



Chevron U.S.A. Production Company
P.O. Box 1392, Bakersfield, CA 93302

W. A. Brommelsiek
Manager - Environmental, Safety, Fire & Health
Western Business Unit

September 25, 1998

Mr. Michael Kenny
California Air Resources Board
Attn: Board Secretary
P. O. Box 2815
Sacramento, CA 95812

RE: COMMENTS ON THE PROPOSED CHANGES METHOD 100

Dear Mr. Kenny,

Chevron U.S.A. Production Company has reviewed the draft revisions to Method 100 and would like to take this opportunity to provide comments. While we understand and agree with the importance of obtaining accurate compliance test data, we need to ensure that the methods that are adopted allow APCD's the flexibility to make certain determinations that will satisfy the requirements of the method while preventing unnecessary expenses when data accuracy is not affected.

In our review, we noted in Section 4.5 (Determination of Gas Concentration Stratification) that we will be required to perform traverses on stacks prior to performing the test to determine if stratification has occurred to determine if multipoint gas sampling is required. We understand that the intent of performing the traverses is to obtain a representative sample of the stack gas. Although we support the intent of this section, we would like to add language to this section that would allow more flexibility in determining gas stratification which would provide the same high level of data accuracy and help control the cost of testing.

The language that we would propose would be a second paragraph and would read as follows:

"As an alternative, a single point may be used if it can be demonstrated that the concentrations of the pollutants being tested at the single point are within 10% of the mean of a traverse from a downstream sample prior to flue gas processing. The data supplied by this demonstration may be used to allow single point testing on similar pieces of equipment with similar test ports."

"In addition to the above methods of determining stratification, approval may be granted for single point testing provided it can be demonstrated to the satisfaction of the agency that the accuracy of the data is maintained within 10% of the mean concentration of the gas."

The intent of the proposed additional language is to provide a way to obtain accurate data without having to install costly stacks on our equipment (e.g., steam generators). Most of our steam generators are not equipped with stacks. In the past, we have tested steam generators from the site glass at the end of the generator (hog trough). We have found that the difference in emissions concentrations at the hog trough from downstream concentrations, where the gas has been well mixed, is negligible. Therefore, if it can be demonstrated that the accuracy of the data is not compromised by testing at the hog trough, Chevron, as well as most other companies, would not have to spend a considerable amount of money with no benefit to data accuracy.

If language similar to the proposal above is put into the method, our proposal to the APCD would be to test a generator equipped with a duct or stack at the hog trough and at the stack using mean of the gas concentration of the traverse at the stack to determine if the concentrations are within 10% of the hog trough gas concentrations. We would use this data to apply to all steam generators that operated under the same parameters (e.g., similar equipment configurations, test port locations, fuel type, etc.).

Please contact Martin Lundy at (805) 633-4458 if you have any questions.

Sincerely,

Martin D. Lundy /dlr

W. A. Brommelsiek

cc: California Environmental Protection Agency
Air Resources Board
P. O. Box 2815
Sacramento, CA 95812
Attn: Ms. Frances Cameron



South Coast Air Quality Management District

21865 E. Copley Drive, Diamond Bar, CA 91765-4182 (909) 396-2000

September 26, 1996

Mr. George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division
California Environmental Protection Agency
Air Resources Board
P.O. Box 2815
2020 L Street
Sacramento, CA 95812-2815

Dear Mr. *George* Lew:

Proposed Revisions to ARB Methods for Measuring Emissions from Stationary Sources

This letter is in reference to your proposed revisions to ARB Methods 5, 7, 100 and 425, and to the proposed new Method 436. The Applied Science and Technology Division of the South Coast Air Quality Management District (SCAQMD) appreciates the opportunity to review and comment on the proposed amendments. We are generally in support of the intent of your proposal to make the methods consistent with the EPA methods. Our comments and suggestion that follow are meant to differentiate ARB methods from SCAQMD methods.

ARB Methods 5, 7, 100, and 425 are methods for measuring pollutants that are similar to SCAQMD Methods 5.2, 7.1, 100.1, and 205.1 respectively. The corresponding methods have subtle differences in aspects of both procedure and quality assurance. Both the ARB and the SCAQMD methods will be used in the South Coast District and there is always a concern that those differences may be used to discredit the validity of the other corresponding method. Since the applicable SCAQMD regulations are based upon data developed from the SCAQMD methods, the continuation of their use would be appropriate so as to neither increase or decrease the stringency of existing SCAQMD regulation. Consequently, our pointing out of certain differences is to emphasize this and not necessarily to propose a change to ARB methods.

Currently, we do not have a method that corresponds to ARB Method 436. Our comments on this method are therefore limited to those that could improve the presentation of the document.

COMMENTS/RECOMMENDATIONS

Method 5, Determination of Particulate Matter Emissions from Stationary Sources

1. Cleaning and recovery procedures in the CARB method include the use of acetone and methylene chloride rinses. SCAQMD does not use this procedure because of toxic waste concerns, potential for additional contamination, and absence of heavy organic materials in stacks located in our District. The SCAQMD method specifies a lower probe and filter temperature (180-200°F) so that the sample stream is maintained above the dew point but sufficiently low to condense sulfuric acid in the front half. This is important because sulfuric acid is considered as a particulate under SCAQMD rules, while dissolved SO₂, measured as sulfuric acid, is subtracted from the impinger catch.
2. The method calls for a glass frit filter support. The glass frit is difficult to recover. It may adsorb or react with some gaseous species. Generally, if the train impingers will be analyzed, Teflon or Teflon-coated steel is preferred.
3. SCAQMD's experience is that SO₂ will react with high sodium glass filters, and can create a measurable weight gain. For this reason, we require Whatman 934AH, quartz, or other equivalent low alkali metal filters.

Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources

1. The SCAQMD method relies on an solution standard calibration as opposed to audit standards for quality assurance purposes.
2. It appears that the "3.3.2. Phenol: white solid" on page 4 was eliminated inadvertently.
3. Because of the minimum 16 hour hold time before sample recovery, an intermediate field sample recovery followed by a final laboratory recovery is an unnecessary complication that results in less thorough rinsing and more sample handling. The recovery step should be collapsed into one laboratory-style recovery.

Method 100, Procedures for Continuous Gaseous Emission Stack Sampling

1. The changes of this method result in closer agreement to the SCAQMD method. We support the use of continuous analyzers for VOC, however, only when the species of hydrocarbons are known for response factor and calibration considerations. This is generally not the case in combustion sources.

September 26, 1996

2. Sections 1.5.5 and 1.5.6 state, "*The difference between the concentration...after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.*" We recommend substituting the words "each test run" in lieu of "a stated period of operation".
3. It is not clear whether the section 2.1.7 applies to a wet analyzer system. We suggest clarification of the language.
4. The range is selected so that the sample gas concentration is between 10 and 95 percent of the range for each pollutant. In order to accept the data at 10 percent, we recommend a four-point calibration instead of the three-point calibration. The low range should be 10 to 20 percent.

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

1. The recommended text in the section for Limit of Detection is "*The LOD is based on the absolute value of the x-intercept of the calibration plot...*" to be consistent with the equation.
2. Specifying the recommended hold time limits and storage conditions would be helpful in the section for sample instability. Recovery within 24 hours, refrigeration and a storage time of two weeks are recommended.
3. A range of 0.5 ug/50 mL to 3.0 ug/50 mL is unnecessarily restrictive for Cr6 M-C range. The range can be expanded to 0.5 to 50 ug/mL, provided that the residuals are less than 10%.
4. It is not clear what the hot plate will be used for in the Cr6-M-C analysis.
5. There appears to be some missing text in section 9.3.2 Water "*Use of ASTM Type I reagent water...*"
6. Specifying the recommended maximum storage time and conditions would be helpful in the section for Cr6 Stock Solution.
7. Unlike the Cr6 M-C and Cr GF-AA calibration procedures, the Cr6 IC-C Analytical Calibration Procedure does not contain a "zero standard". It also does not require a check standard. Both are recommended additions. The number of standards for the calibration curve is not mentioned in the Cr6 M-C Calibration Procedure. There is also no check standard. This information should be added.
8. Filtration is recommended to be optional for the M-C analysis because the samples are often clear and additional sample handling may introduce errors.

9. In order to make the spike recovery work without volume correction in the calculations, there has to be an instruction in the section entitled "Check for Matrix Effects on making the sample and matrix spike.
10. It is not clear in sections 17.2.2 and 19.1.1 whether blanks are referred to as zero standard or reagent blank.

