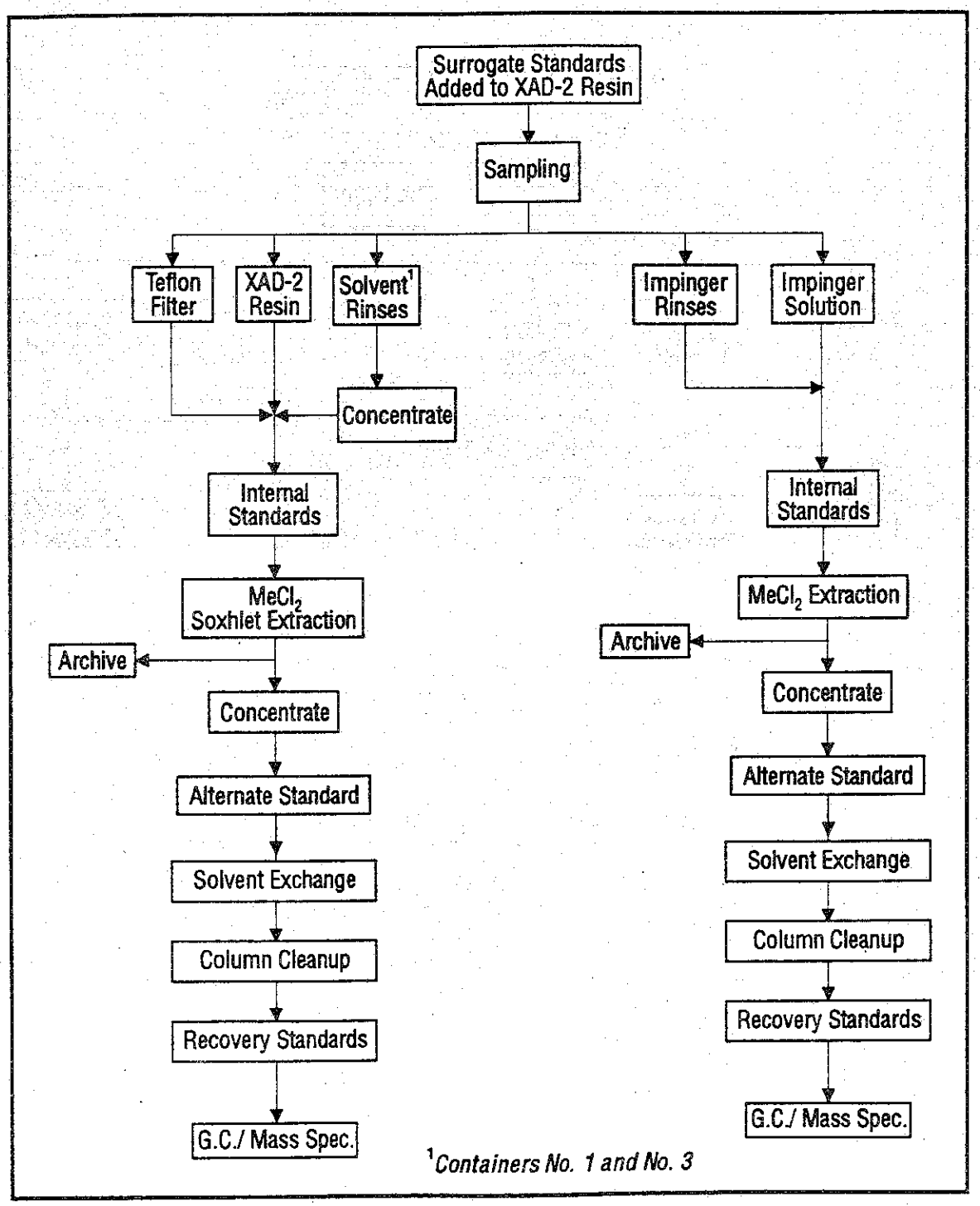

Figure 8
Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Composite Sample

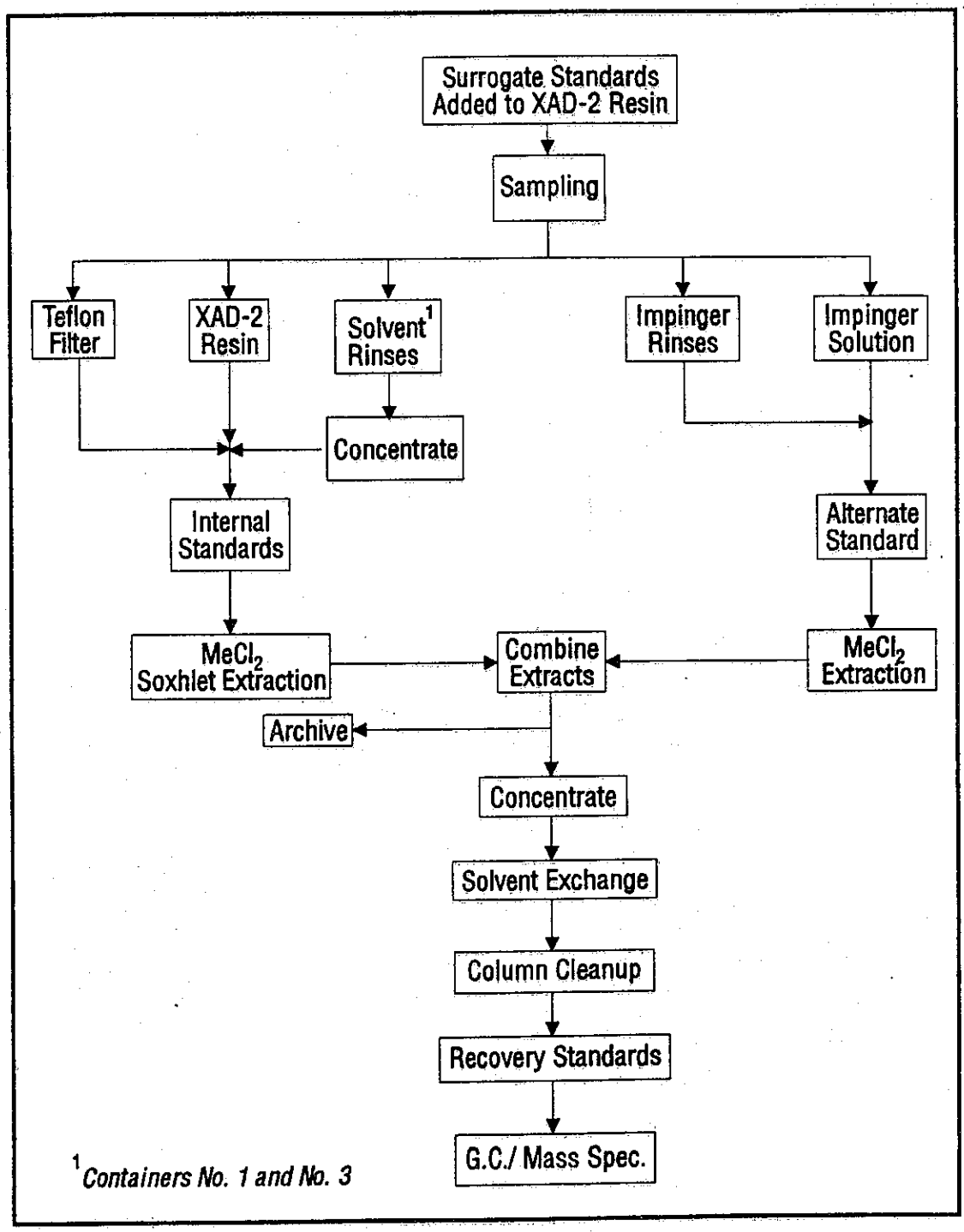

FIGURE 9

EXAMPLE OF PRE-TEST CALCULATIONS FOR PAH EMISSIONS TEST

					PST = 6 hours PSV = 180 dscf	
	PQL (ng/sample)	STC (ng/dscm)	MSV (dscf)	MST (hours)	F	SRL (ng/dscm)
Naphthalene	2400	<1500	>56.5	>1.89	NA	471
2-Methylnaphthalene	330	NA	NA	NA	NA	64.7
Acenaphthylene	5.0	180	0.98	0.03	183	0.98
Acenaphthene	5.0	6	29.4	0.98	6	0.98
Fluorene[1]	83	<6	>489	>16.3	NA	16.3
Phenanthrene	110	120	32.4	1.08	6	21.6
Anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Fluoranthene	5.0	46	3.8	0.13	47	0.98
Pyrene	5.0	46	3.8	0.13	47	0.98
Benzo(a)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Chrysene	5.0	42	4.2	0.14	43	0.98
Benzo(b)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(k)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(e)pyrene	5.0	NA	NA	NA	NA	0.98
Benzo(a)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Perylene	5.0	NA	NA	NA	NA	0.98
Indeno(1,2,3-c,d)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Dibenzo(a,h)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Benzo(g,h,i)perylene	5.0	<6	>29.4	>0.98	NA	0.98
Average Volumetric Sampling Rate (VSR) = 0.5 dscfm = 30 dscf/hr						

PQL = Practical quantitation limit for analyte (based on pre-test analysis of XAD-2 resin)

STC = Source target concentration for analyte. (From previous emissions test. Samples were analyzed by HRGC/LRMS).

MSV = Minimum sample volume required to collect detectable levels of target analyte. (MSV = PQL ÷ STC) *Equation 429-1*

MST = Minimum sample time required to collect detectable levels of target analyte at VSR. (MST = MSV ÷ VSR) *Equation 429-2*

PST = Planned sampling time (6 hours chosen as the longest practical sampling time for the planned emissions test)

PSV = Planned sample volume (PSV = PST × VSR) *Equation 429-4*

F = Safety factor (>1) that allows for deviation from ideal sampling and analytical conditions. (F = PSV ÷ MSV) *Equation 429-5*

SRL = Source reporting limit if the target analyte cannot be detected with the planned test parameters. (SRL = PQL ÷ PSV) *Equation 429-7*

NA This calculation is not applicable either because there is no STC value available or the STC is a detection limit.

[1] PSV is lower than the MSV. Therefore, the analyte is not expected to be detected if it is present at the target concentrations. It will only be detected if the actual concentration is lower than the indicated SRL.

FIGURE 10

CARB METHOD 429 (PAHs) SAMPLING TRAIN SET-UP RECORD

RUN NO. _____ PROJECT NO. _____
PLANT NAME _____ PLANT LOCATION _____
SET-UP DATE _____ SET-UP BY _____
RECEIVED BY _____ DATE/TIME _____

	COMPONENTS	COMPONENT ID	OTHER INFORMATION	
1.	NOZZLE	_____	Material	_____
			Diameter	_____
2.	PROBE	_____	Liner material	_____
			Length	_____
3.	FILTER HOLDER	_____	Before set-up, all openings sealed with	_____
			Filter support type	_____
4.	FILTER	Lot # _____	Filter Type	_____
			Size	_____
			Contamination check?	_____
5.	TRANSFER LINE AND CONDENSER	_____	Transfer line material	_____
	Fittings	_____		_____
6.	XAD-2 RESIN CARTRIDGE	_____	Both ends sealed in lab prior to set-up	_____
			Fittings	_____
			Contamination check?	_____
			Spiked?	_____
7.	IMPINGERS: No. 1	_____	Charge with 100 mL impinger solution and weigh	_____ g
	U-Connector	_____		
	No. 2	_____	Charge with 100 mL impinger solution and weigh	_____ g
	U-Connector	_____		
	No. 3	_____		
	U-Connector	_____	Weigh empty	_____ g
8.	SILCA GEL CARTRIDGE	_____	Tare weight	_____ g
			Appearance	_____

FIGURE 11

CARB METHOD 429 (PAHs) SAMPLING TRAIN RECOVERY RECORD

RUN NO. _____ PROJECT NO. _____
PLANT NAME _____ PLANT LOCATION _____
RECOVERY DATE _____ RECOVERED BY _____

1. **CHECK** whether openings were covered. **RINSE 3x each with Acetone, $MeCl_2$, Hexane.**
   MARK liquid level and **STORE** containers at temp. <4°C away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	$MeCl_2$	Hexane	Storage Container(s) IDs
Nozzle					
Probe liner					
Filter holder front					

2. **STORE** filter(s) at temp. <4°C away from light. **RECORD ALL** sample storage information.

Component	Appearance after sampling	Storage (Temperature & light)	Storage Container(s) ID
Filter			
Filter			
Filter			

3. **CHECK** whether openings were covered. **RINSE 3x each with Acetone, $MeCl_2$, Hexane.**
   MARK liquid level and **STORE** containers at temp. <4°C away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	$MeCl_2$	Hexane	Storage Temp. & light	Storage Container ID
Filter support and filter holder back						
Transfer line						
Condenser						

4. **STORE** Resin cartridges at temp. <4°C away from light. **RECORD ALL** storage information.

ID	Appearance after sampling	Storage temperature & light conditions

5. **WEIGH** impinger contents and silica gel cartridge.
   MARK liquid level and **STORE** impinger contents at temp. <4°C away from light.

Weight	No. 1	No. 2	No. 3	Additional impingers No. 4	No. 5	Silica gel cartridge
Final (g)						
Before sampling (g)						
Gain (g)	(A)	(B)	(C)	(D)	(E)	(F)

Total condensate (A) + (B) + (C) + (D) + (E) + (F) _____ (g)

STORAGE CONTAINER ID(s) _____ _____ _____ _____

6. **RINSE** impingers 3x each with Acetone, $MeCl_2$, Hexane.
   MARK liquid level and **STORE** impinger rinses at temp. <4°C away from light.

Rinse volumes (mL)	No. 1	No. 2	No. 3	Additional impingers No. 4	No. 5	Silica gel cartridge
Acetone						
$MeCl_2$						
Hexane						
STORAGE CONTAINER ID(s)						

FIGURE 12

CHAIN OF CUSTODY SAMPLE RECORD

Project # _____ Date:_____ Start: _____
Stop: _____
Source name: _____ Sample/Run # : _____
Sampling location: _____ Sample type: _____
Chain of Custody Log Record # (s) _____ Operator: _____

SAMPLE STORAGE INFORMATION

SAMPLE PRESERVATION	Comments
Ice/Dry ice?	

CHAIN OF CUSTODY

ACTION	DATE	TIME	GIVEN BY	TAKEN BY

RELATED IDs	DESCRIPTION/COMMENTS	Log #s
FR	Front rinse (nozzle, probe,filter holder front)	
F	Filter in sealed storage container	
BR	Back rinse (filter support, filter holder, sample line & condenser	
C	Resin cartridge	
I	Impinger contents	
IR	Impinger rinses	

FIGURE 13

CHAIN OF CUSTODY LOG RECORD

PROJECT NO. _____ Page _____ of _____

Log #	Sample ID	Date	Time	Comments	Given by	Taken by

Sample Identifier **Sample Description**

FR	Rinses of probe and front half of filter holder
F	Filter in sealed storage container
BR	Rinses of filter support, back half of filter holder, sample transfer line and condenser
C	Aluminum foil wrapped, capped resin cartridge
I	Impinger contents
IR	Impinger rinses

FIGURE 14A

EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR INITIAL CALIBRATION SOLUTION #1
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID: ST1120A1 ACQUIRED: 12/3/94 16:23:24 INSTRUMENT: W
RUN #: PAHCS1 PROCESSED: 12/3/94 OPERATOR: MPA

	RT	RRT	Area	RRF
Naphthalene	8:20	1.006	6.66 E+07	0.75
2-Methylnaphthalene	9:42	1.007	1.44 E+07	1.30
Acenaphthylene	11:04	1.003	1.57 E+07	1.44
Acenaphthene	11:20	1.004	1.05 E+07	0.94
Fluorene	12:06	1.003	8.15 E+06	1.05
Phenanthrene	13:20	1.003	1.99 E+07	1.15
Anthracene	13:23	1.001	7.07 E+06	1.02
Fluoranthene	14:38	1.001	3.18 E+07	1.26
Pyrene	14:55	1.001	3.31 E+07	1.31
Benzo(a)anthracene	16:34	1.002	2.08 E+07	1.13
Chrysene	16:39	1.003	2.26 E+07	1.13
Benzo(b)fluoranthene	18:54	1.004	2.35 E+07	1.69
Benzo(k)fluoranthene	18:58	1.004	2.50 E+07	1.24
Benzo(e)pyrene	19:42	1.004	2.41 E+07	1.20
Benzo(a)pyrene	19:51	1.003	2.11 E+07	1.07
Perylene	20:06	1.004	1.38 E+07	0.70
Indeno(1,2,3-c,d)pyrene	23:60	1.006	2.07 E+07	2.19
Dibenzo(a,h)anthracene	24:01	1.006	1.49 E+07	1.66
Benzo(g,h,i)perylene	25:15	1.005	1.84 E+07	2.23
d_8-Naphthalene	8:17	1.000	3.54 E+08	4.22
d_8-Acenaphthylene	11:02	1.000	1.09 E+08	1.29
d_{10}-Acenaphthene	11:17	1.000	1.11 E+08	1.32
d_{10}-Fluorene	12:04	1.000	7.78 E+07	0.93
d_{10}-Phenanthrene	13:18	1.000	6.92 E+07	0.82
d_{10}-Fluoranthene	14:37	1.000	2.53 E+08	1.03
d_{12}-Benzo(a)anthracene	16:32	1.000	1.83 E+08	0.75
d_{12}-Chrysene	16:36	1.000	2.00 E+08	0.82
d_{12}-Benzo(b)fluoranthene	18:50	1.000	2.77 E+08	1.35
d_{12}-Benzo(k)fluoranthene	18:54	1.000	4.03 E+08	1.95
d_{12}-Benzo(a)pyrene	19:47	1.000	3.93 E+08	1.91
d_{12}-Indeno(1,2,3-c,d)pyrene	23:52	1.000	1.89 E+08	0.92
d_{14}-Dibenzo(a,h)anthracene	23:52	1.000	1.80 E+08	0.87
d_{12}-Benzo(g,h,i)perylene	25:07	1.000	1.65 E+08	0.80
d_{14}-Terphenyl	14:59		2.65 E+08	0.52
d_{12}-Benzo(e)pyrene	19:37	1.000	1.44 E+08	0.37
d_{10}-Anthracene	13:22	1.000	5.82 E+07	0.69
d_{10}-2-Methylnaphthalene	9:38	1.000	8.40 E+07	---
d_{10}-Pyrene	14:54	1.000	2.45 E+08	---
d_{12}-Perylene	20:01	1.000	1.03 E+08	---

FIGURE 14B

EXAMPLE OF INITIAL CALIBRATION (ICAL) RRF SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID: ST1120
RUN #: NA

ACQUIRED: 3-DEC-94
PROCESSED: 3-DEC-94

INSTRUMENT: W
OPERATOR: MPA

	RRF #1	RRF #2	RRF #3	RRF #4	RRF #5	Mean RRF	SD	%RSD
Naphthalene	0.75	0.66	0.61	0.64	0.71	0.67	0.056	8.29%
2-Methylnaphthalene	1.30	1.15	1.10	1.12	1.26	1.19	0.089	7.47%
Acenaphthylene	1.44	1.27	1.24	1.28	1.43	1.33	0.096	7.19%
Acenaphthene	0.94	0.84	0.80	0.83	0.94	0.87	0.067	7.72%
Fluorene	1.05	0.94	0.88	0.92	1.07	0.97	0.082	8.43%
Phenanthrene	1.15	1.06	1.01	1.05	1.23	1.10	0.088	8.00%
Anthracene	1.02	1.00	0.98	0.95	1.14	1.02	0.074	7.25%
Fluoranthene	1.26	1.15	1.08	1.13	1.28	1.18	0.085	7.21%
Pyrene	1.31	1.27	1.13	1.15	1.41	1.25	0.115	9.22%
Benzo(a)anthracene	1.13	1.05	1.05	1.04	1.23	1.10	0.082	7.43%
Chrysene	1.13	1.02	0.97	0.98	1.11	1.04	0.073	7.00%
Benzo(b)fluoranthene	1.69	1.45	1.46	1.42	1.86	1.58	0.194	12.33%
Benzo(k)fluoranthene	1.24	1.25	1.14	1.18	1.26	1.21	0.052	4.32%
Benzo(e)pyrene	1.20	1.12	1.06	1.06	1.19	1.12	0.066	5.89%
Benzo(a)pyrene	1.07	0.99	0.96	0.96	1.14	1.02	0.080	7.81%
Perylene	0.70	0.63	0.58	0.60	0.70	0.64	0.059	9.12%
Indeno(1,2,3-c,d)pyrene	2.19	2.01	1.92	1.99	2.26	2.07	0.143	6.90%
Dibenzo(a,h)anthracene	1.66	1.60	1.56	1.61	1.87	1.66	0.122	7.35%
Benzo(g,h,i)perylene	2.23	2.05	1.96	2.00	2.32	2.11	0.154	7.28%
d_8-Naphthalene	4.22	4.15	4.16	4.18	4.10	4.16	0.044	1.05%
d_8-Acenaphthylene	1.29	1.29	1.28	1.27	1.30	1.29	0.012	0.91%
d_{10}-Acenaphthene	1.32	1.34	1.32	1.30	1.32	1.32	0.013	1.00%
d_{10}-Fluorene	0.93	0.95	0.94	0.95	0.95	0.94	0.011	1.21%
d_{10}-Phenanthrene	0.82	0.82	0.82	0.86	0.88	0.81	0.026	3.09%
d_{10}-Fluoranthene	1.03	1.00	1.07	1.07	0.99	1.03	0.038	3.71%
d_{12}-Benzo(a)anthracene	0.75	0.70	0.70	0.72	0.70	0.71	0.022	3.09%
d_{12}-Chrysene	0.82	0.79	0.81	0.83	0.84	0.82	0.021	2.56%
d_{12}-Benzo(b)fluoranthene	1.35	1.39	1.46	1.27	1.32	1.36	0.072	5.32%
d_{12}-Benzo(k)fluoranthene	1.95	1.95	2.14	1.84	2.11	2.00	0.124	6.23%
d_{12}-Benzo(a)pyrene	1.91	1.96	2.11	1.82	1.99	1.96	0.107	5.46%
d_{12}-Indeno(1,2,3-c,d)pyrene	0.92	0.88	0.98	0.85	0.98	0.92	0.059	6.40%
d_{14}-Dibenzo(a,h)anthracene	0.87	0.84	0.91	0.78	0.89	0.86	0.049	5.71%
d_{12}-Benzo(g,h,i)perylene	0.80	0.76	0.83	0.73	0.80	0.78	0.042	5.36%
d_{14}-Terphenyl	0.52	0.52	0.49	0.48	0.51	0.51	0.018	3.59%
d_{12}-Benzo(e)pyrene	0.37	0.37	0.37	0.36	0.36	0.36	0.005	1.50%
d_{10}-Anthracene	0.69	0.73	0.74	0.80	0.90	0.77	0.080	10.40%
d_{10}-2-Methylnaphthalene	---	---	---	---	---	---	---	---
d_{10}-Pyrene	---	---	---	---	---	---	---	---
d_{12}-Perylene	---	---	---	---	---	---	---	---

FIGURE 14C

EXAMPLE OF CONTINUING CALIBRATION (CONCAL) SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

CONCAL ID: CC1202
CONCAL DATE: 12/3/94

ICAL ID: ST1120
ICAL DATE: 3-DEC-94

INSTRUMENT: W
OPERATOR: MPA

	RRF	ICAL RRF	ΔRRF	RPD %
Naphthalene	0.68	0.67	0.01	1.5
2-Methylnaphthalene	1.42	1.19	0.23	17.6
Acenaphthylene	1.42	1.33	0.09	6.6
Acenaphthene	0.91	0.87	0.04	4.5
Fluorene	0.98	0.97	0.01	1.0
Phenanthrene	1.10	1.10	0.00	0.0
Anthracene	0.98	1.02	-0.04	4.0
Fluoranthene	1.12	1.18	-0.06	5.2
Pyrene	1.18	1.25	-0.07	5.8
Benzo(a)anthracene	1.08	1.10	-0.02	1.8
Chrysene	1.04	1.04	0.00	0.0
Benzo(b)fluoranthene	1.46	1.58	-0.12	7.9
Benzo(k)fluoranthene	1.12	1.21	-0.09	7.7
Benzo(e)pyrene	1.04	1.12	-0.08	7.4
Benzo(a)pyrene	0.95	1.02	-0.07	7.1
Perylene	0.62	0.64	-0.02	3.2
Indeno(1,2,3-c,d)pyrene	2.04	2.07	-0.03	1.5
Dibenzo(a,h)anthracene	1.61	1.66	-0.05	3.1
Benzo(g,h,i)perylene	2.11	2.11	0.00	0.0
d_8-Naphthalene	4.78	1.16	0.68	15.3
d_8-Acenaphthylene	1.20	1.29	-0.09	7.2
d_{10}-Acenaphthene	1.25	1.32	-0.07	5.5
d_{10}-Fluorene	0.85	0.94	-0.09	10.1
d_{10}-Phenanthrene	0.79	0.81	-0.02	2.5
d_{10}-Fluoranthene	1.05	1.03	0.02	1.9
d_{12}-Benzo(a)anthracene	0.69	0.71	-0.02	2.9
d_{12}-Chrysene	0.82	0.82	0.00	0.0
d_{12}-Benzo(b)fluoranthene	1.24	1.36	-0.12	9.2
d_{12}-Benzo(k)fluoranthene	1.91	2.00	-0.09	4.6
d_{12}-Benzo(a)pyrene	1.87	1.96	-0.09	4.7
d_{12}-Indeno(1,2,3-c,d)pyrene	0.84	0.92	-0.08	9.1
d_{14}-Dibenzo(a,h)anthracene	0.80	0.86	-0.06	7.2
d_{12}-Benzo(g,h,i)perylene	0.76	0.78	-0.02	2.6
d_{14}-Terphenyl	0.50	0.51	-0.01	2.0
d_{12}-Benzo(e)pyrene	0.37	0.36	0.01	2.7
d_{10}-Anthracene	0.71	0.77	-0.06	8.1
d_{10}-2-Methylnaphthalene	---	---		
d_{10}-Pyrene	---	1.000		
d_{12}-Perylene	---	1.000		

FIGURE 15A.