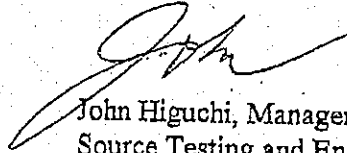
Method 436. Determination of Multiple Metals Emissions from Stationary Sources

1. There are too many options for establishing a reporting limit. It may be helpful to make a distinction between the reporting limit used for test planning, and the reporting limit used for the actual report. Generic detection limits or previously established blanks might be used for test planning (with an appropriate safety factor), but the actual field reagent blank should be used to determine the final reporting limit.
2. The filter position in the train introduces unnecessary sample divisions, additional contamination and more stringent sample digestion. Moving the filter behind the HNO₃/peroxide impingers would allow the entire front half of the sample to be recovered and digested in one fraction, and reduce the amount of HF acid used. Many of the deviations from Method 436 center around the use of HF, partly because of its ability to digest glass and quartz portions of instruments.
3. There were no requirements for pre-cleaning sample storage containers, funnels, flasks, and beakers. The glassware-cleaning instructions found under "Sample Train Preparation" should be applied to all glassware that the sample comes in contact with.
4. We suggest that preparation blanks be reserved under "Sample Train Assembly" rather than under "Sample Recovery". Blanks should be shipped in closed containers with the prepared train. Including this requirement under the train preparation will help ensure that same batch that is used to fill the trains will also be used as the field reagent blank.
5. Sample pH should be tested under "Sample Recovery" rather than under "Analytical Preparation". This will ensure that samples are not accidentally left too basic during shipping. Sample pH should be tested under "Sample Recovery" not "Sample Holding Times". "Sample Holding Times" should immediately precede "Analytical Preparation" to remind the tester and analytical laboratory of the deadlines they are facing.
6. Blanks were consistently referred to as "reagent blanks". This should be corrected to "field reagent blanks" to make the document more consistent.

September 26, 1996 *

These are our comments on and suggestions for improvements of the proposed amendments. If you have any questions, or if we can be of further assistance, please contact me or Mr. Arun Roy Chowdhury at (909) 396-2268.

Sincerely,



John Higuchi, Manager
Source Testing and Engineering Branch
Applied Science and Technology Division
(909) 396-2267

JH:ARC:RC:kn

cc: W. Fray
R. Eden

arb-jew



96-7-2
9/26/96

STATE OF CALIFORNIA
AIR RESOURCES BOARD
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XC: Board member
JDD TAC
MPK Legal
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September 24, 1996

Ms. Pat Hutchens
Clerk to the Board
California Air Resources Board
2020 L Street
Sacramento, CA 95814

Re: Stationary Source Test Method

Dear Ms. Hutchens:

Western States Petroleum Association (WSPA) appreciates the opportunity to comment on the amendments to existing methods and the adoption of new methods. We understand the importance of technically sound and legally defensible methods to determine compliance with districts emission limits for sources. These test methods are used in the preparation of air toxic emission inventory mandated by the Air Toxics "Hot Spots" Information and Assessment Act of 1987. These methods can be used to evaluate air pollution control equipment, and for regulatory criteria development.

Our comments are structured into general comments, technical comments, and editorial comments. The general comments address issues that are common to more than one method. Technical comments address specific test method issues. The editorial comments address typographical and formatting errors in the methods.

If you have questions about these comments, please contact me at 818-543-5349.

Michael Wang
Manager, Operations and Environmental Issues

Attachments
cc:
J. Sickenger
A. Verstuyft

WSPA Comments
Page 1

General Comments

I. ARB Executive Officer: The requirement that modifications to test methods can be approved only by the ARB Executive Officer is a major change in policy. This change is supported by both regulated industry and source test contractors. We requested that the Executive Officer provide guidance on a "modification requiring ARB Executive Officer approval."

We support this change that provides greater consistency in source test requirements statewide. However, without a clarification on modification, cost and delays in testing could increase. In the spirit of greater consistency throughout the state, we urge the ARB to work with the district to eliminate the multiplicity of district specific test methods.

II. Incorporation of Federal Methods by Reference: ARB staff needs to have a simple administrative process to update ARB methods that incorporate updates to Federal Methods by Reference, especially analytical methods. The lack of a process creates a technical and compliance problem, where a method referenced in ARB methods may not be run in the commercial analytical laboratory. EPA in 40 CFR 136 Test Methods for Effluent Monitoring provides an annual update to incorporate ASTM, Standard Methods and other consensus standard methods deemed equivalent to EPA Methods. The amended and new ARB Source Test Methods proposed include out of date or incomplete references to EPA's Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846 Third Edition. The worst example of an out-of-date method reference is the new Method 436, Section 13 that cites the September 1988 version. The official version is January 1995 Update IIa. Update III July 1996 is being proposed for promulgation. Update IV is in draft that includes a major version of inorganic methods affecting Method 436.

A similar update is needed where ASTM methods are included in the ARB methods.

III. Method Detection Limits (MDL), Practical Quantitation Limits (PQL), Reporting Limits (RL), Limit of Detection (LOD). We commend the ARB for recognizing the importance of these limit concepts. However, the ARB staff needs to review the MDL processes used in various methods. Likewise, the ARB staff needs to review the use of PQL and RL to assure consistency across the methods. While there is continuing debate about the MDL concept as described in 40 CFR 136 Appendix B, it is important for ARB to use the MDL process consistently from method to method. PQL and RL are used interchangeably in these methods. It is important for ARB to use these definitions consistently. The LOD (425.3.4.1) adds to the confusion because this is an "instrument" detection limit, however, it is used to determine a RL (425.3.4.2). The theoretical method quantitation limit (TMQL) (429.8.3.1) further confuses the limit concepts. The MDL guidance is 5 times the TMQL (429.8.3.1; 429.A1.1(e)), whereas elsewhere the MDL is typically 2.5-5.0 the S/N (429.A1.1(a)). The MDL discussion in Method 436.2.3 is actually the analytical detection limit. ARB should refer the R.E. Gibbons work on Method Detection Limits.

WSPA Comments

Page 2

The ARB needs to provide guidance on data handling procedure for averaging of field blank/sample blank corrected data reduction (i.e., Method 429.9.2.4.2.). Rules typically used by the source tester are listed below:

A. Average Field Blank Result

1. If a PAH from both field blank (FB) runs was non detect (ND) then the maximum detection limit is reported and the result is flagged as ND.
2. If a PAH from both FB runs was detected then the average concentration is reported and the result is not flagged.
3. If a PAH from one FB is detected and one FB run is ND, then,
 - a. The average result is calculated using one-half the MDL for the ND results and the full MDL for detected results.
 - b. If the average from 3(a) is compared to the highest MDL of the FB.
 - c. If the average from 3(a) is greater than the highest MDL, the average value is reported and the results are not flagged.
 - d. If the average from 3(a) is less than the highest MDL, the highest MDL is reported and the results were flagged.

B. Field Blank Corrected Result.

1. If the field blank average (FB avg) was ND, then the FB is treated as 0 and the measurement is reported as the sample value. The value is not flagged if the sample value is detected and flagged ND, if the sample value is ND.
2. If both the sample and field blank average is detected then,
 - a. The FB avg is subtracted from the sample value.
 - b. The result from 2(a) above is greater than the MDL of the sample value, the value is reported and the result is not flagged.
 - c. The average from 2(a) above is greater than the MDL of the sample value, the value is reported and the result is not flagged.
 - d. The average from 2(a) above is less than the MDL of the sample value, the value is reported and the result is flagged.

WSPA Comments

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3. If the F avg is detected and the sample value is ND, then the sample value is reported and flagged ND.
4. If the FB value was ND then,
 - a. The FB is used at one half the value, and subtracted from the sample value.
 - b. The result from 4(a) above is compared to the MDL of the sample value.
 - c. The result from 4(a) above was greater than the MDL of the sample value, the value is reported and the result is not flagged.
 - d. The result from 4(a) above was less than the MDL of the sample value, the value is reported and the result is flagged.

Method 425.20.3 contains a source reporting limit (SRL). Whereas, 425.20.1 addresses DETECTED and NOT DETECTED chromium6 or chromium, it does not address reporting NOT DETECTED results. The reporting needs to be clarified, especially where data is used for environmental assessment.

IV. Methylene Chloride: The ARB must review, as is EPA, the use of methylene chloride in these methods. Consistent with the Montreal Protocol, EPA is committed to reduction in the use of ozone reducing chemicals. We urge the ARB to look for alternative solvents that pose a lower risk to sampling and analysis personnel, and to the environment. Alternatives to methylene chloride may be required for some source, see Method 5 Section 4.3.1.1 Footnote 2.

WSPA Comments

Page 4

Technical Comments

Section 94105

Method 5 Determination of Particulate Matter Emissions from Stationary Sources:

We strongly recommend this method be amended to account for and credit particulate generated through air pollution control and the test method. The South Coast Air Quality Management District (SCAQMD) Method 5.2 allows credit for ammonium sulfate dihydrate $[(NH_4)_2SO_4 \cdot 2H_2O]$. Ammonium sulfate dihydrate is created in the sampling train from the reaction of ammonia injection for particulate control in electrostatic precipitators (ESP). Ammonia injection creates a similar reaction for nitrogen oxide control in selective catalytic reduction (SCR). Section 4.2.1.1 and Section 6.9 need to be corrected for ammonium sulfate.

The purpose of this Method 5 is to measure particulate and not gas that may combine in the sampling train to form particulate. Further, the sulfate particulate as sulfur oxides may already be monitored in the gas phase depending.

- 4.3 Second paragraph, Option three does not guarantee constant weight is achieved. There needs to be a definition of constant weight.
- 4.3.1.3 Suggest using Na_2SO_4 anhydrous to dry the solvent, and add guidance on the use of a drying agent per EPA Method 1664. Guidance is needed on breaking emulsions with a stirring rod, salt, or alcohol, and what is permissible to ARB.
- 5.3 Addition of standard dry test meter is excellent.

Section 94107

Method 7 Determination of Nitrogen Oxide Emissions from Stationary Sources:

- 3.3.8 Does ARB have assurance from EPA that they will maintain the QA/Performance Evaluation (PE) program? The EPA Office of Water is eliminating their QA/PE program, and the Office of Air is under similar pressure.
- 4.4.1 See above.
- 5.2.3 Is the 7% criteria, absolute or relative?
- 5.6 Type S or P weights?

Section 94114

Method 100 Procedures for Continuous Gaseous Emission Stack Sampling

We commend ARB for the addition of Appendix 100.1 to make this method comparable to EPA Method 205. ARB needs to work with EPA to address the problems with accuracy and bias in NIST traceable reference materials. The recent problems of a greater than $\pm 2\%$ error in sulfur dioxide certification gases can affect gas dilution systems.

WSPA Comments

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We recommend ARB consider permeation systems as an alternative to certified calibration gases or dilution systems. We would be willing to work with ARB staff to develop this protocol. Discussions have been held with SCAQMD personnel.

3.1 See comments above first paragraph

Section 94135**Method 425****Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources**

ARB should include in the scope of the method, the staff's interpretive guidance on the maximum hexavalent chromium in total chromium measurements. The interpretive guidance was that hexavalent chromium was no greater than 5% of total chromium. The interpretive guidance is useful when the hexavalent chromium determinations are spurious.

EPA intends to withdraw Method 7191 as discussed by O. Fordham (EPA-OSW) at EPA 12th Annual Solid Waste Analysis and Quality Assurance Conference, July 1996. There are significant problems with the chromium 6/alkaline medium as discussed by R. Vitale et. al. at EPA 11th Annual Solid Waste Analysis and Quality Assurance Conference, July 1995.

3.4.1 The discussion of limit of detection (LOD) herein is different from a method detection limit (MDL). However, the LOD is used to establish a reporting limit (RL) [3.4.2]. The LOD applies to calibration deviation, and does not account for variation in the method.

11.5(6) The reporting guidance does not make sense for air samples; it is guidance for solid waste type samples

17.1.1(2) See 3.4.1 above

Section 94141**Method 429****Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources**

The ARB should accept SW-846 Method 8270a in selective ion monitoring (SIM) as an alternative to dilution isotope mass spectrometry. Method 8270a SIM is a cost effective alternative to the more expensive ARB method. Method 8270a SIM is recognized by EPA as a performance based method alternative.

2.3.1 The blank contamination needs further discussion.

2.3.2,.3 The requirement for the MDL could be misinterpreted as meaning to be performed with every batch. Whereas, the intent in a current MDL be available. An MDL per every experimental set would be prohibitively expensive. See 8.3.1 and General Comments.

WSPA Comments

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- 4.2.1 Check reference year. See General Comments.
- 4.2.2.1 Define "giant" Soxhlet.
- 4.2.2.4 Define accept criteria for XAD-2 contamination
- 4.2.7 Define acceptable drying time as 0.5-1 hour.
- 4.2.8 Replace with an alternative to chromic acid.
- 4.3.1 Refer to EPA QA Handbook for Air Pollution Monitoring Systems 600/4-79-027a,b,c Volume II with updates.
- 4.3.2 Reference 11.4 superseded see 4.2.8
- 6.0 This section does not address demonstration of proficiency such as running acceptable blind quality control samples and achieving EPA requirements.
- 8.3.1 The TMOQL concept is flawed. See the discussion in General Comments on MDL.
- 9.2.4.2 See General Comments on MDL.

Section 94161

Method 436 Determination of Multiple Metals in Emissions from Stationary Sources

- 1.3.4 Method detection limit. See General Comments
- 2.3 Have laboratory provide recent MDL performed within the last year.
- 7.1 The HF matrix guidance for use of the alumina torch needs clarification.
- 7.3 Mercury analysis is problematic and biased. This has been documented by EPRI, re P. Chu et.al.
- 9.4.1 The holding time preservation requirements should be immediately.
- Fig. 13 The frequency of QA/QC is excessive. The frequency should be 1 per analytical batch or ten actual samples exclusive of QC.
- 11.4.1, 2, .5 Formatting
- 13.3.1,2 Move approximate symbol "~" down to midline. Need a professional word processing editor.
- 17.1.1, 2 Format does not equal 3.4.1.
- 22. EPA intends to withdraw Method 7191. See EPA 12th Annual Solid Waste Analysis and Quality Assurance Conference, July 1996.

WSPA Comments

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Editorial Comments

Section 94105

Method 5 Determination of Particulate Matter Emissions from Stationary Sources:

- 4.1.5 reference Appendix A
- 4.3.1.1 To footnote 2 add the last paragraph of section 4.3 or reference this guidance.
- 4.3.1.2 Mason jar or equivalent
- 5.3 Include reference to EPA's Quality Assurance Handbook for Air Pollution Monitoring Systems EPA 600/4-79-027a,b,c Volume II with updates.
- 6.1 There is a 4 space typographic offset for many terms including ms, Pbar, H; term 13.6 is missing units
- 6.11.1 K3 in definition.
- Fig. 5.3 Typographic error 1/2 space down line at last line
- App: Number equations. Last line is incomplete.

Section 94107

Method 7 Determination of Nitrogen Oxide Emission from Stationary Sources:

- 2.1 Typographic error "±"
- 2.1.1.10 Halocarbon is missing footnote superscript.
- 2.3.2 Coors and Nalge are missing footnote superscript.
- 3.1.1 ASTM method year citation. See General Comments III.
- 5.2.1.1 NBS should be NIST.
- 8 There is no reference to the bibliography.

Section 94135

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

- 7. "Teflon"
- 7.3.1 Dionex include footnote that ARB does not endorse specific products.
- 9.3 line 3 "the IC-C"
- 9.3.3 ASTM method year. See General Comments.
- 11.4 ± 5
- 11.4.1, .2, .5 formatting.
- 17.1.1, .2 format does not equal 3.4.1.
- 22. EPA intends to withdraw Method 7191. See EPA 12th Annual Solid Waste Analysis and Quality Assurance Conference, July 1996

WSPA Comments

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Section 94141

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

- 4.3.5 "Teflon-lined"
- 4.4.3 Either "Leak Check" or "Leak-Check" consistency in use throughout this section; Li = leak check.
- 4.5.5 K2 = m3/ml or ft3/ml; superscripts.
- 5.3 No smoking reference is good, however, it should address atmospheric contamination. See 11.9.
- 6.1 Material Safety Data Sheets is correct terminology.
- 9.1.7-.9 RRF is (note line over top)
11. Bibliography 11.2 and .3 are out of date
- App. A. Revise after review of limits. See General Comments.

Section 94161

Method 436 Determination of Multiple Metals in Emissions from Stationary Sources

- 2.5.1-4 Reference Section 13 SW-846 methods that are out of date. See General Comments.
- 4.2.1 ug/in2
- 4.5.37.2 Ni(NO3)2·6H2O
- 4.7.13 deuterium arc or Zeeman.
- 9.5.3 Omit Standard Methods
- Table 1 "As", "V"
- Table 2 Retitle "Applicable Techniques, Methods, Potential Interferences and Corrective Action"
- As Method 7060 should be 7060A
- As Method 7760 should be 7760A



Air Pollution Control Board
 Greg Cox District 1
 Dianne Jacob District 2
 Pam Slater District 3
 Ron Roberts District 4
 Bill Horn District 5

Air Pollution Control Officer
 R. J. Sommerville

September 25, 1996

GEORGE LEW, CHIEF, ENGINEERING LAB
 MONITORING LABORATORY DIVISION
 CALIFORNIA AIR RESOURCES BOARD
 P. O. BOX 2813
 SACRAMENTO CA 95812

96-7-2
 9/26/96

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 KC: Board Members
 JDS TAC
 MPR legal
 MLD

COMMENTS ON PROPOSED CARB METHOD 431

Attached is a list of concerns and comments our Monitoring and Technical Services Division has developed concerning the proposed CARB Method 431 for testing ethylene oxide. Since the senior chemist responsible for the testing of this pollutant was on vacation until September 17, 1996, our comments are forwarded to you at this time.