EXAMPLE OF SUMMARY REPORT OF LCS RESULTS
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID CARB
Lab ID: 14129/LCS1/LCS2
Instrument: W
Operator: MPA
Reviewer: JCM

Sample Matrix: XAD-2
Date Received: NA
Date Extracted: 11/30/94
Date Analyzed: 12/3/94
Sample amount: Sample

ICAL ID: ST1120
ICAL DATE: 12/3/94
CONCAL ID: NA
CONCAL DATE: NA
Units: NA

Resin Lot #: LC1130M
LCS IDs: NA
LCS DATE: NA

COMPOUND:	LCS1 %R	LCS2 %R	RPD %
Naphthalene	100	103	3.0
2-Methylnaphthalene	96	95	1.0
Acenaphthylene	95	97	2.1
Acenaphthene	92	94	2.2
Fluorene	94	96	2.1
Phenanthrene	93	94	1.1
Anthracene	91	89	2.2
Fluoranthene	90	92	2.2
Pyrene	87	89	2.3
Benzo(a)anthracene	87	86	1.2
Chrysene	83	89	7.0
Benzo(b)fluoranthene	92	93	1.1
Benzo(k)fluoranthene	92	95	3.2
Benzo(e)pyrene	97	99	2.0
Benzo(a)pyrene	89	92	3.3
Perylene	89	89	0.0
Indeno(1,2,3-c,d)pyrene	87	90	3.4
Dibenzo(a,h)anthracene	88	90	2.2
Benzo(g,h,i)perylene	89	91	1.2
Internal Standards (%R)			
d_8-Naphthalene	67	64	
d_8-Acenaphthylene	73	70	
d_{10}-Acenaphthene	76	75	
d_{10}-Fluorene	79	81	
d_{10}-Phenanthrene	88	93	
d_{10}-Fluoranthene	84	80	
d_{12}-Benzo(a)anthracene	96	98	
d_{12}-Chrysene	96	91	
d_{12}-Benzo(b)fluoranthene	88	85	
d_{12}-Benzo(k)fluoranthene	85	84	
d_{12}-Benzo(a)pyrene	92	90	
d_{12}-Indeno(1,2,3-c,d)pyrene	104	105	
d_{14}-Dibenzo(a,h)anthracene	96	96	
d_{12}-Benzo(g,h,i)perylene	102	103	
Alternate Standard (%R)			
d_{10}-Anthracene	83	85	

FIGURE 15B

LCS RECOVERIES FOR BENZO(a)PYRENE

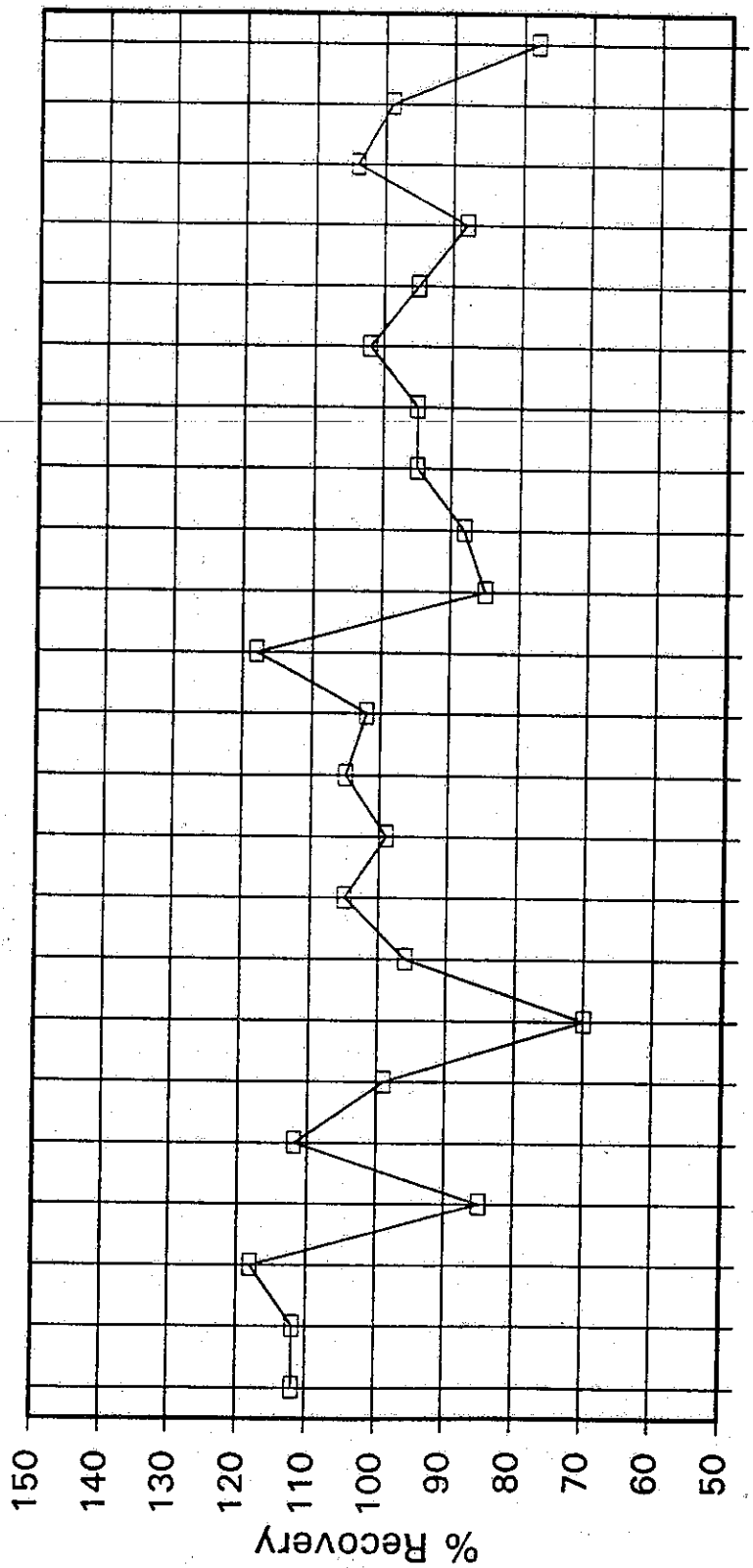

FIGURE 16A

EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Lab ID: 14129-02
Acquired: 12/3/94 16:23:40
Client ID: M429-32

ICAL ID: 12/3/94 16:23:40
ICAL DATE: 12/3/94

Instrument: W
Operator: MPA
Reviewer: JCM

	RT	RRT	Area	RRF	Amt. (ng)	% REC
Naphthalene	8:21		1.053 E+10	0.67	10,478.37	
2-Methylnaphthalene	9:41		1.790 E+08	1.19	140.98	
Acenaphthylene	11:03		9.371 E+08	1.33	712.59	
Acenaphthene	11:19		7.649 E+06	0.87	8.21	
Fluorene	12:05		2.417 E+07	0.97	30.02	
Phenanthrene	13:17		8.402 E+08	1.10	925.53	
Anthracene	13:21		2.905 E+07	1.02	34.54	
Fluoranthene	14:36		5.932 E+08	1.18	254.36	
Pyrene	14:52		7.611 E+08	1.25	307.62	
Benzo(a)anthracene	16:32		3.120 E+06	1.10	1.9	
Chrysene	16:32		9.620 E+06	1.04	6.2	
Benzo(b)fluoranthene	18:49		1.030 E+06	1.58	7.6	
Benzo(k)fluoranthene	Not found		0.0	1.21		
Benzo(e)pyrene	19:36		1.646 E+07	1.12	13.61	
Benzo(a)pyrene	19:46		4.936 E+06	1.02	3.95	
Perylene	20:01		1.823 E+06	0.64	2.32	
Indeno(1,2,3-c,d)pyrene	23:54		5.728 E+06	2.07	4.37	
Dibenzo(a,h)anthracene	23:56		5.875 E+05	1.66	0.59	
Benzo(g,h,i)perylene	25:09		1.584 E+07	2.11	14.95	
d_8-Naphthalene	8:18	1.000	4.794 E+08	1.16	124.92	62.5
d_8-Acenaphthylene	11:01	1.000	1.972 E+08	1.29	166.07	83.0
d_{10}-Acenaphthene	11:16	1.000	2.142 E+08	1.32	176.19	88.1
d_{10}-Fluorene	12:02	1.000	1.658 E+08	0.94	190.71	95.4
d_{10}-Phenanthrene	13:16	1.000	1.652 E+07	0.81	213.39	106.7
d_{10}-Fluoranthene	14:34	1.000	3.955 E+08	1.03	116.22	58.1
d_{12}-Benzo(a)anthracene	16:28	1.000	2.835 E+08	0.71	121.18	60.6
d_{12}-Chrysene	16:31	1.000	2.987 E+08	0.82	111.08	55.5
d_{12}-Benzo(b)fluoranthene	18:45	1.000	3.439 E+08	1.36	165.79	41.4
d_{12}-Benzo(k)fluoranthene	18:50	1.000	4.304 E+08	2.00	141.02	35.3
d_{12}-Benzo(a)pyrene	19:41	1.000	4.895 E+08	1.96	163.67	40.9
d_{12}-Indeno(1,2,3-c,d)pyrene	23:46	1.000	2.529 E+08	0.92	179.71	44.9
d_{14}-Dibenzo(a,h)anthracene	23:45	1.000	2.400 E+08	0.86	182.65	45.7
d_{12}-Benzo(g,h,i)perylene	24:60	1.000	2.006 E+08	0.78	167.24	41.8
d_{14}-Terphenyl	14:55		7.988 E+08	0.51	523	105
d_{12}-Benzo(e)pyrene	19:32	1.000	3.011 E+08	0.36	676.33	135.3
d_{10}-Anthracene	13:20	1.000	6.795 E+07	0.77	95.29	47.6
d_{10}-2-Methylnaphthalene	9:38	1.000	1.844 E+07	---	100	
d_{10}-Pyrene	14:51	1.000	6.576 E+08	---	100	
d_{12}-Perylene	19:56	1.000	3.057 E+08	---	100	

FIGURE 16B

EXAMPLE LABORATORY REPORT OF PAH RESULTS FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID M429-32
Lab ID: 14129-02
Instrument: W
Operator: MPA
Reviewer: JCM

Sample Matrix: M429
Date Received: 11/18/94
Date Extracted: 11/30/94
Date Analyzed: 12/3/94
Sample amount: Sample

ICAL ID: ST1120
ICAL DATE: 12/3/94
CONCAL ID: NA
CONCAL DATE: NA
Units: ng/sample

Resin Lot #: LC1130M
LCS IDs: 14129-LCS1/LCS2
LCS DATE: 12/3/94

COMPOUND:	Conc.	R.L.	Flags
Naphthalene	10478	1600	
2-Methylnaphthalene	141	94	
Acenaphthylene	712	5.0	
Acenaphthene	8.2	5.0	
Fluorene	30	27	
Phenanthrene	930	80	
Anthracene	35	5.0	
Fluoranthene	254	5.0	
Pyrene	307	5.0	
Benzo(a)anthracene	ND	5.0	
Chrysene	6.2	5.0	
Benzo(b)fluoranthene	7.6	5.0	
Benzo(k)fluoranthene	ND	5.0	
Benzo(e)pyrene	14	5.0	
Benzo(a)pyrene	ND	5.0	
Perylene	ND	5.0	
Indeno(1,2,3-c,d)pyrene	ND	5.0	
Dibenzo(a,h)anthracene	ND	5.0	
Benzo(g,h,i)perylene	15	5.0	
Internal Standards (%R)			
d_8-Naphthalene	62		
d_8-Acenaphthylene	83		
d_{10}-Acenaphthene	88		
d_{10}-Fluorene	95		
d_{10}-Phenanthrene	107		
d_{10}-Fluoranthene	58		
d_{12}-Benzo(a)anthracene	61		
d_{12}-Chrysene	56		H
d_{12}-Benzo(b)fluoranthene	41		H
d_{12}-Benzo(k)fluoranthene	35		H
d_{12}-Benzo(a)pyrene	41		H
d_{12}-Indeno(1,2,3-c,d)pyrene	45		H
d_{14}-Dibenzo(a,h)anthracene	46		H
d_{12}-Benzo(g,h,i)perylene	42		
Alternate Standard (%R)			
d_{10}-Anthracene	48		
Surrogate Standard (%R)			
d_{14}-Terphenyl	105		
d_{12}-Benzo(e)pyrene	135		

FIGURE 17A
EXAMPLE OF TESTER'S SUMMARY OF LABORATORY REPORTS

Run #:	31	32	33	Field Blank	Method Blank	LCS #1	LCS #2
	ng/sample					percent recovery	
Naphthalene	4300	10000	460000 *	<1600	<1700	100	103
2-Methylnaphthalene	< 94	140	6400 *	< 94	<78	96	95
Acenaphthylene	140	710	85000 *	9.1	< 5.0	95	97
Acenaphthene	9.2	8.2	500	< 5.0	< 5.0	92	94
Fluorene	27	30	180	< 27	< 27	94	96
Phenanthrene	310	930	43000 *	< 80	< 74	93	94
Anthracene	26	35	2400	5.3	< 5.0	91	89
Fluoranthene	83	250	16000 *	16	< 5.0	90	92
Pyrene	110	310	20000 *	19	< 5.0	87	89
Benzo(a)anthracene	< 5.0	< 5.0	170	< 5.0	< 5.0	87	86
Chrysene	< 5.0	6.2	300	< 5.0	< 5.0	83	89
Benzo(b)fluoranthene	< 5.0	7.6	340	< 5.0	< 5.0	92	93
Benzo(k)fluoranthene	< 5.0	< 5.0	89	< 5.0	< 5.0	92	95
Benzo(e)pyrene	35	< 35	530	6.9	< 5.0	97	99
Benzo(a)pyrene	< 5.0	< 5.0	240	< 5.0	< 5.0	89	92
Perylene	< 5.0	< 5.0	110	< 5.0	< 5.0	89	89
Indeno(1,2,3-c,d)pyrene	< 5.0	< 5.0	100	< 5.0	< 5.0	87	90
Dibenzo(a,h)anthracene	< 5.0	< 5.0	6.4	< 5.0	< 5.0	88	90
Benzo(g,h,i)perylene	< 85	< 85	440	17.0	< 5.0	89	91
Internal Standards (%R)							
d_8-Naphthalene	66	62	57 *	53	55	67	64
d_8-Acenaphthylene	82	83	85 *	73	69	73	70
d_{10}-Acenaphthene	85	88	80 *	81	75	76	75
d_{10}-Fluorene	91	95	102	90	82	79	81
d_{10}-Phenanthrene	106	107	79 *	107	93	88	93
d_{10}-Fluoranthene	79	58	75 *	83	80	84	80
d_{12}-Benzo(a)anthracene	100	61	108	114	93	96	98
d_{12}-Chrysene	91	56	99	102	88	96	91
d_{12}-Benzo(b)fluoranthene	69	41 H	60	85	84	88	85
d_{12}-Benzo(k)fluoranthene	62	35 H	50	78	84	85	84
d_{12}-Benzo(a)pyrene	70	41 H	58	86	89	92	90
d_{12}-Indeno(1,2,3-c,d)pyrene	82	45 H	58	106	106	104	105
d_{14}-Dibenzo(a,h)anthracene	72	42 H	58	92	92	96	96
d_{12}-Benzo(g,h,i)perylene	84	46 H	58	107	104	102	103
Surrogate Standards (%R)							
d_{14}-Terphenyl	125	105	90	123	130		
d_{12}-Benzo(e)pyrene	72	135	112	103	112		
Alternate Standard (%R)							
d_{10}-Anthracene	67	48 H	115	116	101	83	85
Test Date	11/15/94	11/16/94	11/17/94	11/16/94	NA	NA	NA
Date received by lab.	11/18/94	11/18/94	11/18/94	11/18/94	NA	NA	NA
Date extracted	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94
Date analyzed	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94

"<" denotes that the compound was not detected at levels above the indicated reporting limit.
"H" indicates internal Standard Recovery Results below 50%, but signal-to-noise greater than 10:1.
"*" indicates compounds reanalyzed at 1:50 dilution due to saturation.

FIGURE 17B
FIELD DATA SUMMARY FOR PAH EMISSIONS TEST

	RUN ID	31	32	33	
	DATE	11-15-95	11-16-95	11-17-95	
	START/STOP TIME	1015/1435	1020/1645	0855/1525	
	LOCATION	STACK	STACK	STACK	
	STACK DIAMETER	35.5 in.	35.5 in.	35.5 in.	
	NOZZLE DIAMETER	0.3105	0.313 in.	0.3125 in.	
	METER BOX ID	5419	5419	5419	
STANDARD DRY GAS VOLUME	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	V_m	132.65	213.67	228.10	cubic ft
	P_{bar}	29.78	29.98	29.88	inches Hg
	ΔH_{avg}	1.15	1.35	1.56	inches H_2O
	T_m	60.0	60.0	60.0	° F
	K_1	17.64	17.64	17.64	
	Y	1.08	1.08	1.08	
PERCENT MOISTURE	B_{ws}	12.9	15.0	18.4	percent
	Impinger + tare	2183.3	2092.3	2063	grams
	Final wt.	2609.8	2934.9	3210.2	grams
	Net imp. catch	426.5	842.6	1147.2	grams
	Silica gel tare	1561.8	1788.8	1585.7	grams
	Post sampling wt.	1590.0	1826.9	1536.2	grams
	Moisture gain	28.2	38.1	49.5	grams
	Total moisture (V_{lc})	454.7	880.7	1196.7	grams
	$V_{w(std)}$	21.43	41.50	56.39	DSCF(68° F)
	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	K_2	0.0471	0.0471	0.0471	
MOLECULAR WEIGHT	M_d	29.93	29.95	30.08	lb/lbmole
	M_s	28.40	28.16	27.86	lb/lbmole
	O_2	11.25	10.75	10.00	percent
	CO	0.00	0.00	0.00	percent
	CO_2	9.25	9.50	10.50	percent
	N_2	79.50	79.75	79.50	percent
	B_{ws}	12.86	14.98	18.36	percent
GAS VELOCITY	v_s	38.4	40.88	43.2	feet/second
	Δp	0.530	0.56	0.59	inches H_2O
	T_s	420	428	427	° F
	P_g	-0.27	-0.27	-0.27	inches H_2O
	P_s	29.76	29.96	29.86	inches Hg
	M_s	28.40	28.16	27.86	lb/lbmole
	K_p	85.49	85.49	85.49	
	C_p	0.83	0.83	0.83	
VOLUMETRIC FLOW RATE	Q_{std}	8241	8531	8641	DSCF(68° F)
	B_{ws}	12.86	14.98	18.36	percent
	v_s	38.38	40.88	43.23	feet/second
	A	6.8736	6.8736	6.8736	sq. feet
	sec/min	60	60	60	
	K_1	17.64	17.64	17.64	
ISOKINETIC RATIO	I	96	99	104	percent
	T_s	420	428	427	° F
	$V_{m(std)}$	145.19	235.57	250.76	DSCFM(68° F)
	P_s	29.76	29.96	29.86	inches Hg
	v_s	38.38	40.88	43.23	feet/second
	θ	240	360	360	minutes
	B_{ws}	12.86	14.98	18.36	percent
	A_n	0.00053	0.00053	0.00053	sq. feet
	K_4	0.09450	0.09450	0.09450	

FIGURE 17C

EXAMPLE OF EMISSIONS TEST REPORT

	Run #31	Run #32	Run #33
(ng/dscm)			
Naphthalene	1046	1499	64782
2-Methylnaphthalene	<23	21.0	901
Acenaphthylene	34	106	11971
Acenaphthene	2.2	1.2	70
Fluorene	6.6	4.5	25
Phenanthrene	75	139	6056
Anthracene	<6.3	5.3	338
Fluoranthene	20	38	2253
Pyrene	27	47	2817
Benzo(a)anthracene	<1.2	<0.75	24
Chrysene	<1.2	0.92	42
Benzo(b)fluoranthene	<1.2	1.1	48
Benzo(k)fluoranthene	<1.2	<0.75	13
Benzo(e)pyrene	<8.5	<5.3	75
Benzo(a)pyrene	<1.2	<0.75	34
Perylene	<1.2	<0.75	16
Indeno(1,2,3-c,d)pyrene	<1.2	<0.75	14
Dibenzo(a,h)anthracene	<1.2	<0.75	0.90
Benzo(g,h,i)perylene	<21	<13	62
(ng/sec)			
Naphthalene	4068	6036	264180
2-Methylnaphthalene	<89	85	3676
Acenaphthylene	132	429	48816
Acenaphthene	8.7	5.0	287
Fluorene	26	18	103
Phenanthrene	293	561	24695
Anthracene	<25	21	1378
Fluoranthene	79	151	9189
Pyrene	104	187	11486
Benzo(a)anthracene	<4.7	<3.0	99
Chrysene	<4.7	3.7	172
Benzo(b)fluoranthene	<4.7	4.6	195
Benzo(k)fluoranthene	<4.7	<3.0	51
Benzo(e)pyrene	<33	<21	304
Benzo(a)pyrene	<4.7	<3.0	138
Perylene	<4.7	<3.0	63
Indeno(1,2,3-c,d)pyrene	<4.7	<3.0	57
Dibenzo(a,h)anthracene	<4.7	<3.0	3.7
Benzo(g,h,i)perylene	<80	<51	253

Standard Conditions: 68 deg.F (20 deg.C) & 29.92 in. Hg. (760 mm Hg)
"<" indicates that the compound was not detected above the reporting limit.

METHOD 429 - APPENDIX A

DETERMINATION OF THE METHOD DETECTION LIMIT

This procedure is based on the approach adopted by the EPA and included as Appendix B to Title 40, Part 136 of the Code of Federal Regulations (40 CFR 136). The samples shall be subjected to the same extraction, concentration, cleanup, and analytical procedures as those required for the field samples.

A1 Procedure

A1.1 Make an estimate of the detection limit (MDL) of each target compound using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent methylene chloride.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

(e) The concentration equivalent to five times the theoretical quantitation limit (Section 8.3.1 of the test method)

The experience of the analyst is important to this process, but one of the above considerations must be included in the initial estimate of the detection limit.

A1.2 Prepare according to the procedures described in Sections 4.2.2.1 to 4.2.2.4 enough XAD-2 resin to provide, at a minimum, eight aliquots each with mass equal to that required to pack a Method 429 sorbent cartridge. A contamination check must be conducted to identify those PAH for which a MDL cannot be determined by this method.

A1.3 To each of seven (7) aliquots of the clean resin, add an amount of each target analyte equal to the estimated detection limit. The mass of each resin aliquot must be known, and should be approximately 40 grams, the amount required to pack a Method 429 sorbent cartridge. The eighth aliquot shall be a blank.

A1.4 Process each of the eight samples through the entire PAH analytical method. All quality criteria requirements of the analytical method must be satisfied.

A1.5 Report the analytical results. The laboratory report must satisfy all of the reporting requirements of Section 10 of the test method.

A1.6 It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with step A1.3. This will: (1) prevent repeating this entire procedure and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure a good estimate of the method detection, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in step A1.3. Evaluate these data:

(1) If the sample levels are in a desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL according to Section A2.

(2) If these measurements indicate the selected analyte level is not in correct range, reestimate the MDL with a new sample as in A1.2 and repeat steps A1.3 to A1.5.

A2 Calculation

A2.1 Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i^2\right)}{n}\right] \qquad 429\text{-(A)-(34)}$$

$$S = \sqrt[2]{S^2}$$

Where:

X_i, $i = 1$ to n, are the analytical results in the final method reporting units obtained from the n sample aliqouts and Σ refers to the sum of the X values from $i = 1$ to n.

A2.2 (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =0.99)} \times (S) \qquad 429(A)\text{-}(35)$$

Where:

MDL = the method detection limit

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = Students' t-value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table 429(A)-1.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in A2.2(a) are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL
UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

A3 Optional Iterative Procedure

A3.1 This is to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step A1.1, take the MDL as calculated in Step A2.2, spike the matrix at this calculated MDL and repeat the procedure starting with Step A1.3.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right] \qquad 429(A)\text{-}(36)$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step A1.3. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in Equation 429(A)-3 to compute the final MDL according to the following equation:

$$MDL = 2.681 (S_{pooled}) \qquad 429(A)-(37)$$

Where: 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL calculated using Equation 429(A)-4 are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$LCL = 0.72\ MDL$$
$$UCL = 1.65\ MDL$$

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLE 429(A)-1

SELECTED STUDENT'S t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of Replicates	Degrees of Freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390

State of California
California Environmental Protection Agency
Air Resources Board

Method 431

Determination of Ethylene Oxide Emissions from Stationary Sources

Adopted September 12, 1989
Amended: _____

It is proposed that the content of ARB Method 431, Determination of Ethylene Oxide Emissions from Stationary Sources, adopted September 12, 1989, be deleted and replaced by the following revised content. For the text of the current test procedure, which is proposed to be replaced, contact Mr. George Lew, Air Resources Board, Monitoring and Laboratory Division, P.O. Box 2815, Sacramento, California 95812, telephone (916) 263-1630.

Method 431 **Ethylene Oxide**

PROPERTIES: gas at room temp
M.W.: 44.05 B.P.: 10.7 C; V.P.: 146 kPa (20 C)
vapor density: 0.98 (air = 1); explosive range: 3% to 80+% v/v in air

SAMPLING	MEASUREMENT
The direct interface sampling and analysis procedure described in Appendix A may be used to continuously monitor ethylene oxide concentrations at the outlet (and inlet) of the control device using a gas chromatograph with flame ionization detector (GC/FID) or photo-ionization detector (PID). OPTION: Where appropriate, integrated Tedlar bag sampling may be used to monitor the ethylene oxide concentrations. Refer to Appendix I for sampling procedures.	TECHNIQUE: Gas Chromatography, Flame Ionization detector (PID optional). ANALYTE: Ethylene Oxide (EtO) INJECTION: 0.5 cc to 2 cc; sampling loop. TEMPERATURE -INJECTION: 100 C -DETECTOR: 220 C -COLUMN: isothermal 80 C CARRIER GAS: UHP Helium or Nitrogen 30 cc/minute COLUMNS: 6 to 9 foot 1% SP-1000 on 60/80 mesh Carbopack B CALIBRATION: compressed gas cylinder standard, ANALYTICAL RANGE: 0.20 ppmV to 0.50 %v/v

PRINCIPLE: The mass (or concentration) of ethylene oxide delivered to a control unit (inlet) during a sterilization cycle will be estimated (i.e., calculated) using the procedures in Appendix B or measured using the sampling/analysis procedures described above. The mass (or concentration) of ethylene oxide delivered to the control unit (inlet) during an aeration cycle and the mass (or concentration) of ethylene oxide emitted from the control unit (outlet) during a sterilization or aeration cycle will be determined using the sampling/analysis procedures described above and the calculations described in Appendix F.

APPLICABILITY: This method is applicable to the measurement of ethylene oxide in emissions from hospital equipment sterilization and aeration chambers, and appropriately configured commercial sterilizers.

LIMITATIONS: Refer to Appendix H for limitations associated with Tedlar bag and direct interface sampling/analysis of ethylene oxide.

INTERFERENCES: The diluent gas (such as Freon-12, HCFC-124, or others) may interfere with the EtO peak when testing low EtO emissions concentrations. GC operating conditions should be adjusted to provide baseline resolution between EtO and any diluent gas.

REFERENCED METHODS: This method is based on the EPA rule for EtO emissions from sterilizers (December 6, 1994, CFR 40, Part 63.63, pg. 689).

REAGENTS:

1. Ethylene oxide in compressed gas cylinders at levels bracketing the sample concentrations. Sterilant diluent gas may be included in the gas mixtures at levels expected in the emission matrix.
2. Helium, 99.999%, and FID grade hydrogen and air.
3. Air, purified, to be used for dilutions, blank preparation, and standard preparation.

EQUIPMENT:

1. Gas chromatograph, flame ionization detector, integrator, and columns.
2. Sample loops .50, 1.0, and 2.0 cc.

** SPECIAL PRECAUTIONS: Ethylene Oxide is a potential carcinogen. Work should be performed in a well ventilated fume hood. For specific regulatory requirements refer to the California Labor Code, Part 10, Section 9020; Title 8, California Code of Regulations, Section 5220.

CALIBRATION AND QUALITY CONTROL:

Refer to Appendix E for multipoint and daily calibration and quality control procedures. Refer to Appendix E for calibration procedures specific to the direct-interface gas chromatography.

LIST OF APPENDICES:

Appendix A:	Testing Procedures for Sterilizers with Catalytic Oxidation or Hydrolytic Scrubber Type Control Units
Appendix B:	Procedures for Estimating Mass of EtO at the Control Unit Inlet
Appendix C:	Testing Procedures for Aeration Chambers
Appendix D:	Documentation of the Probe Position at the Inlet of Catalytic Oxidation Units
Appendix E:	Calibration and Quality Control Procedures
Appendix F:	Calculations
Appendix G:	Reporting Requirements
Appendix H:	Method Limitations
Appendix I:	Tedlar Bag Sampling and Quality Control Procedures
Appendix J:	Definitions

APPENDIX A
TESTING PROCEDURES FOR STERILIZERS WITH
CATALYTIC OXIDATION OR HYDROLYTIC SCRUBBER
TYPE CONTROL UNITS

The following procedures shall be used to determine the efficiency of catalytic oxidation and hydrolytic scrubber types of control devices used in controlling emissions from an ethylene oxide sterilizer. The following aspects of the ethylene oxide compliance test are discussed below in this Appendix:

-Stack gas moisture determination.
-Stack gas volumetric flow rate determination.
-Determination of ethylene oxide concentration.

The procedures described herein are used to provide control unit inlet and outlet mass or concentration values to be used in calculating a control efficiency, as specified in the Ethylene Oxide Airborne Toxic Control Measure for Sterilizers and Aerators (17 CCR, Section 93108). As described below, stack gas moisture and volumetric flow rate determination may not be required for many control unit configurations. In such cases the control efficiency will be based solely on the concentration reduction across the control device.

Stack Gas Moisture

If volumetric flow measurements are required, measure the moisture content of the exhaust gas using ARB Method 4 during the evacuation and wash stages of at least one cycle (out of the three).

Stack Gas Flow Rate

If volumetric flow measurements are required, measure the volumetric flow rate of the control device exhaust continuously during the evacuation and wash cycles using the procedures found in ARB test methods 2, 2A or EPA Method 2C or 2D, as appropriate. Following are the recommended procedures for flow rate measurements for hydrolytic scrubber and catalytic oxidation type control devices.

Hydrolytic scrubber type control units: ARB Method 2A is required for measuring flow rates from hydrolytic scrubber type control units. It may be necessary to have multiple meters available in order to cover the expected range of flow rates. To calculate the molecular weight of the gas, assume that the composition of the sterilant gas is delivered unchanged from the chamber to the control unit and that the balance of the control unit emission gas is sterilant balance gas (if any) plus the measured moisture content. If there is any dilution of the sterilant gas though, the diluent gas concentration will have to be measured along with the concentration of EtO in the gas streams for volumetric flow to be calculated correctly. Record the flow rate at 1 minute intervals throughout the test cycle, taking the first reading within 15 seconds after time zero. Time zero is defined as the moment when the pressure in the sterilizer is released. (The purpose here is to measure flow rates concurrently with the bag samples or on-site GC). Correct the flow to standard conditions (68 F and 1 atm) and determine flow rate in units of standard cubic feet per minute for the run as outlined in

the test methods listed in this paragraph.

Catalytic oxidation type control units: Volumetric flow measurements may not be necessary for compliance testing of catalytic oxidation control units. In those systems that meet the following criteria the destruction efficiency calculation can be based solely on the EtO concentration measurements (not applicable where the inlet estimation technique is used).

1. no dilution between inlet and outlet sampling locations,

2. identical flow at inlet and outlet sampling locations, and

3. constant flow throughout the duration of the compliance test.

However, volumetric flow measurements may be required by the Districts in order to determine yearly mass emissions for inventory or facility risk assessment purposes. In those cases the following procedures shall be followed. Note that flow measurements need only be obtained at one of the sampling locations, either inlet or outlet, if the above conditions are met.

CARB Method 2 (type S pitot tube) should be used to determine stack gas velocity and volumetric flow rate of stacks greater than 12 inches in diameter. Testing stacks/ducts having cross-sectional diameters less than 12 inches and equal to or greater than four inches, must be conducted according to United States Environmental Protection Agency (USEPA) Stationary Source Sampling Methods 1A and 2C. The differential pressure gauge used to measure velocity head (delta P) must meet the requirements of ARB Method 2, Section 2.2 (also USEPA Method 2, Section 2.2). Pitot tube dimensions and specifications must be demonstrated to meet the requirements of ARB Method 2, Sections 2.7 and 4.2 (also USEPA Method 2, Sections 2.7 and 4.2). The source test reports must (1) include reasonably accurate as-installed drawings of the stack from the sterilizer to the point of emission, and (2) identify sampling locations, including dimensions, for each facility. Volumetric flow measurements will be conducted in the following manner: 1. A complete velocity traverse of the exhaust duct will be conducted in a manner consistent with applicable ARB or USEPA reference methods for flow determinations. 2. An average velocity pressure will be calculated from the individual pressure measurements made at each velocity traverse point as specified in the ARB/EPA reference method. 3. A traverse point, where the measured velocity pressure corresponds to the calculated average pressure, will be used to make single point pressure measurements during direct sampling and analysis of EtO emission. 4. Velocity pressure measurements will be made concurrently with each direct sample drawn out of the exhaust duct for analysis. The emissions flow rate will be determined from the set of pressure measurements made at the single traverse point and compared to the flow rate calculated from the initial, "complete" flow rate measurement procedure. The two flow rates must compare within 10% for the test run to be valid.

Typical cat-ox units operate at 50 and 100 scfm. The exhaust ducting of a typical control unit is 4 to 6 inches and occasionally up to 10 inches in diameter. The larger size ducting gives very low linear gas velocities (e.g., less than 10 ft/sec.) which are difficult to measure using standard pitot tube/manometer techniques. A practical solution is to reduce the diameter of the oversize stack to a temporary 4 inch stack during the test. Also, because

low flow/low velocity pressure conditions are anticipated for the exhaust duct emissions from some control units, use of a pressure transducer whose sensitivity is applicable for low magnitude pressure measurements and whose performance is traceable to a National Institute of Standards and Technology (NIST) reference standard is acceptable. Calibrations of the pressure transducer must be routinely conducted and calibration curves maintained in the company's file.

Determination of Ethylene Oxide Concentration at the Inlet of Control Units

Two options are provided, as outlined below, for determination of the mass of ethylene oxide delivered to the control unit inlet.

Option 1, Inlet Estimation: (sterilization cycle only, cannot be used for aeration tests) The mass of ethylene oxide emitted from the sterilization chamber and delivered to the control unit inlet, during a sterilization cycle, may be calculated using the estimation technique detailed in Appendix B. The procedures shall be performed, on an empty sterilizer, for the duration of the post-evacuation/wash stages under normal operating conditions. A short "soak" (exposure) stage, e.g., manually aborted after no more than ten minutes, should be used to minimize leak and chamber losses. For those sterilization systems where sterilant gas is also added as "make-up" during the exposure stage, the cycle shall be aborted and the chamber exhausted before such "make-up". The use of the inlet estimation technique is not allowed for sterilizer systems using water ring seal pumps (flow through or recirculating) for chamber evacuations. All test conditions must be characterized and reported with the final test results.

Option 2, Inlet Measurement: (must be used for aeration tests)
The mass of ethylene oxide emitted from the sterilization or aeration chamber and delivered to the control unit inlet may be determined by monitoring the chamber exhaust volumetric flow rate and EtO concentration (as described in the Measurement Methods section below) at the control unit inlet. If using this inlet measurement procedure, only the "entire duration of the first evacuation", as defined by the ATCM, must be tested for compliance purposes. The inlet and outlet of the control unit must be tested simultaneously. A loaded chamber must be used when performing compliance tests of sterilization cycles if using this inlet measurement option. If the chamber load is to be used for compliance testing of an aeration run, the "soak" (or exposure) stage may not be shortened, e.g., manually aborted. This inlet measurement procedure must be used for compliance testing of aeration cycles. All test conditions must be characterized and reported with the final test results.

Measurement Methods

The mass of ethylene oxide delivered to the control unit inlet during an aeration cycle and the mass of ethylene oxide emitted from the control unit outlet during a sterilization or aeration cycle must be determined by using one of the following sampling/analysis procedures and the calculations found in Appendix F. For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by following the steps outlined in Appendix D.

Tedlar bag sampling/analysis procedure: The Tedlar bag sampling procedure specified in Appendix I may be used to collect samples of sterilizer/aerator and control unit exhaust gas for subsequent analysis by GC/FID. The sampling quality assurance procedures detailed in Appendix I must be followed. In addition, the following procedures must be followed.

If Option 1, Inlet Estimation, is used then the entire 1st evacuation and wash period must be monitored for EtO emissions at the outlet of a control system. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

If Option 2, Inlet Measurement, is performed then the inlet and outlet monitoring will be conducted simultaneously. For cat-ox control units, integrated bag samples will be taken for at least the duration of the entire first evacuation. For acid scrubber control systems, integrated bag samples will be taken during the 1st evacuation and for the duration of any additional evacuation/wash periods (up to the point where aeration begins). Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

ARB staff recommends that one of the test personnel monitor the sterilizer chamber pressure during the run and communicate, with walkie-talkies, the sampling start and stop times to the sampling test crew.

Excess EtO shall be bubbled through a sulfuric acid (1 N solution) impinger before discharge, or alternatively can be routed back into the control unit inlet gas stream. Ensure that the excess sample gas which has passed through the acid filled impinger is discharged to a safe location and will not imperil test personnel.

The Tedlar bag samples must be analyzed within 24 hours (of the sample stop time) by the procedures listed herein. The mass of EtO associated with each bag sampling interval is calculated as outlined in Appendix F.

Repeat the procedures three times (three cycles). The arithmetic average percent efficiency (see Appendix F: Calculations) of the three runs shall determine the overall efficiency of the control device.

Direct Interface Sampling Analysis: As an alternative to the Tedlar bag sampling procedure described above, a gas chromatograph (with FID or PID) interfaced directly to the emission source may be used to continuously monitor ethylene oxide concentration at the outlet (and inlet) of the control device. For catalytic oxidation type control units, this procedure shall only be used if the sampling frequency is less than 2 minutes. For hydrolytic scrubber units, this procedure shall only be used if the sampling frequency is less than 1 minute. In addition, the following procedures must be followed.

If Option 1, Inlet Estimation, is used then the entire 1st evacuation and wash period must be monitored for EtO emissions at the outlet of a control system. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

If Option 2, Inlet Measurement, is performed then the inlet and outlet monitoring will be conducted simultaneously. For cat-ox control units, direct GC sampling will be conducted for at least the duration of the entire 1st evacuation. For acid scrubber control systems,

sampling will be conducted during the 1st evacuation and for the duration of any additional evacuation/wash periods (up to the point where aeration begins). Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

ARB staff recommends that one of the test personnel monitor the sterilizer chamber pressure during the run and communicate, with walkie-talkies, the sampling start and stop times to the sampling test crew.

When testing 3M sterilizer systems, or other systems with pulsed chamber exhaust, if the inlet mass is measured using the direct-GC approach, testers must use a one liter Greenburg-Smith impinger (empty) in the GC sampling train. The impinger shall be placed between the catalyst bed control unit and the on-site GC. This impinger will be connected by a Teflon line (less than 2 feet) to the catalyst bed's inlet sample port and by a Teflon line (less than 1 foot) to the heated sample line to the GC analyzer. The insertion of this impinger into the sample train will function as a mixing chamber for the sampled sterilizer exhaust gas prior to introduction into the GC analyzer. Sterilizers with pulsed exhaust will be continuously sampled through the modified sample train. The impinger geometry will mix the sampled gas and "smooth out" the variable concentrations associated with the pulsed exhaust gas flow. The impinger must be included in the system leak check, field blank and field spike.

The sample train is leak checked by plugging the sample line at the stack end and running the sample pump. Flow indicated by the rotameter should fall to zero. If it does not, seek and correct loose connections and other potential sources of leakage, then repeat the leak check.

Maintain a constant flow rate of approximately 2 liters per minute through the sample probe and transfer lines. If the sample transfer line is more than 10 feet long it should be heated to approximately 150 F.

Excess EtO shall be bubbled through a sulfuric acid (1 N solution) impinger before discharge, or alternatively, route the excess gas back into the control unit inlet gas stream. Ensure that the excess sample gas which has passed through the acid filled impinger is discharged to a safe location and will not imperil test personnel.

Repeat the procedures three times (three cycles). The arithmetic average percent efficiency (see Appendix F: Calculations) of the three runs shall determine the overall efficiency of the control device.

APPENDIX B

PROCEDURES FOR ESTIMATING MASS OF ETO AT THE INLET

The amount of ethylene oxide, in pounds, loaded into the sterilizer shall be determined by one of the following three procedures. These estimation procedures are valid only if there are no significant leaks or loss of EtO before the control unit. These estimation procedures shall be performed using an empty sterilization chamber. A short exposure stage, e.g., manually aborted, should be used to minimize leak and chamber losses. For those sterilization systems where sterilant gas is also added as "make-up" during the exposure stage, the cycle shall be aborted and the chamber exhausted before such "make-up". These estimation procedures may not be used with sterilization systems using water ring sealed pumps for evacuation of the chamber.

1) For small sterilizer operations using disposable sterilant cartridges, weigh the cartridge to the nearest .5 gram before and after use. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the sterilant mixture. Alternatively, if the cartridge supplier has certified the weight of EtO contained in the cartridge then this weight may be used for the estimation calculation. Or,

2) Weighing the ethylene oxide gas cylinder(s) used to charge the sterilizer before and after charging. Record these weights to the nearest 0.1 lb. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the gas. Or,

3) Calculating the mass based on the conditions of the chamber immediately after it has been charged and using the following equation. A calibrated differential pressure gauge shall be used to monitor the chamber pressure.

$$W_c = \frac{MW \times M \times P \times V}{R \times T}$$

where:

W_c = weight of ethylene oxide charged to the chamber, in pounds (grams)

MW = Molecular weight of ethylene oxide, 44.05 lb/mol (gr/gr-mole)

M = mole fraction of ethylene oxide

P = chamber pressure, psia

V = chamber volume, ft^3 (L)

R = gas constant, 10.73 $(psia*ft)^3/(mol*R)$ ((.08205 L*atm)/(g-mole*K))

T = temperature, R (K)

S = standard conditions are 68 F (R or K) and 1 atm.

APPENDIX C

TESTING PROCEDURES FOR AERATION ROOMS

The following procedures shall be used to determine the efficiency of a control device used to control ethylene oxide emissions from an aeration room. An aeration room is defined as any facility used for the dissipation of ethylene oxide residue from equipment previously sterilized in a sterilizer. The procedures are identical to those used to test sterilization chamber/control units (Appendix A) with the exception of the following.

The test shall be performed by placing a normal load of previously-sterilized equipment into the aeration room. The exposure stage should not be shortened or aborted.

The measurement procedures in Appendix A shall be used to determine the volumetric flow rate and EtO concentration at the inlet and outlet of the control device. (The inlet estimation technique cannot be used.)

If using the direct GC sampling and analysis procedure, sample and analyze a slipstream of the outlet concentration of EtO once every 3 minutes continuously for 1 hour.

The emissions test shall be conducted in the hour immediately following the loading of the aeration room. The test shall consist of one aeration cycle run. The test engineer and/or test administrator shall insure that the aeration room is being tested under normal operating conditions and equipment load. These conditions shall be documented and reported with the final test results.

Testers must have documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and make-up air). Procedures for insuring the correct probe position are listed in Appendix D. This documentation shall be reported along with the test final results.

APPENDIX D

DOCUMENTATION OF INLET PROBE POSITION FOR CATALYTIC OXIDATION UNITS

For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by the following steps:

1. Install the sampling probe in the control unit inlet.

2. During a sterilizer chamber evacuation monitor the volumetric flow rate of the chamber exhaust (e.g., before dilution in the control unit) and control unit exhaust. Also measure the concentration of ethylene oxide (or diluent gas) in the chamber exhaust (e.g., before dilution in the control unit) and at the control unit inlet (e.g., after dilution in the control unit). The expected concentration of EtO at the control unit inlet (at a given time) can be calculated by the following equation (note that the concentration and flow measurements must be taken simultaneously):

$$C_e = (Q_c / Q_{cu}) \times C_c$$

where:

C_e = EtO (or diluent gas) concentration expected at the control unit inlet.
Q_c = volumetric flow rate of the chamber exhaust
Q_{cu} = volumetric flow rate at the control unit outlet
C_c = EtO (or diluent gas) concentration measured in the chamber exhaust

3. The concentration of ethylene oxide measured at the control unit inlet must be within 10% of C_e for the probe to be documented as correctly positioned.

Alternatively, the correct placement of the control unit inlet probe may be documented as follows.

1. Install the sampling probe in the control unit inlet.

2. During a sterilizer chamber evacuation monitor the volumetric flow rate of the control unit exhaust. Also monitor the concentration of ethylene oxide, using the procedures outlined below, at the control unit inlet (e.g., after dilution in the control unit). Monitor both the flow rate and EtO concentration for the duration of the sterilization chamber exhaust (first evacuation and following washes).

3. Calculate the total amount of EtO delivered to the control unit. These calculations are outlined in Appendix F.

4. Calculate the estimated amount of EtO delivered to the control unit by following

the procedures in Appendix B.

5. Perform the above operations 3 times.

6. The concentration of EtO measured at the control unit inlet must be within 10 % of the estimated amount for the probe to be documented as correctly positioned.

The above test must be performed every time the probe is replaced or moved. The documentation showing correct positioning of the inlet probe must be included in the test report.

APPENDIX E

CALIBRATION AND QUALITY CONTROL PROCEDURES FOR ANALYSIS

1. INTRODUCTION

Each laboratory that uses this procedure is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability and an ongoing program of routine calibration and analysis of performance check samples to evaluate and document data quality. Two options are provided for routine calibration; calculation by linear regression or average response factor. The laboratory must maintain records of all performance checks to document the quality of generated data.

2. APPARATUS

2.1 Flowmeter, 100 sccm.

2.2 Tedlar bags, 10 L.

3. REAGENTS

3.1 Calibration standards can be obtained commercially in specially treated compressed gas cylinders. Concentrations of the minor components in each mixture must be traceable to the National Institute of Standards & Technology (NIST) or to a national measurement system approved by the Executive Officer of the Air Resources Board. NIST traceability may be accomplished by the specialty gas vendor via several methods:

(1) By analyzing the gas mixture directly against a NIST Standard Reference Material (SRM). This alternative can be utilized when an SRM with the proper component is available and the concentration is within a factor of two (2) from the gas mixture concentration.