We would seriously appreciate your review of our comments and we would also seriously appreciate an extension of the review time.

If you have any questions concerning the above, please telephone me at 694-3351.

Judith M. Lake
 JUDITH M. LAKE, CHIEF
 Monitoring and Technical Services Division

Comments on Proposed Meth 431

20 September 96

COMMENTS ON PROPOSED METHOD 431

Note: pages are referenced by the following: p5t, p5m, p5b (top, middle, bottom)

Appendix A

p 2 & p3 Testing procedures are for *inlet and outlet of control units, not sterilizers*, so title of App A should be changed. It could still include the fact that the section only addresses the sterilizer evacuation stage.

p 3 For catalytic units, the atmospheric moisture is in great excess of any moisture created by the destruction of ETO. It is also true that the atmospheric moisture is greater than the resulting average moisture from the initial humidification process. Thus, why require a moisture measurement? It should be sufficient to measure the ambient moisture of the surrounding air by wet/dry bulb.

p3 For hydrolytic units, the inlet moisture is still the ambient moisture, and the outlet moisture is at most saturated, and can be assumed to be; it is only slightly above ambient temperature. So, only a wet/dry of the atmosphere should be required, and a temp of the outlet stream.

p3 I make the above comments even when flow measurements are required.

p3 Hydrolytic scrubber type...
Here measuring the moisture of the inlet stream would present health hazards to the personnel as there is a very high conc of ETO.

p3 *INSERT* For the Joslyn system there is no flow rate, so there would be no requirement to measure the flow.

p5t "Determination of ETO Conc at the *Inlet of Control Units*". Here the subtitle reflects that the *control units* are being tested, not the sterilizers. This is correct, but it contradicts the main title.

p5m *Inlet Estimation* What sites where inlet estimation would be necessary (for safety purposes) do NOT have water ring seal pumps? SB stated that Children's Hosp did. The Joslyn system also has a water ring seal pump. These are the places where it was necessary to estimate the inlet conc.

p5b *Inlet Measurement* Why is it necessary to not allow aborting the sterilization time when it is necessary to test the aeration stage? If the evacuation stage has eliminated most of the ETO, it does not seem relevant that the stage was aborted. It will be very expensive time-wise to not abort the sterilization phase. It must be remember that hospitals need the sterilization equipment, and that loss of its use during testing is significant. Preventing the hospital from using the sterilization equipment a second and even third day would be an immense burden to the hospital. If no abortings are permitted, and the aeration phase must be tested twice, it would not be possible to do this in one day. (Does this proposed Meth 431 explicitly state the number of times an aeration cycle must be tested for one aerator?)

p5b *Measurement Methods* Documenting the position of the probe by making extra measurements, which will be discussed in App D will be a burden. Time is of the essence, and it will be expensive to perform those tests. More will be stated when that section is reviewed.

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Tedlar Bags

SPECIAL COMMENTS:

#1) The evacuation cycle on the sterilizers differs significantly in the time period. Since this time is not known before a test is performed, it would be difficult to 1) set a flow rate at which the Tedlar bag should be receiving stack gas, so that it could be mostly filled, and adequate sample obtained, at the end of the evacuation cycle. The same variation in time could be stated about the air washes. Cycle times have ranged from less than 20 minutes to about 60 minutes on different sterilizers that have been tested under SD APCD jurisdiction. This imposes a severe limitation and burden on the tester and planning a test.

#2) But, having samples of ETO in Tedlar bags in any lab presents a hazard. Personnel not associated with testing and now potentially exposed. Also, the disposal of the residual after sample analysis presents a problem.

p6t Inlet Measurement For cat-ox units only the first evacuation is required to be documented. For acid scrubbers the first evacuation and the air washes are required. Is this a contradiction of the Rule? (It is true that the rule is being re-written, but it must be consistent with what the method requires.)

p6t Historically, we have tested the air washes, but in both cases. Also, the data can be separated from the evacuation phase.

p6m *Repeat the procedure three times*

From our records this will make a very long test day. This will be expensive for the hospitals because they will not be able to perform a sterilization on any equipment that test day. It is also true that our data shows that if a control unit is passing, then it is usually well above the limit. If it is not passing, then it becomes quite clear during the first or second subtest. Thus, a suggestion would be that if the unit appears to be overwhelmingly passing, that only two subtests be required on a control device if there is only one sterilizer connected to it. If there are more sterilizers, or if the aeration phase needs to be tested, then a third subtest is appropriate.

p6 *Direct Interface Sampling Analysis*

A frequency of two minutes or less for catalytic units is restrictive. California's most professional testers have tested in San Diego's District and none of them produce data in less than two minutes. It normally takes approximately three minutes to elute a chromatogram with ETO and a diluent such as a chlorofluorocarbon. The frequency of less than one minute for hydrolytic scrubbers is also restrictive. It simply has not been met in the tests performed here.

p6 *Inlet Estimation* - testing the 1st evacuation and wash period (for exhaust only) contradicts Rule 1203 which states that only the evacuation is to be tested. (This may be modified by changing the rule, since the latter is under progress.)

p6 & 7 Inlet Measurement Here for catalytic units, only the evacuation is to be tested, but for hydrolytic units, the evacuation and all subsequent air washes are to be tested. These differences seem incorrect. (A rationale should be offered.) (top of p7) This also contradicts the rule as it is currently written.

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p7b Repeat the procedures three times (cycles). For sites which have only one sterilizer, and one control device, if the equipment is clearly demonstrating that it is passing, it may be a waste of money to prevent the site from using its sterilizing equipment later in the day. (The ETO personnel go home in mid-afternoon, presumably because hospital staffing works best that way; they are not there late in the day to start a sterilization of equipment after a full day of testing.)

Appendix B

p8t Water ring seal pumps are often used on units where inlet estimation is needed (Children's H. and Joslyn units (Palomar))

p8b The expression for the pressure P is allowed only as psia, but the value for the gas constant R is allowed to be expressed in psia, cu ft, and lb-mol, or in cgs units of liter-atm, gm-mol. Thus, it is necessary to let P be expressed in atms also.

Appendix C

p9t "The exposure stage *should* not be shortened or aborted." On p5, it is stated that the exposure stage *cannot* be aborted for aeration cycles. There should be consistency of procedure.

Appendix D

Documentation of Inlet Probe Position (Catalysts)

p10t 2. "...monitor the volumetric flow of the...exhaust...before dilution in the control unit." This will expose test personnel to extremely high levels of ETO. It will be very expensive (a roots meter or a turbine meter may be required, with changes to the site equipment). "...measure the concentration of ETO in ...exhaust...before dilution... This will also expose personnel to extremely high levels of ETO.

Thus, it is suggested, as in other EPA and ARB methods, that the correct positioning of the probe be accomplished in the usual fashion of submitting a detailed, engineering drawing-style of site diagram. With the details possible in engineering drawings, it is clear that a correct position above the catalyst bed can be obtained. This would prevent the exposure to hazardous levels discussed above.

p10b & 11 Requiring a tester to calculate the amount of ETO supposedly delivered to the control unit when the tester is performing an on-site measurement seems contradictory. First, different specifications were given to the testing of these different techniques. Now, it is stated that one must do both if one is doing inlet measurements.

It is suggested that the Inlet Estimation technique is subject to serious error in the readings from a pressure gauge.

Requiring the tester to perform two velocity traverses simultaneously will impose an extensive burden on testers. Remember that consultant testers do NOT receive great remuneration for this testing; thus, for a one-man company to employ a second person to perform this task would put all source testers in the ETO field *out of business*. This does not mean that checking the flow is not a good idea; it simply means it is not economically feasible. Please refer to the above suggestion that an engineering drawing (which is by definition highly accurate) would circumvent all these problems.

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p11 "5. Perform the above operations 3 times." This would require extensive time-consuming activities. It also would be tantamount to not requiring the measurement of the inlet diluted values, since they are only documented to be correct by the measurement of the undiluted values, which are themselves to be done three times.

Appendix E

p13: §4.1 Multipoint calibration

§4.1.1 states that "four different concentrations" must be used. Does one of these include zero gas? The statement should clearly indicate whether it does.

p13m §4.1.3 "Standard deviations are calculated at each level of the multipoint and must be comparable to those published for the method." Where are there published values? Also, by "standard deviations at each level of the multipoint", is it meant the standard deviations of the areas for a given (fixed) concentration of ETO. (If the concentration is fixed, then there is no standard deviation of the ppm.) However, should this be revised to read "relative standard deviation", since the area responses will be depend on the attenuation and amplification settings on the gc. The flow of the hydrogen and combustion air, as well as the flow of the carrier gas will also affect the areas. One could also compute standard deviations (or relative ones) of the calculated concentrations from those areas from the least squares curve. This approach might be more meaningful, since it would give values of the discrepancies of the (calculated) concentrations versus the "true" concentrations.