(2) If SRMs are not available, analyzing the gas mixture against well characterized Gas Manufacturer Primary Standards (GMPS). These GMPS mixtures are analyzed against internal laboratory standards, gravimetric or volumetric, traceable to NIST.

4. INITIAL PERFORMANCE DEMONSTRATION

The following steps must be followed before the analytical method may be used. The performance evaluation must be repeated at least every six months. NOTE: Two options are provided for daily calibration (see Section 5). If response factor method (5.2) is used, both Option 1 and 2 (4.1.2 and 4.1.4) must be conducted during initial performance evaluation. Peak area integration, and not peak heights, must be used for the determination of instrument response.

4.1 Multipoint calibration

4.1.1 Standards are analyzed at least three times at four different concentrations. The concentration levels should be five times the limit of detection on the low end, approximately midway in the linear response range of the method, and near the high concentration end of the linear response limit. Results of the multipoint analyses must be documented and shall include data on intercept, slope, correlation of fit, relative standard deviations, range of concentrations tested, response factor and limit of detection calculations.

4.1.2 Option 1, Least Squares Fit. The least squares analysis of the data should produce a correlation coefficient of at least 0.99. Blank values shall not be subtracted from the raw data and the origin (0.0, 0.0) will not be used in the calculations. If the intercept deviates significantly from zero, the analysis must be reviewed for possible system contamination or other problems.

4.1.3 Standard deviations are calculated at each level of the multipoint and must be comparable to those published for the method.

4.1.4 Option 2, Response Factor. For each calibration target compound, calculate the pooled mean response factor (RF) from the set of four multipoint levels. Calculate the standard deviation and the percent relative standard deviation. The laboratory must demonstrate that RF values over the working range for the target compounds are constant. The percent relative standard deviations of the mean RF's must not exceed 15%. The equation for calculating the pooled mean response factor is listed below.

$$Rf_{pooled} = (RF_{1a} + RF_{1b} + RF_{1c} + RF_{2a} + \ldots\ldots RF_{4b} + RF_{4c}) / 12$$

where 1a through 4c represent the individual response factors calculated from the 12 multipoint runs.

4.1.5 Analytical Limits of Detection (LOD) must be calculated. The LOD for each method must be calculated by the following equation:

$$LOD = |A| + 3S$$

where

A is the least squares x-intercept, in units of ppmV, calculated from the multipoint data (section 4.1.1).

S is the standard deviation of replicate determinations of the lowest standard. At least 3 replicates are required. The lowest standard must be run at 1 to 5 times the estimated detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$S = RSD \times A$

where RSD is the relative deviation of the lowest standard analyzed.

4.1.6 The Limit of Quantitation (LOQ) must be calculated by the following equation:

$LOQ = 3.3 \times LOD$

No analysis results will be reported below the LOQ.

5. ROUTINE CALIBRATION PROCEDURE

Routine users of the method, ie. daily, will use one of the following options for calibrations and result calculations. Compound concentrations used in the calibration curves must bracket levels found in stationary source emission samples. Peak area integration, and not peak height, must be used for determination of instrument response.

5.1 Option 1, Least Squares Fit

A least squares fit, i.e. as determined with the initial multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every eight hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration as a check. The GC response must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

5.2 Option 2, Response Factor

The average response factors, i.e. as determined with the multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every eight hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration (see section 4.1) as a check. The measured RFs must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The response factors are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

For non-routine users of the method, ie. 1 test per month or less, calibration involves generation of at least a 3 point curve during each analysis day and a midpoint calibration check after every 10 samples. Either linear regression or mean response factor calculations can be used. The initial performance evaluation is still required.

6. ROUTINE QUALITY CONTROL

6.1 Laboratory Blanks

A laboratory method blank is a volume of ultra high purity gas carried through the entire analytical scheme. The gas used for blank runs should be certified by the gas supplier or laboratory to contain less than the analytical limit of detection (LOD) of the analytes of interest. The laboratory blank volume must be equal to the sample volumes being processed. Laboratory blanks are analyzed each shift before the analysis of samples may proceed. A blank is also analyzed after the analysis of a sample containing components with concentrations greater than the most concentrated standard used. The laboratory blank results will be reported along with raw sample data in final reports. Sample results should not be corrected for blank contribution. Note that a field blank analysis may be used in place of the laboratory blank. However, if the results of the field blank are greater than LOQ, a laboratory blank will be run to isolate the source of contamination.

6.2 Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples, or at least one sample per batch, will be analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift. The precision ($|Ave. - X_1|/Ave.) \times 100$) of duplicate analyses must fall within predetermined limits, i.e, 3 x RSD as established during the initial performance evaluation.

6.3 Calibration Check Sample

The midpoint standard used in multipoint calibrations must be analyzed every eight hours, or every ten samples, whichever is more frequent, to check instrument performance. The GC response of all analytes must be within 10 % of the mean values established in the multipoint calibration or a new calibration curve must be generated. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

6.4 Performance Evaluation Samples

To demonstrate data quality, performance evaluation samples may be analyzed periodically. At the discretion of the Executive Officer, periodic analysis of performance evaluation samples may be required. If analysis of performance evaluation samples is required by the Executive Officer, the analyses shall be conducted in the following manner. The performance evaluation material shall be used to evaluate both sampling and analytical systems. Performance evaluation samples shall be analyzed at a frequency dependent on how often the method is used. If the method is used on a daily basis, the performance evaluation sample must be analyzed twice a month. If the method is used less frequently, the performance evaluation sample must be analyzed once a month or whenever the method is used (whichever is less). A value of $\pm$10% of the stated concentration of the performance evaluation sample must be recovered for the analyte of interest. The results of these analyses must also be recorded and placed on permanent file for at least three years and shall be made available to the Executive Officer upon request. All performance evaluation samples will be labeled with an

expiration date and may be re-certified by the vendor if they contain sufficient volume (i.e. greater then 60% residual).

6.5 Qualitative Analysis Criteria

The retention time of the target compound must be within 0.06 RRT units of the standard RRT.

6.6 Quantitation Criteria

The column resolution criteria of 20% valley (as measured from the baseline to valley minimum) between a target compound and an interfering compound must be achieved before any quantitation can be allowed. When a compound interferes with the target compound and the degree of the interferences exceeds the column resolution criteria the compound can still be quantified if the following criteria is met. Set the reporting limit for the lowest amount that can be quantified high enough such that the interfering compound accounts for less than 10% of the area of the target compound.

7. REPORTING

Each report of analyses shall be in the following format and will include the following information. Refer to Appendix F for result calculations format.

7.1 Complete identification of the samples analyzed (sample numbers and source). Pertinent information should be submitted to the analytical laboratory via a chain of custody record.

7.2 Date of submittal of the sample, date and time of GC analysis. The latter should appear on each chromatogram included with the report.

7.3 The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).

7.4 The calibration data, including average response factors calculated from the calibration procedure described in Section 5. Include the relative standard deviation, and data showing that the midpoint response factors have been verified at least once during each 8-hour period of operation or with each separate set of samples analyzed.

7.5 All relevant data used to define the reporting limit will be reported. This will include parameters such as sampling volumes, sample injection volume, chromatographic interferences, and Tedlar bag contamination levels. In no case will results be reported below the established reporting limit. Test reports should include a table summarizing reporting limits (per sample) including a description of causes of variation.

8. DIRECT SAMPLING CALIBRATION AND QUALITY CONTROL PROCEDURES

Due to the nature of direct sampling routine calibration procedures are somewhat different. The sequence of in-field calibration, QC, and sample runs listed below is recommended when performing on-site analyses.

1. Run a 3 point calibration (triplicate runs at three levels) bracketing the expected sample concentration before each compliance test. The calibration curve prepared from the averages shall be used for quantitation of the cycle samples as well as determination of the limit of quantitation.

2. Run a field blank, through the entire sampling train, using zero air (ambient air normally can be used for this purpose for ethylene oxide sampling).

3. Run a field spike, through the entire sampling train, using the calibration standard closest to the sample concentrations. The spike gas introduced at the transfer line inlet should be at ambient pressure.
4. Analyze the field samples.

5. Run standard checks after sample analyses are complete for each cycle test. Standard check results must be within 10% of the pretest average values.

APPENDIX F

CALCULATIONS

Calculate the mass of EtO emitted from the control unit during each bag sampling period by using the following equation. Throughout the calculations, sufficient significant figures will be carried to round off to the required destruction efficiency. For example, if the rule requires 99.9% destruction efficiency, the calculations will be carried to 4 significant figures with the result rounded to 3 significant figures.

$$W_b = C \times V \times 44.05 \text{ lb/mol} \times \text{mol}/385.32\text{scf} \times 1/10^6$$

where:

W_b = the mass of EtO emitted corresponding to each bag

C = concentration of EtO in ppm

V = volume of gas exiting the control device corresponding to each bag sample, ft^3. The volume is determined by integration of the area under the curve of volumetric flow rate (corrected) versus time for the period each bag was sampled.

Add the mass corresponding to each bag, W_b, (i.e., mass emitted during the 1st evacuation plus the mass emitted during washes) used during the evacuation for the total mass (W_o).

$$W_o = (\text{Sum})W_b$$

Determine sterilizer control device efficiency (% Eff) using the following equation:

$$\% \text{ Eff} = (W_i - W_o)/W_i \times 100$$

where:

W_i = the total mass of EtO delivered to the control unit; this value can either be estimated using the procedures in Appendix A or measured using the procedures in Appendix B along with the calculations listed above (for W_i). Note that where appropriate, as described in Appendix A, the mass values in the control efficiency equation may be replaced with the corresponding EtO concentration averages.

If the direct GC approach is used, instead of Tedlar bag sampling, plot a concentration versus time curve. Calculate the mass flow at each sampling interval ($\leq$ 2 minutes for catalytic oxidation units, $\leq$ 1 minute for hydrolytic scrubbers) by selecting the concentration, C, and volumetric flow rate, F_v, at each interval. (Concentration and flow measurements must be synchronized.) Use the following equation to determine the mass flow rate W_t of EtO exiting the control device.

$$W_t = C \times F_v \times 44.05 \text{ lb/mol} \times \text{mol}/385.32 \text{ scfm} \times 1/10^6$$

where:

C = EtO conc (ppm), F_v = flow (scfm)

44.05 = molecular weight of EtO lb/lb-mole (g/g-mole)

385.32 = 359 scf/mole ideal gas law constant corrected to 68° F and 1 atm. (24.05 = 22.414 l/mole at 68° F).

Plot a curve of mass flow rate versus time and integrate for total mass of EtO for the control device outlet (W_o) (or inlet W_i).

Repeat the procedures and calculations three times. The arithmetic average percent efficiency of the three runs shall determine the overall efficiency of the control device.

APPENDIX G

REPORTING REQUIREMENTS

The following outline of reporting requirements is meant to be used as a general guide for EtO source test report reviewing purposes.

Sterilizer: manufacturer and model number, volume of the chamber, the type of sterilant gas used, the type of materials sterilized, a cycle process diagram, e.g., a plot of chamber pressure vs. time including footnotes regarding start and stop points of cycle stages and including a detailed explanation of the evacuation flow discharge path (water and vapor) during all stages of the cycle. If pressure/volume calculations are used to determine the weight of EtO charged to the chamber then chamber pressure sensor calibration data shall be included in the report.

Control Unit: type of chamber evacuation pumps used, type of control unit, manufacturer and model number, the size or capacity of the control unit, the operating temperature, a diagram of the control unit and sampling locations. If monitoring is conducted at the inlet of a catalytic oxidation unit then the test report shall include documentation of the correct positioning of the inlet sampling probe.

Test Data: plots of volumetric flow rate versus time (the reviewer should determine whether integrated sampling is appropriate), results of moisture determinations, a plot of the multipoint calibrations used for quantitative calculations, calculations for limit of detection and reporting limits, tables of raw data, final results, and all chromatograms. If the direct GC approach is used then plots of EtO concentration vs. time should be included in the report along with the integrated total mass emission result.

Quality Control: The test report shall include complete identification of the samples analyzed (sample numbers and source), date of submittal of the sample, date and time of GC analysis. The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).

APPENDIX H

METHOD LIMITATIONS

Alternative sampling and analytical methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative. The Executive Officer may require the submission of test data or other information showing that the alternate method is equivalent to Method 431. Any modifications to the sampling and analytical procedures described must also be approved in writing by the Executive Officer.

Tedlar Bag Sampling

Tedlar bag samples must be analyzed within 24 hours of end of the sampling period.

Tedlar bags with fittings other than those listed may not be suitable for EtO sampling. The appropriate recovery and stability tests should be conducted before using other fitting types (especially for bags with stainless steel fittings).

CARB staff have not conducted bag stability studies for EtO in dilute-acid hydrolytic scrubber emissions.

The integrated Tedlar bag sampling procedure is not applicable for testing of sources where both the emission gas volumetric flow rate and target compound concentration are variable. The test engineer and/or the reviewing agency will determine whether integrated sampling is appropriate.

Ethylene oxide may decay if exposed to sunlight. Thus, Tedlar bag samples and standards should be protected from sunlight exposure.

Sampling with Tedlar bags must be planned carefully so that the entire emission curve is monitored. To provide documentation that the sampling is representative of the emission curve, it is strongly recommended that a continuous monitor (e.g., FID) be used along with the bag at the control unit inlet. Sampling times could then be modified as necessary to account for shifts in emissions.

On-Site GC

At many hospitals, the control unit is not accessible from parking areas (i.e., with 150 foot heated lines to a parked GC-van). Thus, the GC, gas cylinders and associated support equipment must be physically moved to a location near the control unit, which may prove inconvenient. Also, adequate power may be difficult to get at some facilities.

Many testers feel that on-site GC is more expensive and more difficult than container sampling. In addition to the equipment required, performance of on-site GC requires that an experienced chemist be involved in the field operations.

Inlet Estimation

The inlet estimation procedure assumes that there is no loss of EtO to the chamber, chamber contents, transfer plumbing or pumps and that there are no leaks before the control unit.

Use of the inlet estimation technique assumes that the composition of the sterilant gas is accurately defined and consistent in individual cylinders/cartridges. Thus, a sample from the gas cylinder(s) used during the test should be analyzed to verify the exact sterilant gas composition for the inlet estimation.

Accurate estimates rely on accurate volume measurements and calibrated pressure gauges. Thus, manufacturer's chamber volume specifications should always be double checked and system pressure monitoring devices should be evaluated for accuracy.

Some sterilization systems add sterilant gas as needed to the chamber during the exposure stage because the chamber pressure may decrease slightly after initial pressurization. This addition of make-up gas would, if significant, invalidate the inlet estimation calculation since with existing systems it would be quite difficult to estimate the amount of make-up gas added. To minimize this source of error, when using the inlet estimation technique, the test should be conducted with an empty chamber and the exposure stage should be aborted after no more than 10 minutes.

Since the estimation technique can only be used for empty chamber tests, an exposed chamber load will not be available if subsequent aeration tests are to be performed. There must be an exposed load in the aerator for a valid test. Thus, an additional sterilization cycle with unaborted exposure stage would have to be run to provide the materials to be aerated. Furthermore, the inlet EtO concentrations must be physically measured with Tedlar bags or direct GC for aeration tests since estimation is not possible. Thus, where aeration tests must be conducted in addition to sterilizer tests, inlet estimation may not provide any time or cost benefit.

The inlet estimation technique should not be used with sterilization systems using water ring seal pumps, either flow through or recirculating.

Acid Scrubber

The stability of ethylene oxide in hydrolytic scrubber unit emission matrix, in Tedlar bags, has not yet been demonstrated (by ARB staff). Stability studies for ethylene oxide in this matrix should be conducted and results reviewed by the ARB before compliance tests are performed using this method.

This method allows the option to measure inlet concentrations (e.g., with bag sampling or by direct GC) instead of using the estimation technique outlined in Appendix B. However, the concentration of EtO at the inlet of hydrolytic scrubber units will be approximately 27% and 100% by volume for systems using 12/88 and 100% EtO sterilant gases, respectively. Due to the safety concerns associated with the high inlet EtO concentrations, it is recommended to use the calculation procedure in Appendix B. Anyone conducting tests at

the inlet of a hydrolytic scrubber should use extreme caution to avoid exposure to personnel and explosions.

The direct interface option may only be used to test hydrolytic scrubber units (inlet or outlet) if sample frequencies are 1 minute or less.

Quantitation of the diluent gas may be necessary at facilities using a sterilant mixture in order to calculate corrected volumetric flow rate.

Catalytic Oxidation

If the control unit inlet total mass is measured rather than estimated, testers must have documented evidence that the inlet probe is placed such that the sampled gases are completely mixed, i.e., chamber exhaust and make-up air (refer to Appendix D). This documentation shall be reported along with the test final results.

When testing 3M sterilizer systems, or other systems with pulsed chamber exhaust, if the inlet mass is measured using the direct-GC approach, testers must use a one liter Greenburg-Smith impinger (empty) in the GC sampling train. The insertion of this impinger into the sample train will function as a mixing chamber for the sampled sterilizer exhaust gas prior to introduction into the GC analyzer.

The direct interface option shall only be used to test catalytic oxidation units (inlet or outlet) if sample frequencies are 2 minutes or less.

Many sterilization systems use water ring seal pumps to evacuate the chamber. Some EtO will be retained in the water as the sterilant gas passes through the pump. Depending on system design, water ring seal pumps can cause a shift in EtO emission from the initial chamber purge to the air washes and even into the aeration cycle. Because of this emission shift, the inlet estimation technique should not be used with systems using water ring seal pumps.

Testers have speculated that EtO concentrations may, in some cases, be stratified in the exhaust duct flow from catalytic oxidation control units. Further investigation is necessary to define this problem. However, if stratification does occur, some sort of sample averaging probe would be required to obtain valid test results.

APPENDIX I

STANDARD OPERATING PROCEDURE FOR THE SAMPLING OF
ETHYLENE OXIDE EMISSIONS FROM STATIONARY SOURCES INTO TEDLAR BAGS

INTRODUCTION

This method should not be attempted by persons unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. APPLICABILITY

This sampling method uses a Tedlar bag to collect ethylene oxide (EtO) samples from applicable source emissions.

2. LIMITATIONS

2.1 Refer to Appendix H.

3. EQUIVALENCY

Alternative sampling methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer or his or her authorized representative. The Executive Officer may require the submission of test data or other information showing the alternate method is equivalent to Method 431.

4. APPARATUS

Apparatus required for sampling is described below. It is recommended that all equipment which comes in contact with sampled gas be made of Teflon or Tedlar unless these materials are found unsatisfactory and other materials demonstrated suitable in specific situations.

4.1 Sample line. Teflon tubing, 6.4 mm (1/4 inch) outside diameter, of minimum length sufficient to connect the probe to bag and not longer than 10 feet. If the sample line must be longer than 10 feet, then the sample line shall be heated and insulated and capable of operation at above 100 C (212° F).

4.2 Teflon valves or fittings shall be used to connect sample train components. Mininert Teflon valves are recommended.

4.3 Sample bags. Bags shall be made of Tedlar film, at least 0.002 in. thick.

4.3.1 Mininert Teflon valves are recommended.

4.3.2 Refer to Section 7 for this Appendix for apparatus used in Tedlar bag

manufacture, cleaning, and contamination testing.

4.4 Rigid container(s) for filling sample bags by application of vacuum.

4.4.1 The container shall be airtight when sealed.

4.4.2 The container shall be opaque except that a small window to check the condition of the bag within is permissible.

4.4.3 The container shall be fitted with couplings to mate with sample bags, sample line and vacuum line and a flow control valve capable of shutting off flow to the bag.

4.4.4 Sample bags may be fabricated with rigid containers as an integral unit.

4.4.5 An appropriate vacuum relief valve is suggested to protect bags and rigid container.

4.5 Pump, leak free, with capacity of at least 2 liters per minute.

4.6 Flow meter, rotameter type or equivalent, with measurement range of 0.05 to 1.0 liters per minute for observing sampling rate.

4.7 Shipping containers to protect bags in transport shall be opaque to protect bags from ultraviolet light. Containers shall have no staples, sharp edges or metal closures which might damage bags. The rigid container for filling bags may be used for bag transport; any window in the container shall be covered with opaque material during such transport.

4.8 Expendable Materials

4.8.1 Standard gas mixture for field spikes. Appropriate cylinder gases containing the pollutant(s) of interest in known concentration.

4.8.2 99.999% N_2 or zero air

5. PROCEDURE

The following describes the procedure for collecting samples from stacks. A field blank and a field spike must be obtained for each source test (Refer to section 6 for discussion).

5.1 (Optional) Determine stack moisture content by ARB Method 4; if moisture content is above the 60°F saturation level, then dilution of the sample bag may be required. If moisture content of stack gas is not determined, then Tedlar bag shall be monitored for condensation during sampling (see Section 5.7).

5.1.1 Procedure for Sample Bag Dilution. Bags should be pre-filled with

99.999% nitrogen or zero air to approximately one-third the final sample volume. The exact volume of dilution gas must be recorded to allow for correction of data. If condensation still occurs, increase dilution as necessary.

5.2 Assemble the sampling train at the sampling site as shown in Figure 1.

5.3 Leak check the sample train. To start the leak check, connect the sample line to the bag, making sure the valve on the bag is closed. Place the bag in the rigid container and close as if for sampling. Turn on the vacuum pump until a reading of 15 inches H_2O is maintained. Make sure that the probe line is **not** plugged and that the ON/OFF valve is open. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before the leak check continues. Turn the pump off, break the vacuum on the rigid container and open the mininert valve on the Tedlar bag. Place the bag back in the container and close as if for sampling. Plug (leak tight) the end of the probe. Turn on the vacuum pump and adjust until a reading of 15 inches H_2O is maintained. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before sampling continues. If impingers are used, extreme care must be used when applying and removing the vacuum to avoid carry over of the liquids in the impingers.

5.4 Break the vacuum on the rigid container. Unplug the end of the probe and place the end of the probe in the stack away from the walls. Care should be taken to avoid dilution of the stack gas sample with ambient air by sealing the open port area around the probe, especially in stacks with negative static pressure.

5.5 Make sure the sampling train is configured correctly, the valve on the sample bag is open and the ON/OFF valve is closed. Turn the vacuum pump on and adjust until a reading of 15 inches H2O is maintained. Begin sampling by opening the ON/OFF valve. Record the sample start time on the field data sheet.

5.6 Monitor the container vacuum and sample flow rate and adjust as necessary. After sampling for the planned interval, close the ON/OFF valve noting the time on the field data sheet. Bags should be filled no more than half full. If condensation occurs, discard sample and resample as per 5.1.1.

5.7 After sample purge is complete, close the ON/OFF valve, turn the pump off, break the vacuum on the rigid container and close the mininert valve on the bag.

5.8 Attach a label to each Tedlar bag sample (and impinger if used) containing the following information:

Job #
Date
Time
Sample/Run #

Plant Name
Sample Location
Log #
Initials of Sampler Operator

5.9 Promptly place the sealed bag in a shipping container; close the container to prevent possible degradation of the sample by ultraviolet light. Several bags may be placed in the same shipping container.

5.10 Fill out the Chain of Custody-Sample Record, Log Book Data sheets, and Field Data sheets. Copies of these forms are attached as Figures 2, 3 and 4.

5.11 Sample Bag Transport Procedure

5.11.1 Transport sample bags in opaque shipping containers.

5.11.2 Airborne transport could potentially result in rupturing of bags containing toxic samples. Surface shipment is advised. If airborne transport is unavoidable then bags should not be filled more than half way to avoid bag rupture.

5.11.3 Deliver bags to laboratory for analysis promptly. The maximum hold time is 24 hours.

6. QUALITY CONTROL

6.1 Sampling Runs, Time and Volume

6.1.1 Sampling runs. The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3) runs per source test.

6.1.2 Sample time. Integrated bag sampling. The sampling must be of sufficient duration to provide coverage of the average operating condition of the source as specified by the ATCM or as directed by the District.

6.2 Routine Sampling Quality Control. This section outlines the minimum quality control operations necessary to assure accuracy of data generated from samples collected in Tedlar bags. These QC operations are as follows:

* Field blank samples
* Field spike samples
* Collocated samples (optional)
* Tedlar bag contamination checks

6.2.1 Field blank samples. At least one field blank sample will be taken per source test. At the discretion of the tester, more blank samples may be

taken. Air or nitrogen from a compressed gas cylinder (ambient air may also be used) is collected in the bag in the manner described in section 5 of this method. This blank sample is transported and analyzed along with the stack gas samples. If field blank values are greater than 20 % of the stack gas values, then the data will be flagged. Field blank values will be reported along with the stack gas results.

6.2.2 Field spike samples. At least one field spike sample will be taken per source test. At the discretion of the field engineer, more spike samples may be taken. Pure air or nitrogen containing known concentration(s) of EtO is drawn from one bag to another through the sampling apparatus. The spiked sample is transported and analyzed along with the stack gas samples. Spike sample recoveries will be reported along with the source test results.

6.2.3 Collocated samples. Collocated sampling will be performed at the discretion of the tester. Samples are collected through two identical sampling systems simultaneously from the same stack sampling port. The analysis results of collocated samples are used to estimate method precision.

6.2.4 Tedlar bag contamination checks. Tedlar bags will be tested for contamination as outlined in Section 10 of this Appendix.

FIGURE 1

TEDLAR BAG SAMPLING TRAIN

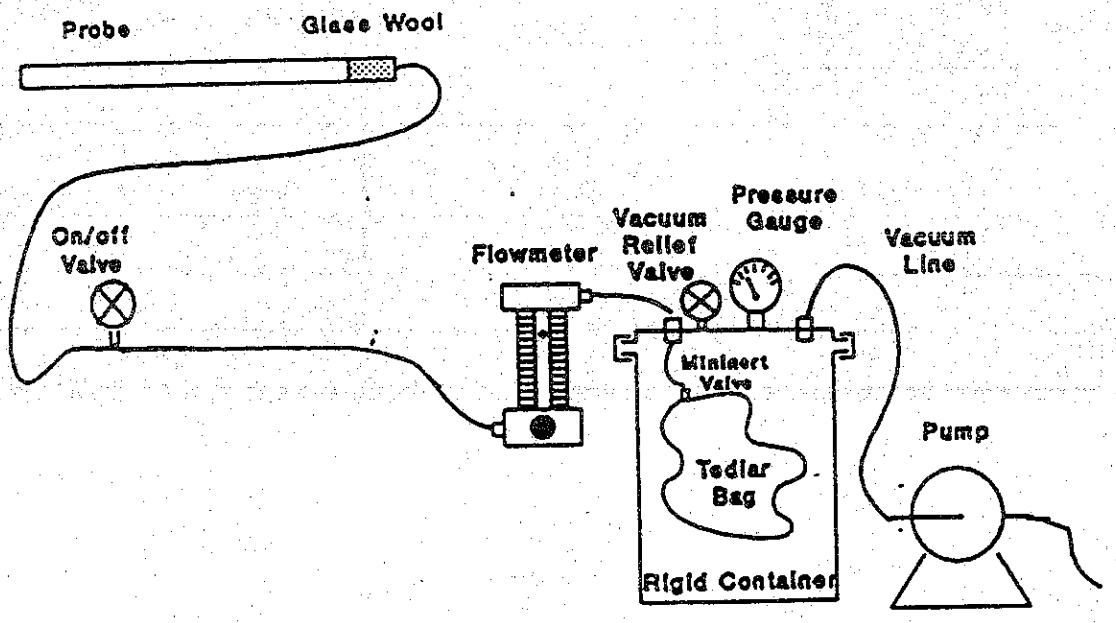

FIGURE 2

CHAIN OF CUSTODY

SAMPLE RECORD

Job Date: _____ Time: _____

Sample/Run# _____

Sample Location _____

Type of Sample _____

Log # _____ Fitting # _____

Initials _____

Action Taken	Start Date	Time	Given By	Taken By

Related I.D. #s	Description

FIGURE 3

CHAIN OF CUSTODY
LOG BOOK

PROJECT NO. _____

Log No.	Sample I.D.	Date	Time	Comment	Valve I.D. Bag Sample	Given By	Taken By

FIGURE 4

FIELD DATA SHEET

Project Name _____

Date _____ Sample ID:_____

LOG ID:_____

Sample Type:_____

BAG QUALITY ASSURANCE

Bag ID No._____ Initial Bag Leak Check_____

Bag Check Analysis (List Results of Bag check Analysis)

FLOWMETERS

Flowmeter ID_____

Date of Flow Meter Calibration Check_____

Sampler ID_____ Sampler Leak check_____

SAMPLE TIME

Time _____ Total time

_____

Flowrate _____ Average Flow

_____

COMMENTS_____

_____

7. Production of Tedlar Bags

New bags are recommended for each sample. Previously-used bags may be used again if cleaned and checked for leaks and contamination as specified below. Tedlar bags may also be purchased already assembled, but must be certified to specified contamination levels before use.

7.1 Materials and Equipment

7.1.1 Tedlar, 0.002 inch thickness.

7.1.2 Fittings for connection to sample line. Mininert Teflon valves are recommended. Quick-disconnect Swagelock fittings are commonly used, but are suspected of possible interferences at low ppb concentrations. Fittings should be composed of inert materials, teflon and stainless steel are recommended.

7.1.3 Septum fitting for injection of surrogates or removal of sample by syringe.

7.1.4 Cork borers for installation of fittings.

7.1.5 Lay-out Table to measure and cut Tedlar to size.

7.1.6 Heat-Seal Apparatus for making seams in Tedlar. Vertrod Thermal Impulse Heat Sealing Machinery or similar device. May require compressed air cylinder.

7.1.7 Pump for evacuation of bags during purging operations, together with fittings or manifold system to connect pump to bags.

7.1.8 Ultrasonic bath for cleaning fittings.

7.1.9 Oven for drying fittings

7.1.10 99.999% Nitrogen for purging bags.

7.1.11 Distilled water.

7.2 Clean Fittings

Use of organic solvents is not recommended due to possible contamination of bags.

7.2.1 Clean fittings by placing them in soapy water in ultrasonic bath for about one hour. Rinse fittings thoroughly with clean water, followed by a rinse with distilled water.

7.2.2 Bake fittings in a 100 F oven for at least 8 hours.

7.3 Manufacture of Tedlar Bag

Tedlar bags should be constructed in a clean area, with care taken to avoid contamination such as exposure to chemical fumes, solvent vapors or motor exhaust.

7.3.1 Cut one piece of Tedlar film from roll on lay-out table using a razor blade. A sheet of Tedlar measuring about 54" by 30" will make about a 30 Liter capacity bag (15 L at half-full).

7.3.2 Fold the Tedlar sheet in half and make two seams using heat-seal apparatus. Seams should be at least ½ inch from edge.

7.3.3 Place piece of cardboard inside bag. Use cork borer to make appropriate size hole for fittings, using cardboard to protect other side of bag. Tedlar film should fit snugly around base of fitting.

7.3.4 Attach previously cleaned sample line fitting. Use Teflon washers on inside and outside of bag to secure fitting.

7.3.5 Attach septum fitting if necessary. (Mininert valves have septum and sample line connections all on one fitting).

7.3.6 Seal remaining seam using heat-seal apparatus.

8. Leak Test

Check all sample bags for leaks by inflating with 99.999% nitrogen to a pressure of 2 to 4 inches of water. Good bags should hold constant pressure as indicated by a manometer for 10 minutes or (alternative test) should remain taut and inflated overnight. A small weight (e.g. Kimwipe box) may be placed on top of bag for the overnight leak check. Report bag acceptability on field data sheet (figure 4); destroy or repair and retest defective bags.

9. Bag Cleaning

Purge the bag with 99.999% nitrogen repeatedly until acceptable contamination values are attained. ARB staff experience has shown that 3 to 8 purges are needed to meet the target contamination levels of <1 ppb for most VOCs of interest.

10. Bag Contamination Check

10.1 Check bags for contamination by filling them halfway (so that check volume approximates actual sample volume) with 99.999% nitrogen, allow to equilibrate for 24 hours, then analyze for EtO.

10.2 Acceptable contamination levels may vary depending on the expected sample concentration. However, bags which contain contaminants at levels greater than the LOD will be rejected.

10.3 Label bags and record contamination levels. Also record contamination levels on field data sheets.

APPENDIX J

DEFINITIONS AND ABBREVIATIONS

Response Factor

The response of the gas chromatograph detector to a known amount of standard.

Performance Evaluation Sample

A sample prepared by EPA, ARB or other laboratories containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are usually known to the analyst.

Calibration Check Sample

A standard, normally the midpoint of multipoint calibrations (see section 422.199.4.1), which is analyzed each shift (or cycle) to monitor detector drift. The values of all analytes must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared.

Analytical Limit of Detection (LOD)

The lowest level at which detector response can be distinguished from noise. Refer to Appendix E for more detail.

Analytical Limit of Quantitation (LOQ)

The lowest level at which a compound can be accurately quantified. This value is 3.3 times the Limit of Detection.

Reporting Limit (RL)

The reporting limit (RL) is the lowest level that can be reliably quantitated within specified limits of precision and accuracy during routine analyses of source samples. Reporting limits will be based on parameters such as sampling volumes, dilutions, sample injection volume and chromatographic interferences.

Field Blank

A field blank is taken in the same way as a sample is taken except that pure air or nitrogen is used as a sample. The field blank is used to determine background levels in the sampling system. The gas used for blank runs should be certified by the gas supplier or laboratory to contain concentrations less than the limit of detection for the analytes of interest.

Field Spike

A standard gas containing ethylene oxide at known and certified concentration is introduced at the sampling probe inlet and transferred through the entire sampling train to be analyzed exactly as a normal stack emission sample. The standard gas used for the field spike should be the calibration standard closest to the actual sample concentrations. The spike gas introduced at the probe inlet should be at ambient pressure. The use of a Tedlar bag provides a simple procedure for introduction of the spike gas into the sample probe. The spike/standard gas can be transferred from a compressed gas cylinder into the Tedlar bag and the bag then attached (leak-tight) to the probe inlet. Spike gas can then be pulled through the sample train as under normal conditions.

Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples are analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift.

State of California
California Environmental Protection Agency
Air Resources Board

Proposed

Method 436

Determination of Multiple Metals Emissions from Stationary Sources

Adopted: _____

It is proposed that the content of ARB Method 436, Determination of Multiple Metals Emissions from Stationary Sources, be adopted as shown in the following text.

Method 436

Determination of Multiple Metals
Emissions from Stationary Sources

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TABLE OF CONTENTS (con't)

TABLE OF CONTENTS (con't)

Method 436

DETERMINATION OF MULTIPLE METALS EMISSIONS FROM STATIONARY SOURCES

1 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), vanadium (Vn) and zinc (Zn) stack emissions from stationary sources. This method is not suitable for the determination of hexavalent chromium or particulate matter emissions.

Any modification of this method shall be subject to approval by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in two impingers (analyzed for all metals), and acidic potassium permanganate solution in two impingers (analyzed only for Hg).

Sampling train components are recovered into separate front and back half fractions and acid digested using conventional Parr^{R} Bomb or microwave digestion techniques to dissolve inorganics and to remove organic constituents that may create analytical interferences. The analytical sensitivity achieved for a given sample will depend upon the sample matrix, types and concentrations of other chemical compounds in the sample matrix, as well as the original sample mass and instrument sensitivity.

After digestion, portions of the probe, filter and nitric acid/hydrogen peroxide digestion solutions are combined into a single front half composite and analyzed for Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, P, Pb, Sb, Se, Tl, Vn and Zn by inductively coupled plasma atomic emission spectroscopy (ICPAES) or direct aspiration atomic absorption spectroscopy (DAAAS). The acidic potassium permanganate impinger digestion solution, the HCl rinse solution and an aliquot from the front half composite sample are analyzed for mercury (Hg) by cold vapor atomic absorption spectroscopy (CVAAS).

Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, cobalt, lead, selenium and thallium, if these elements require greater analytical sensitivity than can be obtained by ICPAES. Additionally,

if desired, the tester may use DAAAS for analysis of all metals if the resulting reporting limits meet the goal of the testing program. Similarly, inductively coupled plasma mass spectroscopy (ICPMS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Tl and Zn.

The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance (QA) measures, as necessary, including actual sample matrix effects checks. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition shall be used to establish the quality of the data. The QA requirements of this method are detailed in Section 9.

1.3 DEFINITIONS

1.3.1 End User

For the purposes of this method, the regulating agency or its authorized representative shall be considered the end user if a determination of metals emissions from a stationary source is required as part of a regulatory process. Otherwise the end user shall be the party who defrays the cost of performing this method. The pre-test protocol must identify the end user.

1.3.2 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). The tester shall ultimately be responsible for performance of this method whether directly or indirectly through co-ordination of the efforts of the sampling and analytical groups.

1.3.3 Source Target Concentration

This is the target concentration for each emitted metal of interest specified by the end user of the test results. The target concentration shall be expressed in units of target metal mass per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/m^3 or $\mu g/m^3$).

1.3.4 Method Detection Limit

The method detection limit (MDL) is based on the precision of detection of the analyte concentration near the instrument detection limit.

1.3.5 Reporting Limit

The reporting limit (RL) is a limit for each metal at or below which data must not be reported. It is based on the minimum analyte mass that must be collected in the sampling train to allow detection during routine laboratory operation within

the precision established by the MDL determination. The RL will be calculated as 5 times the MDL for those metals not detected in pre-test reagent blanks. The RL for detected metals will be calculated as 5 times the pre-test reagent blank detection level.

Note:

If reagent blanks are not analyzed prior to testing, the RLs are calculated as 5 times the MDL or detection level, whichever is greater, determined for the field blank sample train. If the field blank detection levels yield unacceptable RLs, then the RLs may be established by analysis of the field reagent blank samples.

2 RANGE, PRECISION, METHOD DETECTION LIMIT, REPORTING LIMIT AND INTERFERENCES

2.1 ANALYTICAL RANGE

For the analyses described in this methodology and for similar analyses the ICPAES response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (μg/ml) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 μg/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of cadmium should be diluted to that level before analysis.

2.2 METHOD PRECISION

The precision (relative standard deviation) for each metal detected in an EPA method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.3 METHOD DETECTION LIMIT (MDL)

ICPAES analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICPMS analytical detection limits (based on SW-846, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

The detection limit for Hg by CVAAS (on the resultant volume of the digestion of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used.

The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Method detection limits for the target metals using the various analytical techniques referenced in this method are estimated in Table 1. The MDLs shown in Table 1 assume complete digestion and a final sample volume of 300 ml. For example, if the sample fraction volume is reduced from 300 ml to 30 ml, the MDL for that fraction is improved by a factor of ten. Actual MDLs are sample dependent and will vary based on the final sample volume, the sample matrix and the skill of the analyst.

2.4 REPORTING LIMIT (RL)

The tester shall calculate the reporting limits (RLs) for the target metals. This value will be 5 times the MDL determined for the pre-test blank contamination checks or 5 times the field blank sample results if no pre-test analyses are performed. If the field blank analytical results yield unacceptable RLs, then the field reagent blanks may be analyzed to calculate RLs.

The RL is a required parameter for pre-test minimum sample volume and minimum sample time determination. Therefore, when no pre-test contamination checks are performed, the minimum RL for each target metal shall be estimated as 5 times the MDL shown in Table 1 or 5 times the MDL estimated by the laboratory performing sample analysis.

2.5 INTERFERENCES

2.5.1 ICP

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Background and overlap corrections may be used to adjust for spectral interferences. Refer to EPA SW-846, Method 6010 and Method 6020 for details on potential interferences for this method.

2.5.2 GFAAS

The chemical, physical and spectral interferences associated with GFAAS are described in EPA SW-846, Method 7000, Section 3.2. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

2.5.3 DAAAS

The chemical, physical and spectral interferences associated with DAAAS are described in EPA SW-846, Method 7000, Section 3.1.

2.5.4 CVAAS

The chemical, physical and spectral interferences associated with CVAAS are described in EPA SW-846, Method 7470, Section 3.0.

3 RECOMMENDED PRE-TEST PREPARATION

The procedures presented in Section 3.1 through Section 3.5 are recommended procedures only. They are intended to help the tester maximize method performance by providing algorithms for estimating sample volume and times based upon predetermined analytical and process parameters. Failure to perform these procedures should not, by itself, constitute a fatal error when evaluating or auditing Method 436 test results. However, their omission could result in unacceptable test results.

3.1 RESPONSIBILITIES OF THE END USER AND TESTER

3.1.1 The End User

Before testing may begin, the end user of the test results shall specify the source target metals concentrations to be determined by this method using the guidelines of Section 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (Section 3.2) have been met.

3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

The tester shall obtain all relevant data that are required for pre-test calculations of sampling parameters. The tester shall develop and write a pre-test protocol before performing this method to help ensure satisfactory results.

The tester shall be responsible for ensuring that all sampling and analytical reporting requirements are met.

3.2 PRE-TEST PROTOCOL

The pre-test protocol should include the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of each emitted metal of interest (3.2.1),

(2) preliminary analytical data (3.3) for each target metal, and

(3) planned sampling parameters (3.5).

The protocol should demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. In addition, the pre-test protocol should include information on equipment, logistics, personnel and other resources necessary for an efficient and coordinated test.

At a minimum, the pre-test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be approved by the end user of the results and the tester.

The tester should not proceed with the performance of the remainder of this method unless the pre-test protocol is approved by the tester and the end user.

3.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

3.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

3.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

3.2.1.3 Interests of the End User, the Tester and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user must then provide applicable emissions results if they are available from previous tests of the facility to be tested. Otherwise, an estimate of metals emissions from the source must be obtained from the results of tests performed at similar sources. This target concentration is necessary for the calculation of the target sampling parameters required by Section 3.5.

3.3 PRELIMINARY ANALYTICAL DATA

3.3.1 Results of Blank Contamination Checks

Ideally, the tester should obtain from the analyst the results of pre-test metals contamination checks performed on the filter and reagent batches to be used for sample collection. The analytical report must satisfy the reporting requirements of Section 11.

In some instances, logistical and/or practical considerations may preclude obtaining preliminary contamination checks. In these cases, the tester shall use the analytical results for the field blank sample or the field reagent blank samples to calculate the RL. However, the tester must be aware that calculating the RL in this manner may yield an unacceptable RL resulting in unsatisfactory test data.

3.4 EXPECTED RANGE IN TARGET CONCENTRATIONS

The tester shall calculate the mass or concentration of each target metal expected in the sample that will be submitted for analysis (Section 1.3.3)

Metal analytes in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration metal could contain levels of other metals that exceed the upper limit of the method.

In some cases the solution is two analyses - first with undiluted composite, and then again after appropriate dilution of the composite. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained.

3.5 SAMPLING RUNS, TIME, AND VOLUME

3.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

3.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable target metal mass for quantitation. It must be based on a) the reporting limit (1.3.5), b) the source target concentration (3.2.1), and c) sampling limitations. Use Equation 436-1 to calculate the target MSV for each target metal analyte.

$$MSV(dscm) = RL \times \frac{1}{STC} \qquad 436\text{-}1$$

Where:

MSV	=	Minimum sample volume, dscm
RL	=	The reporting limit, ng/sample (Section 1.3.5)
STC	=	The source target concentration, ng/dscm (Section 3.2.1)

3.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected volumetric sampling rate. Use Equation 436-2 to calculate the minimum sampling time. required to collect the minimum sample volume calculated in section 3.5.2. The tester should use an average volumetric sampling rate (VSR) appropriate for the source to be tested. If the sampling rate (VSR) cannot be achieved in the field (Section 5.1.7), the sampling time shall be revised in Equation 436-2 to achieve the target MSV. The sampling time must be such that the emissions test is conducted during representative operating conditions of the source.

$$MST(hours) = \frac{MSV}{VSR} \times \frac{1}{60} \qquad 436\text{-}2$$

Where:

MST	=	Minimum sampling time, hours
VSR	=	Expected average volumetric sampling rate, dscmm
60	=	Factor to convert minutes to hours

The end user must decide whether the MSTs are all practically feasible. Based on this decision, the tester must use either Section 3.5.4 (a) or 3.5.4 (b) to calculate a planned sample volume (PSV).

3.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the RL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either (a) or (b). If the end user has decided that the MSTs are practically feasible, the tester must calculate the PSV according to Section 3.5.4 (a) and Equation 436-3.

(a) Calculate the PSV using the largest of the target MSV values calculated in Section 3.5.2 and the largest value for F that will give a practical sample volume. Use this PSV to calculate the planned sampling time (Section 3.5.5) and Equation 436-5.

(b) If the MSTs are not all practical, the tester and the end user must agree on a maximum practical sampling time (Section 3.5.5). This value must then be used for the PST in Equation 436-4 to calculate the PSV. The PST will be less than the MST and the PSV will be less than the MSV. Therefore, the primary reporting objective of the test cannot be achieved for all of the target metals. If the primary reporting objective cannot be achieved for all of the target metals, it must be discussed in the protocol and the alternative reporting objective (section 3.5.6) must be approved by the end user of the results.

436-3

$$PSV\,(dscm) = MSV \times F$$

436-4

$$PSV\,(dscm) = PST \times VSR$$

Where:

PST	=	Planned sampling time from Section 2.5.5 (b)
MSV	=	Minimum sample volume, dscm
F	=	A safety factor (≥ 1) that allows for deviation from ideal sampling and analytical conditions

The amount that is actually collected will be determined by practical sampling limitations, the intended use of the data and the level of uncertainty that the end user can tolerate in the measurement of the target concentrations

3.5.5 Planned Sampling Time (PST)

Two options are available depending on whether the primary objective can be achieved for all of the target metals.

(a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target metals and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field, the sampling time must be recalculated using the actual VSR and the target PSV in equation 436-5.

(b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$PST = \frac{PSV}{VSR} \times \frac{1}{60} \qquad 436\text{-}5$$

$$F = \frac{PST}{MST} \qquad 436\text{-}6$$

Where:

PST	=	Planned sampling time, hours
PSV	=	Planned sample volume, dscm
VSR	=	Expected average volumetric sampling rate, dscmm
60	=	Factor to convert minutes to hours

3.5.6 Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for the source for each target metal. The SRL shall be calculated using Equation 436-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$SRL = \frac{RL}{PSV} \qquad 436\text{-}7$$

Where:

SRL	=	Preliminary estimate of source reporting limit, ng/dscm
RL	=	Reporting limit, ng/sample
PSV	=	Planned sample volume, dscm

4 APPARATUS

The sampling and recovery apparatus, reagents and analytical equipment necessary for satisfactory performance of this method are described in this section.

The identification and quantitation of target metals in stationary source emissions tests are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Section 9 are used to monitor the performance of the sampling method, identify problems, and take corrective action.

4.1 SAMPLING TRAIN

The following sampling apparatus is required. The tester may use alternative apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 1. It is similar to the ARB Method 5 Train. The train consists of a nozzle, heated probe, heated filter, a series of five or six impingers emersed in an ice bath and a silica gel impinger or cartridge. A cyclone or similar device in the heated filter box may be used for sampling environments with high particulate matter concentrations.

The optional first impinger is initially dry and strongly recommended for sources with high moisture content. Its purpose is to prevent dilution of impinger reagent contained in the second and third impingers by serving as a moisture trap.

4.1.1 Probe Nozzle

Same as ARB Method 5, Sections 2.1.1 and 2.1.2, constructed of quartz or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° or less and the taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in ARB Method 5, Section 5.1.

4.1.2 Probe

The probe should be lined or made of quartz, borosilicate glass, or Teflon with a heating system capable of maintaining an exit gas temperature during sampling of 120 ± 14 °C (248 ± 25 °F), or other such temperature as approved by the Executive Officer. For high temperature applications (≥260 °C, 500 °F) a non-heated probe liner or a single glass tube consisting of a combined probe and nozzle may be used.

4.1.3 Preseparator

A cyclone, high capacity impactor or other device may be used if necessary to remove the majority of particles before the gas stream is filtered. This catch must be used for any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other materials may be used subject to approval by the Executive Officer.

4.1.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon filter support or other non-metallic, non-contaminating support and glass to glass seal or Teflon gasket. Glass filter supports may be used where stack gas temperatures exceed 260°C (500°F). Other holder and gasket materials may be used subject to approval by the Executive Officer.