§4.1.5 Here the equation

$$\text{LOD} = |A| + 3S$$

is given. A is the least squares intercept (in ppmv) of the independent variable (usually x). Now S is stated to be the standard deviation of the lowest standard. By making this remark here, it implies that the standard deviation is that of the calculated ppm values (calculated from the ls curve). (Otherwise one would be adding sd's of areas to ppm's of the intercept, a meaningless concept.)

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p14: §5. Routine Calibration Procedure should be LABORATORY Calibration procedure (not implying field procedure)

It is stated that routine users are those who perform these tasks "daily"; but no consultant in this state does that, because they have travel time to the sites. Thus, the definition needs revision.

The phrase "eight hours" is used; presumably this originated because offices and labs used to operate on an eight hour basis. However, consultants in the field operate on a variable shift, and even the APCD operates on a 10 hour day. Therefore, instead of interrupting work near the end of the day, the statement should be changed to state "at the end of the normal day's analysis period." (This would prevent someone from running all night without performing a check.)

p14b §6. Calibration Check Sample

p15m §6.3

"The midpoint standardmust be analyzed every eight hours, or every ten samples, ..." Once again, most field consultants do not work on an eight hour schedule, but a variable one, so this should be changed the same as in §5.

p16m §7.4 The verification data about the above comments of §5 and §6 needs to be modified to change the 8 hour criterion.

For field testing this should be stated that the calibration check should be performed after each subst.

p18 APPENDIX F CALCULATIONS

p18a The description of the calculation for the weight of ETO in the inlet or outlet is very unwieldy. Better wording needs to be used.

p18b For the direct go approach, once again the 2 minute and 1 minute intervals for sampling are unrealistic, but are mentioned here. ARB is requested to submit this data for review, since no one we know has presented any such analyses times.

p20 REPORTING REQUIREMENTS

p20 Reporting has been discussed in part in §7, on page 16; part of that discussion is repeated here. Perhaps better organization is needed for presentation in this Method. Remember this method is going to be around for several years. It's better to correct a mistake now than to be burdened with such a need after this method is adopted.

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p21 METHOD LIMITATIONS

p21m Tedlar bag sampling.

The method now recommends that a continuous FID also be used in conjunction with the Tedlar bags, so determine when the sampling period should end. This is time consuming, defeats the original purpose of using Tedlar bags instead of FIDs and is unnecessary because the cycle time is over when the indicator dials on the equipment display different stages of the process.

p21b "Many testers feel that on-site GC is more expensive and more difficult than container sampling." There are only three known testers in the State of California; one of them is so extremely busy that he no longer does ETO tests. Thus, "many" is an inappropriate qualifier. This statement seems as if it is a personal attitude. It may not be supported by the facts. Tedlar bag testing could consist of spending one day in the field and the subsequent day in a lab. This may be more expensive than spending one day in the field doing both the sampling and the analyses. Thus, whether this paragraph is valid should be investigated.

p22 Inlet Estimation

p22t It states that the site ETO cylinders should be analyzed to verify the exact composition of the gas before using it in the sterilization chamber. The ETO in the site cylinder is highly concentrated. The calibration curve for high concentrations is not (usually linear). Thus, the tester would have to have several high concentration standards in the SAME (close) range as the site ETO gas. This would be expensive; it also would expose the personnel to usage of high concentrations.

p22m Pressure gauges are usually not too accurate. Sites usually have them calibrated only on initial installation of the equipment. To calibrate them specifically for a compliance test seems expensive because 1) personnel from the manufacturer have to fly from the east coast to do it, and 2) scheduling such a site visit to correspond to a District ETO test is difficult.

p22b Once again the inlet estimation technique is stated as invalid with water ring seal pumps. But, it is for those very sites for which the estimation technique is useful.

p22b Acid Scrubber

Here it is suggested that for acid scrubbers the inlet estimation technique be used because the sterilant gas consists of a high concentration of ETO. This point has been made by myself in several instances above. However, in those instances, for redundant "quality control" checks, the proposed ARB Method 431 insists that personnel be exposed to high concentrations of ETO.

p23t Once again the 1 minute restriction is stipulated for hydrolytic scrubbers.

p23m Catalytic Oxidation

p23m Documentation of probe placement for inlet measurement is once again discussed. I have the same criticism of this that was presented earlier.

p23m Once again the direct measurement technique is stated to be valid only for 2 minute or less analyses times. This is impossible as has been discussed.

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p23b Water ring seal pumps are again discussed. The same criticism mentioned above applies.

p23b Stratification in catalytic units. This can be circumvented by use of accurate engineering diagrams, as has been discussed above.

p24 APPENDIX I Procedure for Tedlar Bag Sampling

p24m §3. Equivalency

15b

It is stated that alternative methods may be used if substantially equivalent, and if approved by the Executive Officer or his representative. What does substantially equivalent mean, and what does representative mean?

p25b Moisture determinations are once again mentioned. At no time in our determinations of moisture has the percentage been above 3%. It has been slightly above 1% and once about 2%. Thus, a wet dry bulb on the environment in the sterilization room should be sufficient.

p26m §5.3, last sentence.

"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." There are no liquids in any impingers for which this carry-over is pertinent. To deliberately put a liquid in an impinger in the sample train would be to capture ETO and prevent it from being sampled into a Tedlar bag.

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p27 6. QUALITY CONTROL

§6.1.1 Sampling runs and §6.1.2 Routine Sampling Quality Control. All this was discussed earlier and seems redundant here.

p28m §6.2.2 Field spikes in nitrogen would probably affect the gc FID response and give an erroneous result. Our experience has shown that whether a sample is in an air matrix or a nitrogen matrix affects the ppm value of the organic substance found by the FID.

§6.2.2 (Once again) A field spike is expensive because the tester now has to have ETO cylinders in the lab and one for the field.

p29 FIGURE 1 TEDLAR BAG SAMPLING TRAIN

The train as depicted in the diagram has a rotameter between the probe and the Tedlar bag. This rotameter will be contaminated with ETO between subtests (runs). Thus, it should be placed between the can and the sample pump.

p32 FIGURE 4 FIELD DATA SHEET

The calculations is §F only use Total Flow, not average flow, so the calculation and reporting of an average flow is unnecessary. Since it is unneeded by the calculations in the method, requiring it seems inappropriate.

p33 §7. Production of Tedlar bags

Discarding Tedlar bags is expensive. It would be less expensive to clean them. But, having samples of ETO in Tedlar bags in any lab presents a hazard. Personnel not associated with testing and now potentially exposed. Also, the disposal of the residual after sample analyses presents a problem.

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9/26/96



RESEARCH TRIANGLE INSTITUTE

Center for Environmental Measurements and Quality Assurance

September 24, 1996

Pat Hutchens, Board Secretary
Air Resources Board
2020 L Street
Sacramento, California 95814

Dear Ms. Hutchens,

This letter comments on the proposed amendment to Air Resources Board Source Test Method 100, Procedures for Continuous Gaseous Emission Stack Sampling under Section 94114. These comments represent my own professional opinion based on research that I have conducted at the Research Triangle Institute (RTI). This research has involved both gaseous calibration standards and gas dilution systems. My expertise in these two areas has prompted these comments. They do not necessarily represent RTI's official position on the proposed rule.

In 1993, RTI revised the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (Publication No. EPA-600/R93/224) while under contract to US EPA's Atmospheric Research and Exposure Assessment Laboratory. I was the main author of this revision of the protocol. As part of this effort, I conducted a laboratory evaluation of gas dilution systems for analyzer calibration and calibration gas analysis. The results of this research were published in Air & Waste in April 1994. A copy of this article is enclosed for your inspection. In the 1980s, RTI conducted numerous audits of compressed gas calibration standards and EPA protocol Gases. I am enclosing copies of two articles concerning these audits that were published in Journal of the Air Pollution Control Association in 1987 and 1989.

Summary Comments

In general, the proposed use of gas dilution systems in the preparation of gas mixtures for field instrument calibrations is a good idea. Such systems provide more flexibility and convenience than compressed gas calibration standards. They should also be cheaper than compressed gas calibration standards over the long run.

The proposed amendment should be strengthened. Its performance specifications and field evaluation procedures are not described in enough detail to insure that gas dilution systems will perform in an acceptable manner. The proposed amendment does not address the uncertainty of gas concentrations that are produced by gas dilution systems. If gas dilution systems are to be useful for



field instrument calibrations, the uncertainty of the gas mixtures' concentrations must be approximately the same as that for high-quality compressed gas calibration standards, such as EPA Protocol Gases.

Gas dilution systems have not been evaluated sufficiently to characterize their performance and uncertainty. No one has demonstrated that they can yield results, on a routine basis, that are comparable those obtained with undiluted EPA Protocol Gases. These systems need to be evaluated more extensively in both the laboratory and the field than is specified in the proposed amendment.