The filter holder shall be contained in a heated enclosure capable of maintaining a temperature of 120 ± 14 °C (248 ± 25 °F) around the filter holder during sampling. A temperature gage capable of measuring temperature to within 3 °C (5.4 °F) shall be installed so the temperature around the filter holder can be monitored and regulated during sampling.

4.1.5 Sample Transfer Line

For sample train configurations where the first impinger is not directly connected to the filter holder, a sample transfer line must be used. The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings capable of forming vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6 Impinger Train

The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The impinger train shall consist of five or six impingers, depending on whether or not a moisture knockout impinger is used. Impingers are connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings and immersed in an ice bath. The first impinger is optional and is recommended as a

water knockout trap for use during test conditions where high stack gas moisture content might result in considerable dilution of the impinger solutions.

The impingers to be used in the metals train are described as follows. When the first impinger is used as a water knockout, it shall be of the Greenburg-Smith design modified to have either a short or long stem, appropriately sized for the expected moisture catch and installed empty. The second impinger (or the first HNO_3/H_2O_2 impinger) shall be of the Greenburg-Smith design modified to have a long stem as described for the first impinger in ARB Method 5, Section 2.1.7. The third impinger (or the impinger used as the second HNO_3/H_2O_2 impinger) shall be of the Greenburg-Smith design with the standard tip as described for the second impinger in ARB Method 5, Paragraph 2.1.7.

The fourth impinger shall be installed empty and shall be of the Greenburg-Smith design modified to have a short stem. The function of the fourth impinger is to prevent commingling of the solution in the second and third impingers with the solution in the fifth and sixth impingers. The fifth and sixth impingers shall be of the Greenburg-Smith design modified to have a long stem and shall contain a known quantity of acidic potassium permanganate ($KMnO_4$) solution (Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

In summary, the first impinger is empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 4.3.1), the fourth shall be empty, the fifth and sixth shall contain a known quantity of acidic potassium permanganate solution (Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out (first) impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

4.1.7 Silica Gel Cartridge

A silica gel cartridge or impinger shall be placed at the exit of the sixth (last) impinger. The silica gel may be contained in an impinger in the ice bath or an external cartridge if desired. The cartridge or impinger shall contain 200 to 300 grams of silica gel or equivalent desiccant for use in determining stack gas moisture and to prevent damage to the metering system.

4.1.8 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe to allow

constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs as part of an assembly, the configuration must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free configurations are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.9 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.10 Metering System

Vacuum gage, leak-free pump, thermometers accurate to within 3 °C (5.4 °F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 1. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.11 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft.) elevation increase or vice versa for elevation decrease.

4.1.12 Gas Density Determination Equipment

Temperature sensor and pressure gage, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred and alternative configurations of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.13 Teflon Tape

For capping openings and sealing connections on the sampling train. Teflon or other non-contaminating caps, sleeves or seals may also be used.

4.2 SAMPLING MATERIALS AND REAGENTS

A reagents used in performance of this test method shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, unless otherwise approved by the Executive Officer.

4.2.1 Filters

Filters shall contain less than 1.3 $\mu g/in.^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks should be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders such as the Pallflex 2500QAT-UP shall be used. However, if glass fiber filters which meet these requirements become available, they may be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles.

4.2.2 Water

Deionized, distilled. Water conforming to ASTM Specification D1193-77, Type II (incorporated by reference) is recommended. It is required that the water be analyzed for all target metals prior to field use (see Section 7.1.3). All target metal concentrations shall be less than 1 ng/ml.

4.2.3 Nitric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide

Thirty Percent (V/V).

4.2.6 Potassium Permanganate

4.2.7 Sulfuric Acid

Concentrated.

4.2.8 Silica Gel and Crushed Ice

Same as ARB Method 5, Sections 3.1.2 and 3.1.4 respectively.

4.3 SAMPLING REAGENT PREPARATION

4.3.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2

Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water, and then

add 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.3.2 10 Percent H_2SO_4 (V/V)

Mix carefully, with stirring, 100 mL of concentrated H_2SO_4 into 800 mL of water, and add water with stirring to make a volume of 1 L: this solution is 10 percent H_2SO_4 (V/V).

4.3.3 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V)

Prepare fresh daily. Dissolve, with stirring, 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/mL of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of $KMnO_4$ with H_2SO_4, there could be pressure buildup in the solution storage bottle. Therefore, these bottles shall not be fully filled and shall be vented to relieve excess pressure and reduce explosion potential. Venting should be performed in a manner that will not allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.3.4 Nitric Acid (HNO_3), 0.1 N

Carefully add, with stirring, 6.3 mL of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of each target metal.

4.3.5 Hydrochloric Acid (HCl), 8 N

Carefully add, with stirring, 690 mL of concentrated HCl to a graduated cylinder containing 250 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of Hg.

4.4 GLASSWARE CLEANING REAGENTS

4.4.1 Nitric Acid, Concentrated

Fisher ACS grade or equivalent.

4.4.2 Water

As specified in Section 4.2.2.

4.4.3 Nitric Acid, 10 Percent (V/V)

Carefully add, with stirring, 500 mL of concentrated HNO_3 to a graduated cylinder containing approximately 4000 mL of water. Dilute to 5000 mL with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5 SAMPLE DIGESTION AND ANALYSIS REAGENTS

Target metals standards, except Hg, may also be made from solid chemicals as described in EPA Methods 6010 or 7470 (SW-846). Refer to Citations 1, 3 or 4 of the Bibliography for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to Section 6.2.5 of ARB Method 101A.

4.5.1 Hydrochloric Acid, Concentrated

4.5.2 Hydrofluoric Acid, Concentrated

4.5.3 Nitric Acid, Concentrated

Baker Instra-analyzed or equivalent.

4.5.4 Nitric Acid, 50 Percent (V/V)

Carefully, with stirring, add 125 mL of concentrated HNO_3 to 100 mL of water. Dilute to 250 mL with water. Mix well. Reagent shall contain less than 2 ng/mL of each target metal.

4.5.5 Nitric Acid, 5 Percent (V/V)

Carefully, with stirring, add 50 mL of concentrated HNO_3 to 800 mL of water. Dilute to 1000 mL with water. Reagent shall contain less than 2 ng/mL of each target metal.

4.5.6 Water

As specified in Section 4.1.2.

4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution

See EPA SW 846, Method 7470 for preparation.

4.5.8 Stannous Chloride

See EPA SW 846, Method 7470 for preparation.

4.5.9 **Potassium Permanganate, 5 Percent (W/V)**

See EPA SW 846, Method 7470 for preparation.

4.5.10 **Sulfuric Acid, Concentrated**

4.5.11 **Potassium Persulfate, 5 Percent (W/V)**

See EPA SW 846, Method 7470 for preparation.

4.5.12 **Nickel Nitrate, $Ni(NO_3)_2\ 6H_2O$**

4.5.13 **Lanthanum Oxide, La_2O_3**

4.5.14 **Al Standard (AAS Grade), 1000 ug/ml**

4.5.15 **Ag Standard (AAS Grade), 1000 ug/ml**

4.5.16 **As Standard (AAS Grade), 1000 ug/ml**

4.5.17 **Ba Standard (AAS Grade), 1000 ug/ml**

4.5.18 **Be Standard (AAS Grade), 1000 ug/ml**

4.5.19 **Cd Standard (AAS Grade), 1000 ug/ml**

4.5.20 **Co Standard (AAS Grade), 1000 ug/ml**

4.5.21 **Cr Standard (AAS Grade), 1000 ug/ml**

4.5.22 **Cu Standard (AAS Grade), 1000 ug/ml**

4.5.23 **Fe Standard (AAS Grade), 1000 ug/ml**

4.5.24 **Hg Standard (AAS Grade), 1000 ug/ml**

4.5.25 **Mn Standard (AAS Grade), 1000 ug/ml**

4.5.26 **Ni Standard (AAS Grade), 1000 ug/ml**

4.5.27 **P Standard (AAS Grade), 1000 ug/ml**

4.5.28 **Pb Standard (AAS Grade), 1000 ug/ml**

4.5.29 **Sb Standard (AAS Grade), 1000 ug/ml**

4.5.30 **Se Standard (AAS Grade), 1000 ug/ml**

4.5.31 Tl Standard (AAS Grade), 1000 ug/ml

4.5.32 Vn Standard (AAS Grade), 1000 ug/ml

4.5.33 Zn Standard (AAS Grade), 1000 ug/ml

4.5.34 Mercury Standards and Quality Control Samples

Prepare fresh weekly a 10 μg/mL intermediate mercury standard by adding 5 mL of 1000 μg/mL mercury stock solution to a 500 mL volumetric flask; dilute to 500 mL by first adding 20 mL of 15 percent HNO_3 and then adding water to the 500 ml volume. Prepare a 200 ng/mL working mercury standard solution fresh daily: add 5 mL of the 10 μg/mL intermediate standard to a 250 mL volumetric flask and dilute to 250 mL with 5 mL of 4 percent $KMnO_4$, 5 mL of 15 percent HNO_3, and then water.

Use at least five separate aliquots of the working mercury standard solution and a blank to prepare the standard curve in the linear range of the instrument. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 μg/mL standard and diluting until in the calibration range.

4.5.35 ICP Standards and Quality Control Samples

Calibration standards for ICP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICP ANALYSIS	
Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Co, Cu, Fe,
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 μg/mL solutions with 5 percent nitric acid. Use a minimum of one standard and a blank to form each calibration curve. Also prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve. Suggested standard levels are 25 μg/mL for Al, Cr and Pb, 15 μg/mL for Fe, and 10 μg/mL for the remaining elements. Standards containing less than 1 μg/mL of metal should be

prepared daily. Standards containing greater than 1 μg/mL of metal are typically stable for a minimum of 1 to 2 weeks. For ICPMS, follow Method 6020 in SW-846.

4.5.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Cobalt, Lead, Selenium, and Thallium

Prepare a 10 μg/mL standard by adding 1 mL of 1000 μg/mL standard to a 100 mL volumetric flask. Dilute to 100 mL with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/mL standard by adding 1 mL of the 10 μg mL standard to a 100 mL volumetric flask and dilute to 100 mL with the appropriate matrix solution. Prepare other standards by dilution of the 100 ng/mL standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 μg/mL standard and diluting until it is in the range of the samples. Standards containing less than 1 μg/mL of metal should be prepared daily. Standards containing greater than 1 μg/mL of metal are typically stable for a minimum of 1 to 2 weeks.

4.5.37 Matrix Modifiers

4.5.37.1 Nickel Nitrate, 1 Percent (V/V)

Dissolve 4.956 g of $Ni(NO_3)_2 * 6H_2O$ in approximately 50 mL of water in a 100 mL volumetric flask. Dilute to 100 mL with water.

4.5.37.2 Nickel Nitrate, One tenth (0.1) Percent (V/V)

Dilute 10 mL of 1 percent nickel nitrate solution to 100 mL with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

4.5.37.3 Lanthanum

Carefully dissolve 0.5864 g of La_2O_3 in 10 mL of concentrated HNO_3 and dilute the solution by adding it with stirring to approximately 50 mL of water and then dilute to 100 mL with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

4.5.38 Whatman 40 and 541 Filter Papers (or equivalent)

For filtration of digested samples.

4.6 SAMPLE RECOVERY APPARATUS

Same as ARB Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman. and Glass Funnel), respectively, with the following exceptions and additions:

4.6.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs

For quantitative recovery of materials collected in the front half of the sampling train.

4.6.2 Sample Storage Containers

Glass bottles (see the precaution in Section 4.3.3 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 500 ml and 1000 ml, shall be used for storage of acidified $KMnO_4$ containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

4.6.3 Graduated Cylinder

Glass or equivalent.

4.6.4 Funnel

Glass or equivalent.

4.6.5 Labels

For identification of samples.

4.6.6 Polypropylene Tweezers and/or Plastic Gloves

For recovery of the filter from the sampling train filter holder.

4.7 SAMPLE PREPARATION AND ANALYTICAL EQUIPMENT

4.7.1 Volumetric Flasks, 100 ml, 250 ml, and 1000 ml

For preparation of standards and sample dilution.

4.7.2 Graduated Cylinders

For preparation of reagents.

4.7.3 **Parr[R] Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent)**

For sample digestion.

4.7.4 **Beakers and Watchglasses**

250 mL beakers for sample digestion with watchglasses to cover the tops.

4.7.5 **Ring Stands and Clamps**

For securing equipment such as filtration apparatus.

4.7.6 **Filter Funnels**

For holding filter paper.

4.7.7 **Whatman 541 Filter Paper (or equivalent)**

For filtration of digested samples.

4.7.8 **Disposable Pasteur Pipets and Bulbs**

4.7.9 **Volumetric Pipets**

4.7.10 **Analytical Balance**

Accurate to within 0.1 mg.

4.7.11 **Microwave or Conventional Oven**

For heating samples at fixed power levels or temperatures.

4.7.12 **Hot Plates**

4.7.13 **Atomic Absorption Spectrometer (AAS)**

Equipped with a background corrector.

4.7.13.1 **Graphite Furnace Attachment**

With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium). Pyrolytically-treated graphite platforms and tubes are recommended.

4.7.13.2 Cold Vapor Mercury Attachment

With a mercury hollow cathode lamp or electrodeless discharge lamp. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10 °C such that no condensation forms on the wall of the quartz cell. Same as EPA Method 7470. See **Note No. 2:** Section 7.3 for other acceptable approaches for analysis of Hg in Which analytical detection limits of 0.02 μg Hg/ml were obtained.

4.7.14 Inductively Coupled Plasma Spectrometer

With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

5 SAMPLE COLLECTION AND RECOVERY PROCEDURES

The complexity of this method is such that, to obtain reliable results, tester and analyst must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment; analytical calculations; reporting and the specific procedural descriptions throughout this method.

5.1 SAMPLING

5.1.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

5.1.2 Sample Train Preparation

Follow the same general procedure given in ARB Method 5, Section 4.1.1, except that the filter need not be desiccated or weighed. First rinse all sampling train glassware (including filter support) with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water and allow to air dry. Glassware may be dried in oven if desired. Cover all glassware openings where contamination can occur with a non-contaminating material (**do not use aluminum foil**) until the sampling train is assembled for sampling.

5.1.3 Preliminary Determinations

Same as ARB Method 5, Section 4.1.2.

5.1.4 Sample Train Assembly

Assemble the sampling train as shown in Figure 1. Follow the same general procedures given in ARB Method 5, Section 4.1.3 except place 100 mL of HNO_3/H_2O_2 solution (Section 4.3.1) in each of the second and third impingers as shown in Figure 1. Place 100 mL of the acidic $KMnO_4$ absorbing solution (Section 4.3.3) in each of the fifth and sixth impingers as shown in Figure 1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger or cartridge. Alternatively, the silica gel may be weighed directly in the impinger or cartridge just prior to train assembly. It is recommended that each impinger also be weighed just prior to train assembly to allow weight difference determinations for moisture calculations. Use the sampling train set-up and recovery sheet shown in Figure 5 or similar data form to record set-up parameters.

5.1.5 Sample Train Configuration Options

Several options are available to the tester based on the source specific sampling requirements and conditions.

5.1.5.1 Elimination of First Impinger

The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 100 ml.

5.1.5.2 Mercury Determination

The tester shall include an empty fourth impinger between the two HNO_3/H_2O_2 impingers and the two impingers containing acidic potassium permanganate solution for all test runs for which mercury is to be determined. Use the procedure described in Section 7.1.1 of ARB Method 101A, if necessary, to maintain the desired color in the last permanganate impinger. Mercury emissions can be measured, alternatively, in a separate train using ARB Method 101A.

<u>Precaution:</u> Take extreme care to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent acidic hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.5.3 Preseparator

Subject to the approval of the Executive Officer, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

5.1.5.4 Teflon Tape

Teflon tape or seals or other non-contaminating material should be used if necessary to ensure leak-free sampling train connections. The use of silicone grease is prohibited.

5.1.6 Leak-Check Procedures

Follow the leak-check procedures given in ARB Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.7 Sampling Train Operation

Follow the procedures given in ARB Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of ARB Method 5.

Note: When sampling for Hg, the tester must take steps to maintain the desired color of the acidified permanganate solution in the last impinger, such as described in Section 7.1.1 of ARB Method 101A. Alternatively, the tester may replace the last impinger, as necessary, with an impinger containing 100 ml of fresh acidified permanganate solution to prevent discoloration. If additional permanganate solution is used during a sample run, it must be combined with the original permanganate solution during sample recovery.

5.1.8 Field Blank Train

Each source test must include at least one field blank train. Prepare and configure the blank train in a manner identical to the actual sampling trains. The field blank train shall be taken through all of the steps from preparation through leak check without actual sampling. Upon completion of the leak check, the entrance and exit of the blank train shall be sealed with non-contaminating material and the blank train must remain in the test area for a length of time equivalent to an actual Method 436 sampling period.

Recover the field blank train in the same manner as described for stack samples in Section 5.2.

5.1.9 Calculation of Percent Isokinetic

Same as ARB Method 5, Section 4.1.6.

5.2 SAMPLE RECOVERY

Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. Record all post-test sample recovery parameters on the set-up and recovery sheet shown in Figure 5 or a similar data sheet.

Allow the probe to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, with the undesired result of drawing liquid from the impingers into the filter or commingling of the impinger contents.

The tester may opt to disassemble the sampling train into components before moving the sampling train from the sampling area to the cleanup site. If so, remove the probe or probe-filter assembly from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

The sample is recovered and treated according to the schematic shown in Figure 2. Assure that all items necessary for recovery of the sample do not contaminate the sample. Do not use any metal-containing tools or materials when recovering the train.

Note: some gloves may contain dust which is high in zinc and may contaminate samples.

5.2.1 Container No. 1 (Filter)

Carefully remove the filter from the filter holder and place it in its labeled petri dish container. Use acid-washed polypropylene or Teflon coated tweezers or clean, single-use surgical gloves rinsed with water to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering the filter. Seal the labeled petri dish.

5.2.2 Container No. 2 (Probe and Filter Holder Front Half Rinses)

Quantitatively recover material deposited in the nozzle, probe liner and front half of the filter holder by thoroughly rinsing and brushing with a measured volume of 0.1 N nitric acid and place the wash into a tared, labeled sample storage container. Perform the rinses as described in ARB Method 5, Section 4.2 using 0.1 N nitric acid in place of acetone. It is recommended that two people recover the probe to minimize sample losses. Brush until the 0.1 N nitric acid rinse shows no visible particles, after which make a final rinse of the inside surface with 0.1 N nitric acid.

Record the volume of the combined rinse to the nearest 2 ml. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water and discard these rinses.

5.2.3 Container No. 3 (Impingers 1 through 3, Contents and Rinses)

Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container.

Wipe off the outside of each impinger to remove excess water and other material. Record the weight of each impinger or measure the liquid in the first three impingers volumetrically to within 0.5 mL using a graduated cylinder and record the volume of liquid. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with a measured volume of 0.1 N nitric acid. Repeat this rinsing, then inspect the impingers for any abnormal conditions. Rinse each piece of glassware used to connect the impingers twice with a measured volume of 0.1 N HNO_3; transfer this rinse into a tared labeled Container No. 3. Record the total rinse volume. Combine the rinses and impinger solutions, measure and record the final weight or final volume of Container 3. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.4 Container No. 4 (Impinger 4 - Middle knock-out)

Wipe off the outside of the impinger to remove excess water and other material. Record the weight of the fourth (previously empty) impinger or measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Quantitatively rinse the impinger with a measured volume of 0.1 N HNO_3. Record the volume of rinse used. Add the rinse and impinger catch to a tared, labeled Container 4, seal the container and mark the fluid level. Record the final weight of the container or record the final volume of its contents.

5.2.5 **Containers Nos. 5A and 5B (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 5 & 6)**

Wipe off the outside of each impinger to remove excess water and other material. Record the weights of the permanganate impingers (fifth and sixth) or measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas.

Place the contents of impinger 5 into a labeled glass storage bottle identified as container 5A. Using measured volumes of fresh $KMnO_4$, rinse impinger 5 and its and connecting glassware a minimum of three times and pour the rinses into container 5A. Using 50 ml total of water, rinse impinger 5 and its connecting glassware a minimum of three times and pour the rinses into container 5A, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5A. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Place the contents of impinger 6 into a labeled glass storage bottle identified as container 5B. Using measured volumes of fresh $KMnO_4$, rinse impinger 6 and its and connecting glassware a minimum of three times and pour the rinses into container 5B. Using 50 ml total of water, rinse impinger 6 and its connecting glassware a minimum of three times and pour the rinses into container 5B, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Note: **Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.**

Do NOT rinse with 8 N HCl if no visible deposits remain after rinsing with the fresh $KMnO_4$.

5.2.6 **Container No. 6 (HCl Rinse)**

Examine impingers 5 and 6 for sample residue. If residue is observed, rinse these impingers with 25 mL of 8 N HCl. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers

combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Properly seal and label container No. 6.

5.2.7 Container No. 7 (Silica Gel)

Observe the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. If a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g. Alternatively, transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.

5.2.8 Container No. 8 (0.1 N Nitric Acid Blank)

At least once during each field test, place 100 mL of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank)

At least once during each field test, place 200 mL of 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank)

At least once during each field test place 100 mL of the acidified potassium permangante solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Blank)

Collect only if HCl rinse described in Section 5.2.6 was conducted. At least once during each field test, place carefully and with stirring, 25 mL of the 8 N

hydrochloric acid used to rinse the acidified potassium permanganate impingers into 200 mL water in a labeled container for use in the back half field reagent blank for mercury and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.12 Container No. 12 (Filter Blank)

Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish and make the appropriate entries in the reagent blank field data sheet shown in Figure 6. Store and transport on wet ice together with the sample filters. This will be used as the field reagent blank.

5.3 SAMPLE STORAGE

5.3.1 Filters

All filters shall be stored in their labelled petri dish away from possible contamination sources. Source filters should be separated from field and reagent blank filters to prevent cross contamination.

5.3.2 Liquid Samples

All liquid samples shall be stored in their respective labelled sample jars away from possible contamination sources. Source samples should be separated from field and reagent blank samples to prevent cross contamination. The tester should also consider separating the acidified $KMnO_4$ samples due to their volatile nature.

6 ANALYTICAL PREPARATION

6.1 FIELD SAMPLES AND REAGENT BLANKS

Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If leakage has occurred, either void the sample or use methods, subject to the approval of the Executive Officer, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3. Record the data necessary to process, digest and prepare the sample containers for analysis using the data sheets supplied in Figure 7 through Figure 11.

6.1.1 Container No. 1 (Filter)

Divide the filter with its filter catch into portions weighing approximately 0.5 g each. Place the filter pieces into the analyst's choice of either individual microwave pressure relief vessels or Parr^R Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For

microwave heating, microwave the sample vessels for approximately 12 to 15 minutes of total heating time at 600 watts in intervals as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). For conventional heating, heat the Parr^R Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.2, below.

Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

6.1.2 Container No. 2 (Probe Rinse)

Determine the pH of this sample. If the pH is higher than 2, acidify the sample with concentrated nitric acid to pH 2 or lower within five (5) days of sample collection. Then rinse the sample into a beaker with water and cover the beaker with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Digest the sample in microwave vessels or Parr^R Bombs by carefully adding 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid and then continuing to follow the procedures described in Section 6.1.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 6.1.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 150 mL (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 15 mL aliquot (or 10% of the Fraction 1 volume) and label as Fraction 1B. Label the remaining 135 mL portion (or 90% of the Fraction 1 volume) as Fraction 1A. Analytical Fraction 1A is analyzed using ICP or AAS for all metals except Hg. Analytical Fraction 1B is analyzed using CVAAS for front half Hg.

6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as Fraction 2A. Combine Analytical Fractions 1B and 2B to create Analytical Fraction B.

Determine the pH of Fraction 2A within five (5) days of sample collection. If necessary, acidify using concentrated nitric acid to pH 2 or lower. Rinse the sample into a beaker with water and cover with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Then follow either of the digestion procedures described in Sections 6.1.3.1 and 6.1.3.2 below.

6.1.3.1 Conventional Digestion Procedure

Add 30 mL of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 mL of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 mL of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

6.1.3.2 Microwave Digestion Procedure

Add 10 mL of 50 percent nitric acid and heat for 6 minutes total heating time in alternating intervals of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 6.1.1. Allow the sample to cool. Add 10 mL of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 mL of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

Fraction 1A is combined with Fraction 2A to form Analytical Fraction A and analyzed using ICP or AAS for all metals except Hg. Fraction 1B is combined with Fraction 2B to form Analytical Fraction B and analyzed using CVAAS to determine front half mercury.

6.1.4 Container No. 4 (Impinger 4)

Measure and record the volume of impinger 4 to within 0.5 ml and place in Container No. 4. Label the contents of container No. 4 as Analytical Fraction E. Analytical Fraction E will be separately analyzed for Hg using CVAAS.

6.1.5 Container Nos. 5A and 5B (Impingers 5 & 6)

Measure and record the volume of impinger 5 to within 0.5 ml and place in Container No. 5A. Measure and record the volume of impinger 6 to within 0.5 ml and place in Container No. 5B. Keep the samples in containers Nos. 5A and 5B separate from each other.

To remove any brown MnO_2 precipitate from the contents of Container No. 5A, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5A to be Analytical Fraction C. Analyze Analytical Fraction C for Hg within 48 hours of the filtration step.

Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

Filter the contents of Container No. 5B through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5A through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction D. Analyze Analytical Fractions C, D and E according to the procedures in Section 7.3.

6.1.6 Container No. 6 (HCl Rinse)

This sample will exist only if the HCl rinse was necessary. Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction F. This sample is analyzed as described in Section 7.3.

6.1.7 Container No. 7 (Silica Gel)

Weigh the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g using a balance (this step may be conducted in the field).

6.1.8 Field Reagent Blanks

The field reagent blank samples in Container Numbers 8 through 12 produced previously in Sections 5.2.8 through 5.2.12, respectively, are used to correct sample values when authorized by the Executive Officer. These field reagent blanks shall be processed, digested, and analyzed as shown in Figure 4 and described as follows. Digest and process Container No. 12 contents per Section

5.3.1. Combine Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.3. Combine the diluted digestates from Containers 8, 9 and 12. Use aliquots as Fractions A and B Blanks. Container No. 10 and Container No. 11 contents are Fraction C Blank and Fraction E Blank respectively. Analyze Fraction C and E Blanks (if applicable) per Section 7.3.

7 SAMPLE ANALYSIS

For each sampling train, four to six individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3. Fractions A and B consist of the digested samples for the train from the probe rinse through impinger 3. Fraction A is for ICPAES, ICPMS or AAS analysis as described in Sections 7.1 and/or 7.2. Fraction B is for determination of front half mercury as described in Section 7.3.

Fraction C consists of the impinger contents and rinses from permanganate Impinger 5. Fraction D consists of the impinger contents and rinses from permanganate Impinger 6 combined with the digested MnO_2 precipatate from impinger 5. These samples are analyzed for mercury as described in Section 7.3. Depending on the test, there may be a separate sample from Impinger 4 (Fraction E) and/or an HCl rinse (Fraction F). These samples should be analyzed for mercury and included in the total back half mercury catch. The total back half mercury catch is determined from the sum of Fraction C, Fraction D, Fraction E and Fraction F. Report the analytical results on the Laboratory Analytical Results data sheet shown in Figure 12.

7.1 ICPAES AND ICPMS ANALYSIS

Analyze analytical fraction A by ICPAES using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 9.4.1. Recommended wavelengths for analysis are as follows:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Cobalt	228.616
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorous	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICPMS analysis by following Method 6020 in SW-846.

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

7.2 AAS by Direct Aspiration and/or Graphite Furnace

Analysis of metals in Fraction A using graphite furnace or direct aspiration AAS is often a preferred option. Use Table 2 to determine which techniques and methods should be applied for each target metal. Table 2 also lists possible interferences and ways to minimize these interferences. Calibrate the instrument according to Section 8.3 and follow the quality control procedures specified in Section 9.4.2.

7.3 Cold Vapor AAS Mercury Analysis

Analyze analytical fractions B, C, D (if applicable) and E (if applicable) separately for Hg using CVAAS following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F, or, optionally using **NOTE No. 2** at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. Dilute the aliquot to 100 ml with water. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see **NOTE No. 1** at end of this Section). The total amount of Hg in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of SW-846 Method 7470 or Method 303F. (See **NOTE No. 2** at the end of this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15 HNO_3 percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE No. 1: When Hg levels in the sample fractions are below the RLs given in Table 1, select a 10 ml aliquot for digestion and analysis as described.

NOTE No. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIMS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this Section 5.4.3.: (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

8 CALIBRATION

Maintain a laboratory log of all calibrations.

8.1 Sampling Train Calibration

Calibrate the sampling train components according to the indicated sections of ARB Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

8.2 Inductively Coupled Plasma Spectrometer Calibration

Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. Check the instrument calibration once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed. Perform ICPMS calibration by following Method 6020 in SW-846.

8.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses

Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

9 QUALITY CONTROL

9.1 PRE-TEST DETERMINATIONS (RECOMMENDED)

Determine the linear range and minimum detectable and quantifiable limits of the analytical instrument selected for the respective target metals. Determine the reporting limit, minimum sample volume, planned sample volume and planned sample time according to Section 3 of this method.

9.2 FIELD REAGENT BLANKS (IF ANALYZED)

Follow the steps in Figure 4 of this method.

9.2.1 Filter, Front and Back Half

Combine one filter from the same lot as those used for sample collection (Container No. 12) with the reduced digestate from container 8. Combine 15 ml of this sample with a 15 ml aliquot from Container No. 9 and analyze for Hg. Combine the remainder of this sample with digested portion of Container No. 9 and analyze for multimetals.

9.2.2 Potassium Permanganate and Hydrochloric Acid

Analyze the contents of Container No. 10 and Container No. 11 (if applicable) for Hg.

9.2.3 Reagent Water Check

Analyze a minimum of triplicates of the water described in Section 4.1.2 for concentrations of target metals. All target metal concentrations shall be less than 1 ng/ml.

9.3 SAMPLING

9.3.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

9.3.2 Blank Train

At least one blank train per field test shall be prepared, leak-checked and recovered in the field. The blank train shall be labelled and analyzed as if it were a sample train. The blank train results are used primarily for determining reporting limits (RL's) and as a check for on-site contamination. They also provide information regarding the magnitude of source emissions relative to background.

9.3.3 Dedicated Impingers

Impingers should be coded for easy identification. Impingers used for potassium permanganate should not be used as nitric acid impingers for other tests to avoid contamination.

9.4 SAMPLE HANDLING

9.4.1 Holding Times

Store all liquid samples in acid solutions of pH 2 or lower as soon as practicable after sampling. It is recommended that pH paper be used in the field after

recovery of the sample train to verify pH 2 or lower condition. Five days is the maximum time allowed between sampling and storage in pH 2 acid solutions. All liquid samples should be stored in a secure location immediately after sample train recovery.

Analyze appropriate sample fractions for mercury within 28 days of sample date. Analyze Fraction A for target metals other than mercury within two months of sampling date.

9.5 ANALYTICAL QC

Analytical QA/QC requirements for ICP and AA analysis are summarized in Figure 13.

9.5.1 ICPAES and ICPMS Analysis

Follow the respective quality control descriptions in Section 8 of Methods 6010 and 6020 of SW-846. For the purposes of a three run test series, these requirements have been modified as follows: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 20% of average or repeat all analysis). All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese, Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc

Analyze all samples in duplicate. Perform a matrix spike on one sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. Analyze a quality control sample to check the accuracy of the calibration standards. The results must be within 20 percent or the calibration repeated. All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.3 Cold Vapor AAS Analysis for Mercury

Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (within 15% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F Fraction B blank, fraction C blank and fraction E blank (if applicable) values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

10 CALCULATIONS

10.1 DRY GAS VOLUME

Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of ARB Method 5.

10.2 VOLUME OF WATER VAPOR AND MOISTURE CONTENT

Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of ARB Method 5.

10.3 STACK GAS VELOCITY

Using the data from this test and Equation 2-9 of ARB Method 2, calculate the average stack gas velocity.

10.4 METALS (Except Hg) IN SOURCE SAMPLE

10.4.1 Total Metals (except Hg); Analytical Fraction A

Calculate separately the amount of each metal collected in Analytical Fraction A of the sampling train using the following equation:

$$M_A = C_{a1} F_d V_{soln,1} \qquad \text{Eq. 436-8}$$

where:

M_A = Total mass of each metal (except Hg) collected in the front half of the sampling train (Analytical Fraction A), μg.

C_{a1} = Concentration of metal in Analytical Fraction A as read from the standard curve, μg/ml.

F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction A is diluted to 10 ml to place it in the calibration range, F_d = 5).

$V_{soln,1}$ = Total volume of digested front half sample solution (sum of Analytical Fractions 1A and 2A), ml.

10.4.2 Total Metals (Fraction A), Method Blank Corrected (except Hg)

In cases when the Executive Officer allows correction of analytical results for method (laboratory) blank metals concentrations, calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_A - M_{Ab}) \qquad \text{Eq. 436-9}$$

where:

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, μg.

M_{Ab} = Blank correction value for mass of metal detected in the Fraction A method (laboratory) blank, μg.

10.5 Hg IN SOURCE SAMPLE

10.5.1 Front-Half Hg; Analytical Fraction B

Calculate the amount of Hg collected in the filter and probe rinse combined with

impingers 1 through 3 to form Analytical Fraction B of the sampling train by using Equation 436-10:

$$Hg_{fh} = \frac{Q_B}{V_B} (V_{soln,B}) \qquad \text{Eq. 436-10}$$

where:

Hg_{fh} = Total mass of Hg collected in Analytical Fraction B (filter, probe rinse and first three impingers of the sampling train), μg.

Q_B = Quantity of Hg, μg, TOTAL in the ALIQUOT of Analytical Fraction B analyzed. **NOTE**: For example, if a 10 ml aliquot of Analytical Fraction B is digested, but only 1 ml is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_B.

$V_{soln,B}$ = Total volume of Analytical Fraction B, ml.

V_B = Volume of aliquot of Analytical Fraction B analyzed, ml. **Note**: For example, if the 10 ml aliquot of Analytical Fraction B mentioned above was first diluted to 50 ml with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to Section 7.3 and analyzed, V_B would be 0.2 ml (10 ml/50 ml).

10.5.2 Back Half Hg; Analytical Fractions C, D and E

10.5.2.1 Calculate the amount of Hg collected in Analytical Fraction C (impinger 5) and Analytical Fraction D (impinger 6) by using Equation 436-11:

$$Hg_{C,D} = \frac{Q_{C,D}}{V_{C,D}} (V_{soln,C,D}) \qquad \text{Eq. 436-11}$$

where:

$Hg_{C,D}$ = Total mass of Hg collected in Analytical Fraction C or D, μg.

Q_{bhC} = Quantity of Hg, μg, TOTAL in the ALIQUOT of Analytical Fraction C or D analyzed. **NOTE**: For

example, if a 10 ml aliquot of Analytical Fraction C is digested, but only 5 ml is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 5 ml aliquot for Q_C.

$V_{soln,C,D}$ = Total volume of Analytical Fraction C or D, ml.

$V_{C,D}$ = Volume of Analytical Fraction C or D analyzed, ml. **Note**: For example, if the 10 ml aliquot of Analytical Fraction C mentioned above was first diluted to 100 ml with 0.15 percent HNO_3 as described in Section 7.3 to bring it into the proper analytical range, and then 5 ml of that 100ml was digested and analyzed, V_C would be 0.1 ml (10 ml/100 ml).

10.5.2.2 Calculate each of the back-half Hg values for Analytical Fractions E (middle knockout impinger) and F (HCl rinse) by using Equation 436-12:

$$Hg_{E,F} = \frac{Q_{E,F}}{V_{E,F}} (V_{soln(E,F)}) \qquad \text{Eq. 436-12}$$

where:

$Hg_{E,F}$ = Total mass of Hg collected separately in Fraction E or F, μg.

$Q_{E,F}$ = Quantity of Hg, μg, TOTAL, separately, in the ALIQUOT of Analytical Fraction E, or F analyzed, (see previous notes in Sections 10.5.1 and 10.5.2 describing the quantity "Q" and calculate similarly).

$V_{E,F}$ = Volume, separately, of Analytical Fraction E or F analyzed, ml (see previous notes in Sections 10.5.1 and 10.5.2, describing the quantity "V" and calculate similarly).

$V_{soln(E,F)}$ = Total volume, separately, of Analytical Fraction E or F, ml.

10.5.2.3 **Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 436-13:**

$$Hg_{bh} = Hg_C + Hg_D + Hg_E + Hg_F \qquad \text{Eq. 436-13}$$

where:

Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg.

10.5.3 **Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 436-14:**

Note: Blank corrections may only be applied with the approval of the Executive Officer or his or her authorized representative.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 436-14}$$

where:

Hg_t = Total mass of Hg collected in the sampling train, μg.

Hg_{fhb} = Blank correction value (if applicable) for mass of Hg detected in front half method blank, μg.

Hg_{bhb} = Blank correction value (if applicable) for mass of Hg detected in back-half method blank, μg.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0.0 to 0.6 μg, then use the total to correct the sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 0.6 μg, use the greater of I. or II:

I. 0.6 μg.

II. the lesser of (a) ($Hg_{fhb} + Hg_{bhb}$), or (b) 5 percent of the sample value ($Hg_{fh} + Hg_{bh}$).

10.6 INDIVIDUAL METAL CONCENTRATIONS IN STACK GAS

Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 436-15:

$$C_s = \frac{M_t}{V_{m(std)}} \qquad \text{Eq. 436-15}$$

where:

C_s = Concentration of a metal in the stack gas, μg/dscm.

M_t = Total mass of that metal collected in the sampling train, μg; (substitute Hg_t for M_t for the Hg calculation).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

10.7 ISOKINETIC VARIATION AND ACCEPTABLE RESULTS

Same as Method 5, Sections 6.11 and 6.12, respectively.

11 REPORTING REQUIREMENTS

At a minimum, any test report must include all of the calculations described in Section 10 and all of the sampling and laboratory data resulting from Section 5. Example forms for documenting field testing and laboratory work are provided as Figures 5 through 12. The quality assurance data required by Section 9 must be reported in detail (see Figure 13). This test report shall be maintained by the tester for at least three years. For all tests required or requested by the local Air Pollution Control District/Air Quality Management District, ARB, U.S. EPA or other government agency, these records shall be made available to the Executive Officer upon request.

12 ALTERNATIVE TEST METHODS

Alternative test methods may be used provided that they are equivalent to Method 436 and approved in writing by the Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

13 BIBLIOGRAPHY

EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

ARB Methods 1 through 5, California Code of Regulations, Title 17, Part III, Chapter 1, Subchapter 8, Article 2.

ARB Method 101A, California Code of Regulations, Title 17, Part III, Chapter 1, Subchapter 8, Article 2.

EPA Method 29, Code of Federal Regulations, Title 40, Part 60, Appendix B, April 25, 1996.

TABLE 1

MINIMUM DETECTION AND QUANTITATION LIMITS (ug/sample)
USING ICP, GFAAS, DAAAS AND CVAAS
ASSUMING INSTRUMENT DETECTION LIMITS PUBLISHED IN EPA SW-846*

ANALYTICAL METHOD	ICP		GFAAS		DAAAS		CVAAS	
LEVEL OF SENSITIVITY	MDL	RL	MDL	RL	MDL	RL	MDL	RL
METAL								
Aluminum (Al)							--	--
Antimony (Sb)	9.6	48	0.9	4.5	60.	300.	--	--
Arsenic (As)	16	80.	0.3	1.5	0.6	3	--	--
Barium (Ba)	0.6	3	--	--	30.0	150.	--	--
Beryllium (Be)	0.09	0.45	0.06	0.3	1.5	7.5	--	--
Cadmium (Cd)	1.2	6	0.03	0.15	1.5	7.5	--	--
Cobalt (Co)	2.1	10.5	0.3	1.5	15	75	--	--
Chromium (Cr)	2.1	10.5	0.3	1.5	15	75	--	--
Copper (Cu)	1.8	9	--	--	6.0	30.	--	--
Lead (Pb)	12.6	63	0.3	1.5	30.0	150.	--	--
Manganese (Mn)	0.6	3			3.0	15	--	--
Mercury (Hg)	--	--	--	--	--	--	0.06@	0.3@
Nickel (Ni)	4.5	22.5	--	--	12	60.	--	--

TABLE 1 (CON'T)

Phosphorous (P)	22.5	112.5			--	--	--	--
Selenium (Se)	22.5	112.5	0.6	3	0.6	3	--	--
Silver (Ag)	2.1	10.5	--		3.0	15	--	--
Thallium (Tl)	12	60.	0.3	1.5	30.0	150.	--	--
Vanadium (Vn)							--	--
Zinc (Zn)	0.6	3	--	--	1.5	7.5	--	--

* assumes volume of sample from total train = 300 ml prior to aliquot for analysis

@assumes instrument detection limit of 0.2 ng Hg/ml

MDL - Minimum detection limit

RL - Reporting limit = MDL x 5

TABLE 2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Sb	Aspiration	7040	217.6	100 mg/mL Pb, Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample and standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
AS	Furnace	7060	193.7	Arsenic volatization	Spiked samples & add nickel nitrate solution to digestates prior to analyses. Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al	Add 0.1% fluoride Use method of standard additions
Cd	Aspiration	7130	228.8	Absorption & Light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7191	357.9	Alkali metal Absorption & scatter	KCl ionization suppressant in sample & stand Consult manufacturer's literature

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	Add calcium nitrate for a known constant effect and to eliminate effect of phosphate
Cu	Aspiration	7210	324.7	Absorption & light scattering	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care should be taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 ul of phosphorous acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co & Cr Non linear response	Background correction required Matrix matching or a nitrous-oxide/acety flame Sample dilution or use 352.4 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples & reference materials & add nickel nitrate to minimize volatilization. Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorption & light scattering AgCl insoluble Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample & standards monitored for aspiration rate

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatization by spiked samples or standard audit Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Strontium removes Cu and phosphate Care should be taken to avoid contamination

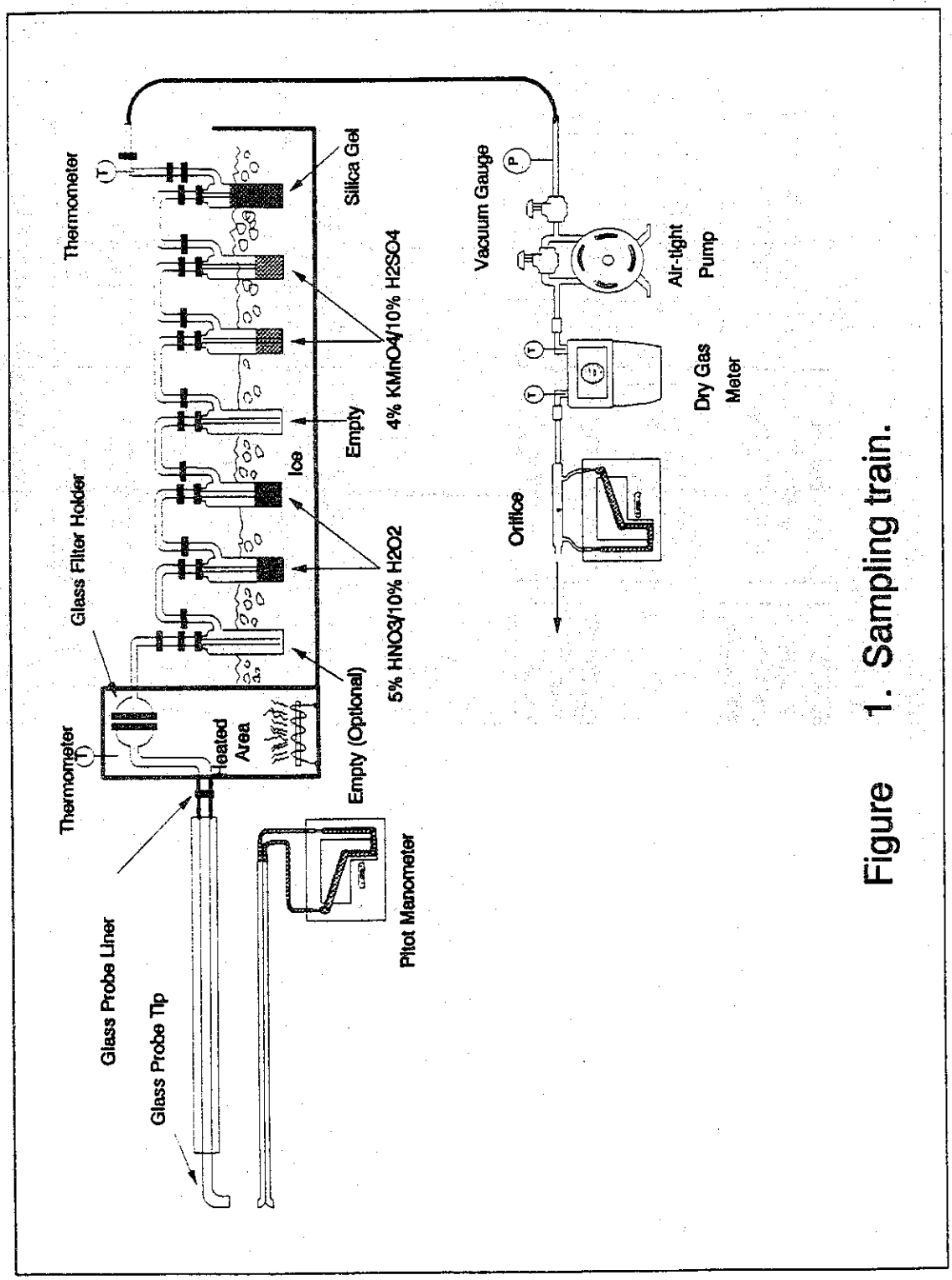
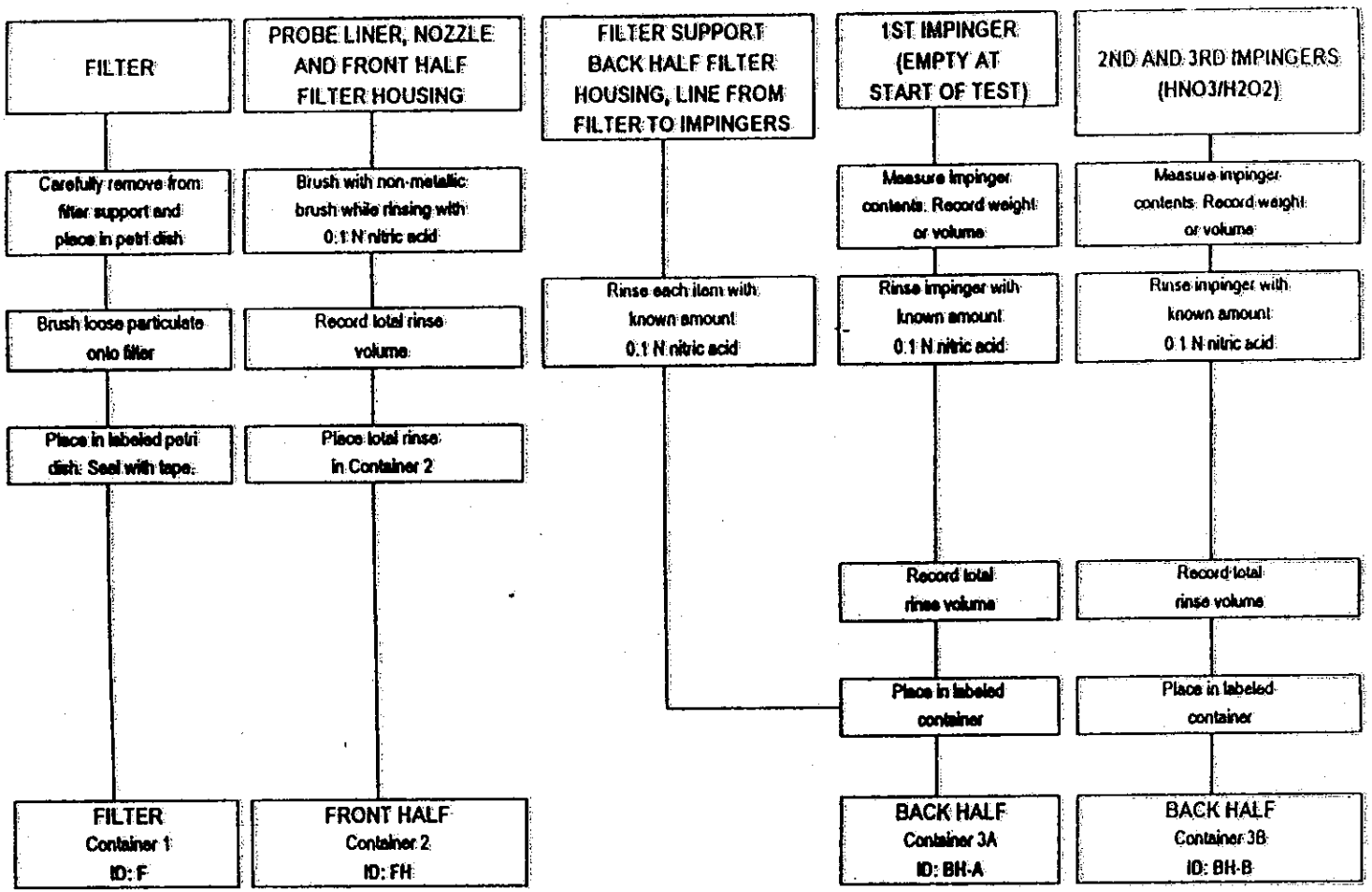


Figure 1. Sampling train.