The performance specifications and field evaluation procedures are written largely for gas dilution systems utilizing thermal mass flow controllers. They should be rewritten to accommodate the operational characteristics of gas dilution systems utilizing other technologies (e.g., capillary tubes, positive-displacement pumps, and periodic injection techniques). It is important that they be written in a manner that is transparent to the gas dilution technology. They should not give the appearance that the Air Resources Board favors any specific gas dilution technology. Any technology should be acceptable to the board as long as the user can demonstrate that it meets a uniform performance specification.

Proposed Appendix 110.1 is a very close relative of EPA Method 205 and shares many of its problems. The following specific comments on the proposed appendix are adapted from comments that were submitted to US EPA in 1994 when Method 205 was being finalized.

<u>Part</u>	<u>Comment</u>
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1.1	Applicability
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	Gas dilution systems have not been evaluated sufficiently to demonstrate that they will perform with a degree of confidence similar to that documented for EPA Protocol Gases. Research to evaluate the uncertainty of gas dilution systems is limited. In my knowledge, the only research in this area are publications by RTI and by Queen's University in Canada and unpublished research by Steiner Environmental, Inc. that was mentioned in the background information for Method 205. This research is reviewed in the following paragraphs. Not enough is known about the performance and uncertainty of gas dilution systems. Their routine use for field instrument calibrations is not justified without more rigorous performance specifications and tests than are given in the proposed appendix.
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RTI conducted a laboratory evaluation of gas dilution systems for analyzer calibration and calibration gas analysis (Wright and Murdoch, 1994). It was funded wholly by the U.S. EPA through Contract No. 68-D1-0009. The evaluation had a limited scope and looked at only four representative gas dilution systems and only three types of pollutant gas mixtures. I believe that this evaluation is the only recent publication concerning the uncertainty of gas dilution systems.

The RTI evaluation compared multi-point calibration data produced by pollutant gas mixtures from gas dilution systems and by undiluted National Institute of Standards and Technology Standard Reference Materials (NIST SRMs). It included systems utilizing capillary tubes, positive-displacement pumps, and thermal mass flow controllers.

The accuracy of these gas dilution systems was estimated by comparing the slope of the least-squares regression line for the diluted gas mixtures with the corresponding slope for the undiluted gas mixtures. In general, the accuracy estimates for the four gas dilution systems were similar after outlier data were discarded. Excluding such outlier data, the absolute values of the 20 remaining accuracy estimates ranged from 0.11 to 3.33 percent with a mean absolute value of 1.24 percent. For 12 of these accuracy estimates, there was no statistically significant difference, at a 95-percent confidence level, between the slopes of the regression lines for the diluted and undiluted gas mixtures. The accuracy estimates for individual gas dilution systems exhibited some variation from day to day and from one pollutant gas mixture to the next. The greatest observed day-to-day variation was from +2.62 to -1.97 percent.

The precision of the gas dilution systems was estimated by the relative uncertainty, at a 95-percent confidence level, for concentrations that are predicted from the regression equation for diluted gas mixtures. In general, the precision estimates for the four gas dilution systems were similar after outlier data were discarded. Excluding such outlier data, the 20 remaining precision estimates for mid-range dilutions ranged from 0.31 to 5.22 percent with a mean value of 1.61 percent. The precision estimates varied with the number of measurements in the calibration and with relative position on the calibration curve. The estimates for individual gas dilution systems exhibited some variation from day to day and from one pollutant gas mixture to the next. The greatest observed day-to-day variation was from 3.81 to 5.22 percent.

The number of experiments conducted during RTI's evaluation was too small to allow one to draw any definitive conclusions concerning the accuracy and precision of gas dilution systems. The evaluation uncovered significant operational problems with several gas dilution systems: a plugged capillary; interference with the pollutant analyzer's response; and a leak in one gas dilution system. These problems reduced the accuracy and precision of the gas dilution systems.

A Wösthoff gas dilution system was used at Queens University (Bate et al., 1969) to prepare ambient-level concentrations of CO₂ in air from cylinders of CO₂ and air. This 3000-to-1 dilution was produced by four positive-displacement pumps operated in series. A nondispersive infrared CO₂ gas analyzer was calibrated over the range from 270 to 370 parts per million (ppm) using the diluted gas mixtures. An SRM that was certified as containing 308 ppm CO₂ plus or minus (+/-) 3 ppm was measured as containing 306.6 +/- 0.7 ppm by the calibrated analyzer. The agreement between these two values is 0.5 percent. The authors state: "Our results certainly corroborate that the accuracy of the calibration CO₂ gas mixtures produced by the pumps was equivalent to that of the NBS standards".

Unpublished research by Steiner Environmental, Inc. (Steiner, 1991) appears to form the technical basis for Method 205. An Environics Model 201 gas dilution system with thermal mass flow controllers was used to prepare three pollutant gas mixtures from EPA Protocol Gases and nitrogen. Although multi-point calibrations generated extensive linearity check data, such data cannot be used to assess the accuracy of the gas dilution system because the measurements are not compared against any external reference standard. They can only be used to assess the internal consistency of the concentrations of gas mixtures that are produced by the gas dilution system.

Measurements of undiluted EPA Protocol Gases were used as quality control checks following the calibrations. The certified concentrations of these external reference standards were compared with measured concentrations using the calibrated analyzers. Data from these quality control checks can be used to assess the accuracy of the gas dilution system and are given on the next page:

Quality Control Measurements for a Gas Dilution System by Steiner Environmental, Inc. using EPA Protocol Gases			
Pollutant Gas	Certified Concentration	Measured Concentration	Percentage Difference
O2	4 %	3.95 %	-1.25 %
O2	8 %	7.98 %	-0.25 %
NOx	12.34 ppm	12.65 ppm	+2.51 %
NOx	78.49 ppm	77.4 ppm	-1.39 %
NOx	80.72 ppm	79 ppm	-2.13 %
NOx	81.35 ppm	84 ppm	+3.26 %
CO2	8 %	8.04 %	+0.50 %
CO2	8 %	8.2 %	+2.50 %
CO2	14.01 %	14.1 %	+0.64 %

The accuracy of the Environics gas dilution system was estimated by the percentage difference between the certified and measured concentrations for the quality control check samples. The absolute values of the accuracy estimates varied from 0.25 to 3.26 percent with a mean absolute value of 1.60 percent. The accuracy estimate exceeded +/- 2 percent for four (or 44 percent) of the nine Steiner Environmental quality control check samples.

Consequently, the Environics gas dilution system would have failed the proposed appendix's specification that the gas dilution system shall produce calibration gas mixtures which have measured values within +/- 2 percent of the predicted values. The Air Resources Board needs to consider whether there is adequate information to support its belief that gas dilution systems will meet the proposed specifications on a routine basis.

References

- R.S. Wright and R.W. Murdoch, "Laboratory Evaluation of Gas Dilution Systems for Analyzer Calibration and Calibration Gas Analysis", Air and Waste, vol. 44, pp. 428-430, 1994.
- G.C. Bate, A. D'Aoust, and D.T. Canvin, "Calibration of Infra-red CO2 Gas Analyzers", Plant Physiology, vol. 44, pp. 1122-1126, 1969.

J. Steiner, Letter to Rima Dishakjian of U.S. EPA concerning Environics gas dilution system, January 15, 1991.

1.2 Principle

The specification that the gas analyzer is to be calibrated should be strengthened. A gas dilution system cannot be verified using a gas analyzer whose calibration curve is not well-characterized. The gas analyzer should be calibrated over its full range using four or more undiluted EPA Protocol Gases and the measured concentrations may differ from the predicted values by no more than ± 5 (or more) percent. The 5-percent specification is based on the uncertainty of the EPA Protocol Gases used to calibrate the gas analyzer (see below).

The effect of the uncertainty of the calibration gases could be reduced by the statistical analysis of the calibration data. The proposed specification could be replaced by one based on the 95-percent confidence interval for concentrations predicted from the linear regression of the multipoint calibration data (see the EPA Traceability Protocol for details).

3.1 Gas Dilution System

The ± 2 -percent specification for the gas dilution system is unrealistic given the uncertainty of the EPA Protocol Gas (± 5 percent) that is being diluted and the uncertainty of the gas analyzer calibration (± 5 percent) that is used to verify the gas dilution system. Error propagation analysis should be conducted to calculate the overall uncertainty associated with the proposed verification procedure.

A potential weakness in the use of gas dilution systems for field instrument calibrations is the introduction of a source of measurement uncertainty in addition to that associated with the calibration gas itself. The concentration of the calibration gas being diluted has its own level of uncertainty. The use of a gas dilution system can only increase the total measurement uncertainty associated with the diluted gas mixture. If the uncertainty of the calibration gas is itself near unacceptable levels, then the use of a gas dilution system may result in unacceptable overall uncertainty. This issue has not been adequately addressed in the proposed appendix. High-accuracy compressed gas calibration standards and high-accuracy gas dilution systems must be used if the resulting diluted gas mixtures are to have high accuracy.