FIGURE 2

SAMPLE TRAIN RECOVERY



NOTE: Containers 3A and 3B may be combined if desired. Alternatively, more containers may be required.

FIGURE 2 (cont.)

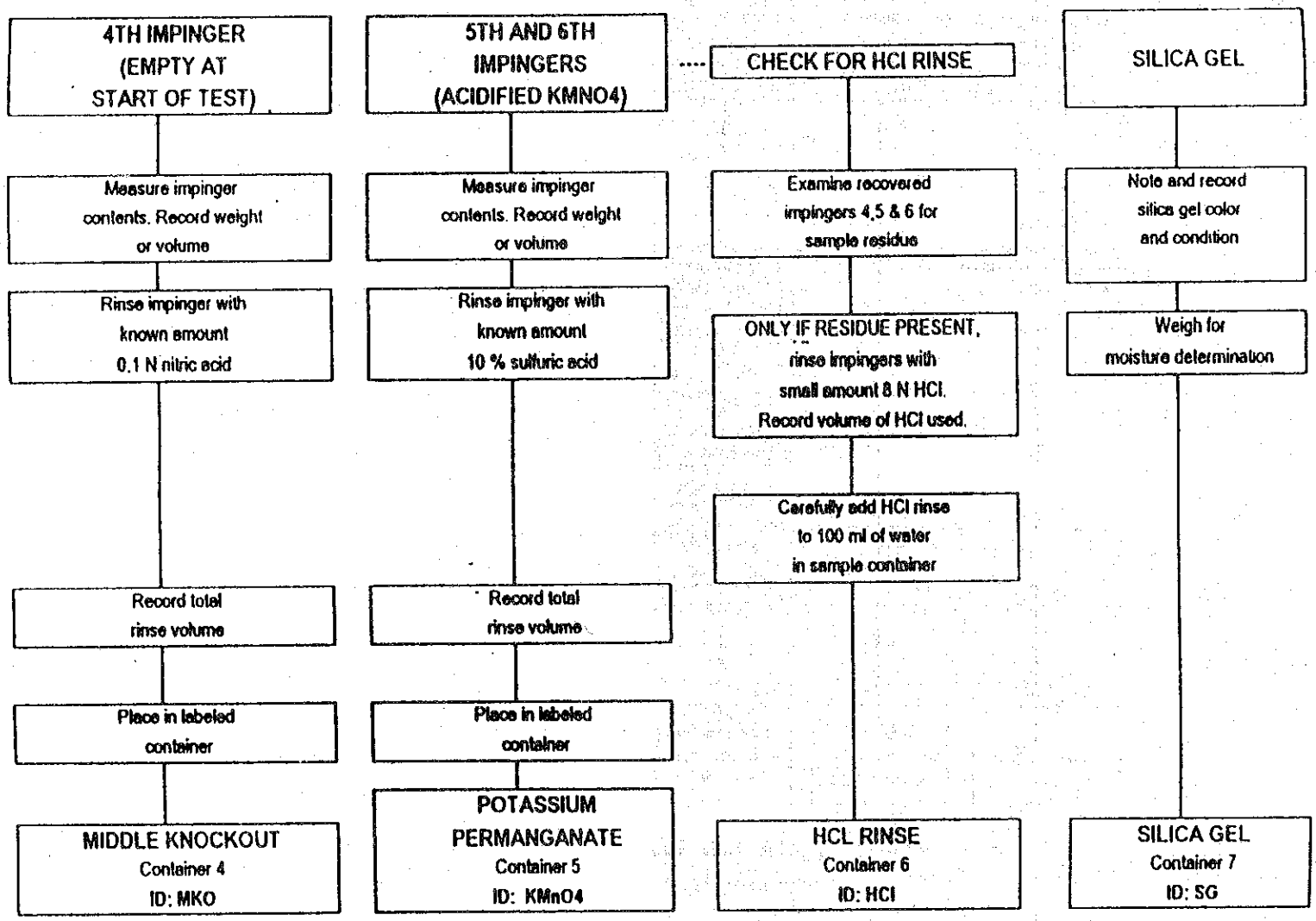


FIGURE 3

SAMPLE ANALYSIS SCHEME

SAMPLE PREPARATION AND ANALYSIS FLOWCHART

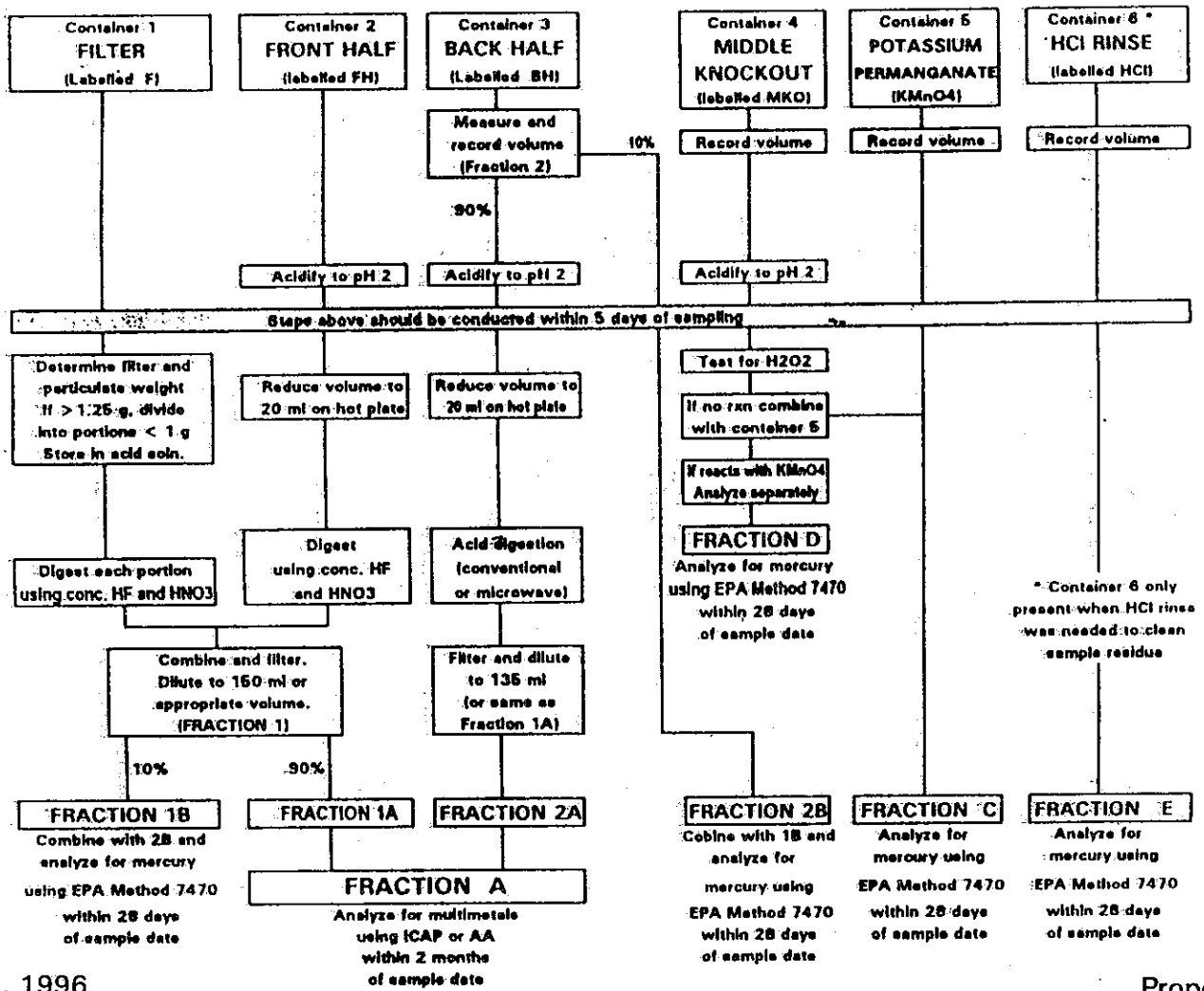


FIGURE 4

REAGENT BLANK ANALYSIS SCHEME

FIELD REAGENT BLANK SAMPLE PREPARATION AND ANALYSIS

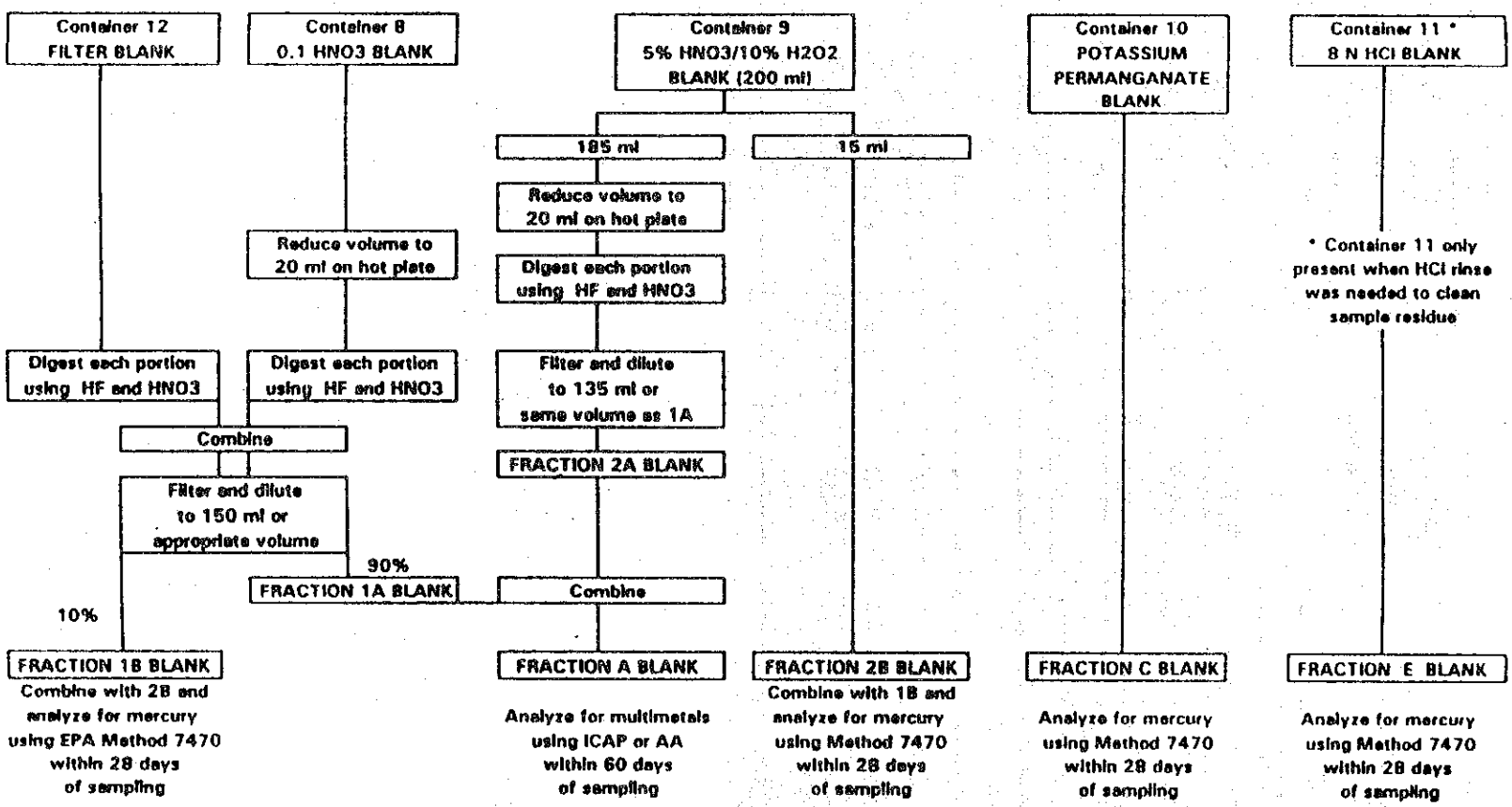


FIGURE 5
RUN SET-UP AND RECOVERY SHEET

PROJECT NO: _____

Method #: _____ Set-up date: _____ Recov. date: _____

Run ID: _____ Set-up time: _____ Recov. time: _____

Set-up by: _____ Recov. by: _____

Probe ID: _____ Probe liner material _____

Filter Box ID: _____

Filter holder ID: _____

	Filter Brand & Model	Filter Lot No.	Filter Size	Appearance After Sampling	Container ID
Filter					

	Rinse Solution and Amt. (mL)	Appearance	Container ID
Front Half			

	Imp. Type	Imp. Soln.	Initial Vol. (mL)	Initial Wt. (g)	Wt. after Sampling (g)*	Wt. differ. for moisture (g)*	Rinse Soln. and Amt. (mL)	Container ID
Imp. 1 ID								
Imp. 2 ID								
Imp. 3 ID								
Imp. 4 ID								
Imp. 5 ID								
Imp. 6 ID								
HCl rinse								
Silica gel								

TOTAL H2O (g): _____

*can use volume differences in place of wt. differences if desired

COMMENTS: _____

FIGURE 6
REAGENT BLANKS - FIELD DATA SHEETS

PROJECT NO. _____

CONTAINER NUMBER	REAGENT	DATE	PREP. BY	AMOUNT (ml)	SAMPLE ID	NOTES
8	0.10 HNO3			(100 ml)		
9	5% HNO3/ 10% H2O2			(200 ml)		
10	KMnO4/ H2SO4			(200 ml)		vent if necessary
11	8 N HCl			(25 ml in 200 ml H2O)		only if HCl rinse used
12	Filter					

Reagent blanks must be taken from same lot of reagents used to prepare and recover sampling trains

FIGURE 7
SAMPLE TRAIN PROCESSING BEFORE DIGESTION

PROJECT NO._____
SAMPLE DATE:_____
TRAIN ID:_____

PROJECT LEADER:_____
PHONE:_____

DATE AND TIME	PREPARED BY	SAMPLE ID	CONT-AINER ID	REQUIRED DOCUMENTATION	FINAL SAMPLE ID	TYPE OF CONTAINER	NOTES
			1 FILTER	Filter and particulate weight_____ (If greater than 1.25, divide) Cover with approx._____ ml 0.10 N HNO3.			HF REQ. FOR DIG
			2 PROBE WASH	Check pH using_____, pH is _____ (If need, approx. conc. HNO3 added____ ml) Reduce vol. to @ 20 ml on hot plate.			HF REQ. FOR DIG
			3 IMPING. 1 TO 3	Total volume:_____ml Remove aliquot for Hg (10%)_____ml Check pH using_____, pH is _____ (If need, approx. conc. HNO3 added____ ml) Reduce vol. to @ 20 ml on hot plate.			
			4 MIDDLE KNOCK OUT	Total volume_____ml Add drop of KMnO4 to check for H2O2: If rxn - place in container for Hg analysis If no rxn - combine with Container 5			
			5 KMnO4	Check for precipitate formation			
			6 HCl rinse	No pre-analysis processing			

COMMENTS:_____

FIGURE 8
REAGENT BLANK PROCESSING BEFORE DIGESTION

PROJECT NO._____
SAMPLE DATE:_____

PROJECT LEADER:_____
PHONE:_____

DATE AND TIME	PREPARED BY	SAMPLE ID	CONT-AINER ID	REQUIRED DOCUMENTATION	FINAL SAMPLE ID(S)	TYPE OF CONTAINER	NOTES
			8 0.10 N HNO3	Combine with Container 9			
			9 5% HNO3/ 10% H2O2	Total volume (8 + 9):_____ml Remove aliquot for Hg (@10%)_____ml Check pH using_____, pH is _____ (If need, approx. conc. HNO3 added____ ml) Reduce vol. to @ 20 ml on hot plate.			
			10 KMnO4	Check for precipitate formation			vent if necessary
			11 HCl rinse	No pre-analysis processing			
			12 FILTER	Filter and particulate weight_____ Cover with approx. _____ ml 0.10 N HNO3.			HF REQ.

COMMENTS:_____

FIGURE 9
MICROWAVE DIGESTION

PROJECT NO._____
SAMPLE DATE:_____

PROJECT LEADER:_____
PHONE:_____

DATE	TIME	BY	LAB ID	SAMPLE ID	MICRO VESSEL ID	REAGANTS ADDED (ml)					MICRO POWER (WATTS)	TOTAL HEATING TIME	NOTES
						FILTERS & PROBE WASH		IMPINGERS					
						conc. HNO3	conc. HF	50% HNO3	30% H2O2	HOT H20			

COMMENTS:_____

FIGURE 10

METHOD 436

FINAL DIGESTATE VOLUMES

Project No. _____

Sample Date: _____

DATE	TIME	INITIALS	LAB ID	SAMPLE ID	MICROVESSEL ID	Final Digestate Volume (ml)	Final Digestate ID

Comments: _____

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FIGURE 11

METHOD 436
POST MICROWAVE DIGESTION, PRE-ANALYSIS SAMPLE TRAIN FLOWCHART

IT IS VERY IMPORTANT THAT CONTAINERS FROM THE SAME SAMPLE TRAIN BE COMBINED FOR ANALYSIS !!!

SAMPLE TRAIN RUN ID: _____

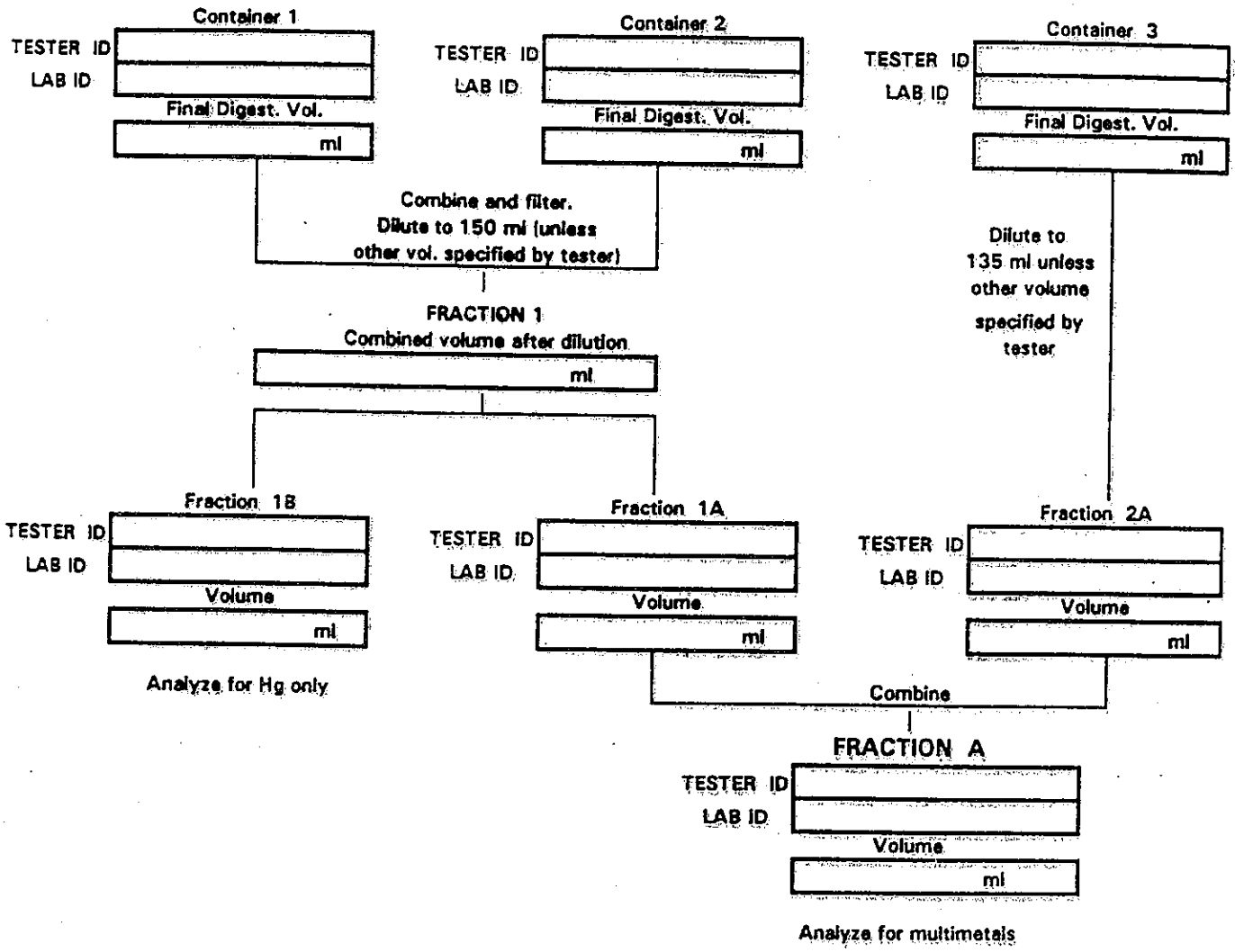

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FIGURE 12
LABORATORY RESULTS

Company name: _____
_____
Address: _____
_____
_____
Attn: _____

P.O. Number: _____
Location: _____

Report date: _____
Sample date: _____
Sample Recv. Date: _____
Report #: _____
Page: _____

Analysis Performed: [ ] ICP/AES [ ] ICP/MS [ ] GFAAS [ ] DAAAS [ ] CVAAS

Sample Train ID: _____

FIELD COMPOSITE ID									
LAB ID									
Metal	units								
Aluminum	ug/ml								
Antimony	ug/ml								
Arsenic	ug/ml								
Barium	ug/ml								
Beryllium	ug/ml								
Cadmium	ug/ml								
Chromium	ug/ml								
Cobalt	ug/ml								
Copper	ug/ml								
Lead	ug/ml								
Lithium	ug/ml								
Magnesium	ug/ml								
Manganese	ug/ml								
Mercury	ug/ml								
Molybdenum	ug/ml								
Nickel	ug/ml								
Phosphorus	ug/ml								
Potassium	ug/ml								
Selenium	ug/ml								
Silver	ug/ml								
Sodium	ug/ml								
Strontium	ug/ml								
Thallium	ug/ml								
Thorium	ug/ml								
Vanadium	ug/ml								
Zinc	ug/ml								

Data certified by: _____

Report approved by: _____

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FIGURE 13
ANALYTICAL QA/QC

ICP/AES: (EPA Method 6010)

REQUIREMENT	CRITERIA
2 instrument check standard runs	within 10% or repeat calibration
2 calibration blank runs	within 3 std. dev. of mean blank value or repeat calibration
1 interference check sample	within 25% of true value
1 quality control sample	within 25% of calibration curve
1 duplicate analysis	within 20% or repeat all analyses

AA: (EPA Method 7000 series)

REQUIREMENT	CRITERIA
Analyze all samples in duplicate	
1 sample matrix spike	within 25% or method of stand. add.
1 quality control sample	within 20% or repeat calibration

DEFINITIONS

Instrument check standards: prepared by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves.

Calibration blanks: prepared by diluting 2 mL of (1:1) HNO_3 and 10 mL (1:1) HCl to 100 mL with Type II water.

Interference check sample: prepared to contain known concentrations of interfering elements that will provide an adequate test of correction factors.

Quality control sample: prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

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