The Air Resources Board should specify an overall uncertainty that is acceptable for concentrations produced by gas dilution systems and it should specify a method for calculating the uncertainty associated with each step in the calibration chain back to NIST primary gas and flow standards.

3.2 Annual Certification Procedure

This procedure is biased towards gas dilution systems using thermal mass flowmeters. It prevents any use of capillary tube gas dilution systems because the flowrates through individual capillary tubes cannot be measured. The only flowrate that can be measured in these devices is the total flowrate. The procedure should be revised to make its requirements transparent to the gas dilution technology.

The proposed appendix specifies that gas dilution systems be calibrated on a yearly basis against a NIST-traceable primary flow standard with an uncertainty of 0.25 percent. This specification is not realistic unless one has access to such a high-accuracy flow calibration device (e.g., a Sierra Instruments, Inc. Cal-Bench Primary Gas Flow Calibration System) or unless one sends the gas dilution system back to the manufacturer or to NIST for certification. The yearly recertification cost for the gas dilution system is a significant and hidden cost that the Air Resources Board must account for in its assessment of the economic impact of the proposed method.

The board should consider establishing a clearer definition of what specifically constitutes a "NIST-traceable primary flow standard". William D. Dorko (301-975-3916) and George E. Mattingly (301-975-5939) of NIST are in the process of investigating the traceability issue for gas dilution systems. It would be in the board's long-term interest to coordinate its efforts with those of NIST and to promulgate a rule that incorporates NIST's work regarding traceability for gas dilution systems.

What assurance does one have that one year is the proper recalibration interval for a mass flow controller? Is there any existing research to support this or any other recalibration interval? What assurance is there that mass flow controllers' calibrations will be stable for an entire year? It would be more reasonable to specify that gas dilution systems be compared to NIST-traceable standards prior to each field test. Is it acceptable for a user to

recalibrate mass flow controller using NIST-traceable standards that are on hand or must the user return the gas dilution system to its manufacturer for yearly recalibrations?

- 3.4 The analytical accuracy specifications for high-level and mid-level calibration gases are unrealistic. Only NIST SRMs or NIST Traceable Reference Materials (NTRMs) have an uncertainty of ± 1 percent. EPA Protocol Gases have an uncertainty of approximately ± 5 percent (see below). The specifications should not allow the use of calibration gases that are "certified" as having ± 1 -percent accuracy unless the specialty gas producer follows an accepted analytical protocol for calibration gas certification such as the EPA Traceability Protocol.

The proposed requirement for annual recertification of calibration gases is overly restrictive and does not reflect the current stability of compressed gas mixtures. In 1993, the certification period for EPA Protocol Gases was increased to 36 months for nonreactive gas mixtures. Most EPA Protocol Gases containing reactive gas mixtures have a certification period of 24 months. The proposed requirement should be similarly increased.

RTI has extensive experience in accuracy assessments of commercial cylinder gases and EPA Protocol Gases (Decker et al., 1981, Wright et al., 1987, 1988, and 1989, and Coppedge et al., 1992). Currently, EPA is conducting an ongoing audit of EPA Protocol Gases (Hines, 1994). The results of the EPA Protocol Gas audits from 1985 through 1994 are generally consistent. Overall, 73 percent of the EPA Protocol Gases were accurate to within ± 2 percent of their certified concentrations and 93 percent of these standards were accurate to within ± 5 percent.

The accuracies of commercial cylinder gases are generally consistent and are significantly worse than those of EPA Protocol Gases. Audits from 1978 through 1981 revealed that only 42 percent of the commercial cylinder gases were accurate to within ± 2 percent of their certified concentrations and only 66 percent of these standards were accurate to within ± 5 percent.

Although these two sets of audits were conducted at different times and accuracies are likely to have improved over time, one may reasonably extrapolate from these audit results to conclude that present-day EPA Protocol Gases are likely to be significantly more accurate than present-day

commercial cylinder gases. No other data are available that would support an alternate conclusion.

Given these audit results, the proposed appendix's implicitly-allowed use of "certified +/- 1-percent accuracy" commercial cylinder gases for may result in reduced accuracies for field instrument calibrations. The accuracy associated with the use of undiluted present-day EPA Protocol Gases for such calibrations may be on the order of +/- 5 percent (assuming a roughly 95-percent confidence level). The use of lower-accuracy commercial cylinder gases with gas dilution systems are very likely to result in less accurate calibrations.

Note that EPA revised its traceability protocol for gaseous calibration standards in 1993 (EPA, 1993). The revised traceability protocol has more stringent analytical and quality control procedures than earlier versions of the protocol. It is expected that the accuracy of EPA Protocol Gases will improve significantly in the future, but future audits are needed to assess the accuracy of standards produced using the revised traceability protocol.

The revised traceability protocol explicitly allows the use of a gas dilution system in the analysis of candidate EPA Protocol Gases. This gas dilution system may use capillary tubes, positive-displacement pumps, thermal mass flow controllers, or other suitable devices to dilute the reference standard. If a gas dilution system is used, it must have a specified accuracy of not greater than 1.0 percent of the undiluted reference standard concentration. The accuracy of the gas dilution system must be checked by the analyst at periodic intervals by comparing diluted reference standards to undiluted reference standards having approximately the same concentration. Additionally, the 95-percent uncertainty for the regression-predicted concentration of a diluted candidate standard must be less than or equal to 1 percent of the concentration of the diluted reference standard.

References

C.E. Decker, M.L. Saeger, W.C. Eaton, and D.J. von Lehmden, "Analysis of Commercial Cylinder Gases of Nitric Oxide, Sulfur Dioxide, and Carbon Monoxide at Source Concentrations" in Continuous Emission Monitoring- Design, Operation, and Experience, Air Pollution Control

Association, Pittsburgh, Pennsylvania 15230, APCA
Publication No. SP-43, 1981.

R.S. Wright, E.L. Tew, C.E. Decker, D.J. von Lehmden, and
W.F. Barnard, "Performance Audits of EPA Protocol Gases and
Inspection and Maintenance Calibration Gases", Journal of
the Air Pollution Control Association, vol. 37, pp.384-385,
1987.

R.S. Wright, C.E. Moore, C.E. Decker, and W.F. Barnard,
"Second Performance Audit of Inspection and Maintenance
Calibration Gases" in Mobile Sources: Emerging Issues, Air
Pollution Control Association, Pittsburgh, Pennsylvania
15230, APCA Publication No. TR-11, 1988.

R.S. Wright, C.V. Wall, C.E. Decker, and D.J. von Lehmden,
"Accuracy Assessment of EPA Protocol Gases in 1988", Journal
of the Air Pollution Control Association, vol 39, pp. 1225-
1227, 1989.

E.A. Coppedge, T.J. Logan, M.R. Midgett, R.C. Shores, M.J.
Messner, R.W. Murdoch, and R.K.M. Jayanty, "Accuracy
Assessment of EPA Protocol Gases Purchased in 1991", Journal
of the Air and Waste Management Association, vol. 42, pp.
1617-1619, 1992.

A. Hines, "Analysis of Protocol Gases: An On-going Quality
Assurance Audit (Results Through July 1994)", unpublished
document downloaded from EPA's Ambient Monitoring Technology
Information Center electronic bulletin board, 1994.

Environmental Protection Agency, EPA Traceability Protocol
for Assay and Certification of Gaseous Calibration
Standards, EPA Publication No. EPA-600/R93/224, 1993.

4 Field Evaluation of the Gas Dilution System

A positive-displacement pump is a variable flow device that
is capable of numerous different dilution ratios. Its
performance should be verified using two or more dilutions.

As stated previously, the +/- 2-percent analytical accuracy
specifications for the gas dilution system and for the mid-
level calibration check are unrealistic given the
uncertainties of calibration gases, gas analyzer
calibrations, and the gas dilution systems.

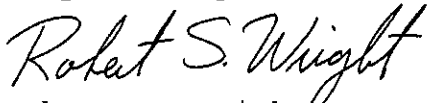
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The specifications should be strengthened because each of the two specifications allows a measured response to vary by +/- 2 percent from a predicted value, rather than specifying the agreement between the two gas concentrations themselves. The proposed appendix would allow one measured response to vary by + 2 percent and the other measured response to vary by - 2 percent to result in an overall disagreement of 4 percent between the two gas concentrations.

The specifications could be replaced by ones based on the statistical analysis of the multipoint calibration data and the multipoint dilution data. For example, a hypothesis test could be performed to determine whether a statistically significant difference exists between the slopes of the regression lines for the calibration data and the dilution. The specifications should be revised and should incorporate a procedure to calculate the overall uncertainty of the gas dilution system given the uncertainty of all the calibration steps leading back to NIST primary gas and flow standards.

Thank you for your attention to these comments. Please call me at (919) 541-6263 if you have any questions concerning them.

Respectfully,



Robert S. Wright,
Environmental Scientist

cc: C.E. Decker, RTI
R.K.M. Jayanty, RTI
W.C. Eaton, RTI

Laboratory Evaluation of Gas Dilution Systems for Analyzer Calibration and Calibration Gas Analysis

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Gas dilution systems can be used for multipoint calibrations of pollutant gas analyzers and for the analysis and certification of compressed gas calibration standards. This laboratory evaluation obtained estimates of the accuracy and precision of four representative gas dilution systems. Diluted and undiluted gas mixtures containing carbon monoxide, nitric oxide or sulfur dioxide in nitrogen were sampled by pollutant gas analyzers. Accuracies were estimated from the difference between the slopes of regression lines from measurements of the diluted and undiluted gas mixtures. These accuracy estimates ranged from -3.3 to 10.0 percent. Precisions were estimated from the 95-percent uncertainty for regression-predicted concentrations. These precision estimates ranged from 0.3 to 14.9 percent of the predicted concentration for mid-range dilutions.

Calibration gases often are diluted during the multipoint calibration of pollutant gas analyzers and during the analysis and certification of compressed gas calibration standards. Gas dilution systems are devices that allow two gas streams to be mixed together continuously and quantitatively. Such systems could be used for multipoint calibrations and analyses of gas mixtures. However, systematic and random errors associated with the dilution would be added to the total measurement uncertainty. Could one use gas dilution systems for these applications with acceptable levels of accuracy and precision?

Under U.S. Environmental Protection Agency (EPA) sponsorship, Research Triangle Institute (RTI) conducted a laboratory evaluation of four representative gas dilution systems. The goal of the evaluation was to estimate the accuracies and precisions of the systems using measurements by pollutant gas analyzers. These estimates were obtained from the statistical analysis of multipoint calibrations using undiluted and diluted gas mixtures.

Gas Dilution Systems

The EnviroNics Model 2020 continuous emissions monitoring calibration system uses thermal mass flow controllers to regulate the flow rates of a compressed gas calibration standard and dilution nitrogen, which are blended together. The system was configured to operate in both of the dilution regions that were used in the evaluation (i.e., 1 to 9 percent and 10 to 90 percent of the standard's concentration). Its specified flow rate accuracy is ± 0.5 percent of the full-scale range and its specified flow rate repeatability is ± 0.2 percent of the full-scale range.

The Milton Roy Model 821S gas divider uses 10 identical, parallel capillary tubes and solenoid valves to blend the calibration standard and the dilution nitrogen. The system was configured to operate in the 10 to 90 percent dilution region. Its specified dilution accuracy is ± 0.2 percent of the standard's concentration and its specified repeatability is ± 0.1 percent of the point.

The Wösthoff Model 1KM67 gas mixing pump uses three piston-driven, positive-displacement pumps to blend the calibration standard and the dilution nitrogen. The standard goes through

one pump and the nitrogen goes through the other two pumps. Switchable gears vary the pistons' stroke frequency and thereby vary the diluted gas concentration. The pumps and gears in the instrument used for this evaluation were lubricated with silicone oil. The system was configured to operate in the 1 to 9 percent dilution region. Its specified accuracy under calibration conditions is ± 1.0 percent relative to the selected dilution level.

The Wösthoff Model 5KA37 gas mixing pump uses five piston-driven, positive-displacement pumps to blend the calibration standard and the dilution nitrogen. The pumps are an oil-less type and have a fixed stroke frequency. Three stopcocks are used to switch the gas streams entering three of the five pumps and thereby vary the diluted gas concentration. The system was configured to operate in the 1 to 9 percent dilution region. Its specified accuracy under calibration conditions is ± 0.5 percent relative to the selected dilution level.

Experimental Procedures

Gas mixtures containing carbon monoxide (CO), nitric oxide (NO), or sulfur dioxide (SO₂) in nitrogen were measured during the evaluation. These measurements were made using the analytical instrumentation listed in Table I. Several gas dilution systems were compared over several days. All measurements that were obtained on the same day were considered to be comparable and no measurements were compared across different days.

Multipoint calibrations were performed using undiluted and diluted gas mixtures. The undiluted gas mixtures were National Institute of Standards and Technology Standard Reference Materials (NIST SRMs) and zero-grade nitrogen. These gas mixtures were the reference standards for the accuracy estimates. The diluted gas mixtures were obtained by dilution of EPA Protocol Gases, which are prepared and analyzed by specialty gas producers using an EPA-specified traceability protocol. RTI verified the certified concentrations of these standards relative to the concentrations of the SRMs.

The calibration data were analyzed using least-squares regression techniques under the assumption of a constant random error

term. For several multipoint calibrations, a quadratic equation fitted the data better than a straight-line equation. The accuracy of the gas dilution systems was estimated by comparing the slope of the regression line for the diluted gas mixtures with the corresponding slope for the undiluted gas mixtures.

$$\text{Accuracy} = 100 \left[\frac{\text{Diluted Slope} - \text{Undiluted Slope}}{\text{Undiluted Slope}} \right]$$

This value is constant across the range of predicted concentrations. Statistical tests were performed to check if the diluted slope was significantly different from the undiluted slope.

The precision of the gas dilution systems was estimated by the relative uncertainty of concentrations that are predicted from the regression equation.¹

$$\text{Precision} = 100 \left[\frac{95\% \text{ Uncertainty for Predicted Concentration}}{\text{Predicted Concentration}} \right]$$

Although the 95-percent uncertainty is approximately constant across the range of predicted concentrations, the precision esti-

Table I. Analytical instrumentation for laboratory evaluation of gas dilution systems.

Gas Mixture	Pollutant Gas Analyzer	Analyzer Range (ppm)	
		For Dilution of 10% to 90% of Std. Conc.	For Dilution of 1 to 9% of Std. Conc.
CO/N ₂	Bendix 8501-5CA	1000	50
NO/N ₂	Thermo Electron 10AR	250	25 and 100
	Columbia Scientific 1600	—	5
SO ₂ /N ₂	Thermo Electron 40	1000	50

Table II. Comparison of precision estimates associated with different predicted concentrations for the same multipoint calibration.

NO Analyzer Range (PPM)	Gas Dilution System Conc.	Precision (percent) for One Sample Measurement		
		At Dilution of 90% of Std. Conc.	At Dilution of 50% of Std. Conc.	At Dilution of 20% of Std. Conc.
250	EnviroNics 2020	0.59	0.97	5.14
	Milton Roy 821S	0.50	0.85	4.53

Table III. Comparison of precision estimates associated with various number of measurements of calibration standards and sample.^{a,b}

Measured Values Used in the Regression Calculations	No. of Values in Regression	Precision at Dilution of 50% of Std. Conc.	
		1 Sample Measurement	3 Sample Measurements
Odd Values ^c	5	1.85	1.24
Even Values ^d	5	1.20	0.81
All Values	10	0.97	0.61

^aGas Dilution System EnviroNics 2020

^bAnalyzer Range 250 ppm NO

^cOdd Values 10, 30, 50, 70, 90% of Std. Conc.

^dEven Values 0, 20, 40, 60, 80% of Std. Conc.

mate varies inversely with the predicted concentration. This variation is illustrated in Table II which gives precision estimates obtained from the multipoint calibration of the NO analyzer on its 0 to 250 parts per million (ppm) range. The precision at the upper end of the regression line is approximately 0.5 percent, but the precision at the lower end is approximately nine times larger. In this paper, precision estimates are generally listed for dilutions of 5 or 50 percent of the diluted standard's concentration.

The precision estimates also vary with the number of measurements in the multipoint calibration and with the number of measurements of the sample being analyzed. This variation is illustrated in Table III, which gives precision estimates obtained from various subsets of the 250 ppm NO multipoint calibration. The precision estimates for a 5-point calibration and one sample measurement are approximately two to three times larger than the precision estimate for a 10-point calibration and three sample measurements. This example demonstrates that precision estimates for a gas dilution system can be improved by increasing the number of measurements.

Several unexpected events occurred during the evaluation. Excessive zero drift in the NO analyzer was discovered and repaired. Several days' data were discarded because of this zero drift. One of the capillaries in the Milton Roy 821S system became plugged during the evaluation and this system could no longer be used. The slope of the diluted SO₂ regression line for the Wösthoff 1KM67 system was significantly different from the slopes of the undiluted gas mixtures and the other systems' diluted gas mixtures. This difference may be due to interference of silicone oil from the Wösthoff 1KM67 system on the ultraviolet fluorescence SO₂ analyzer. Additionally, oil was seen coming from the system's nitrogen pump and a dropout trap was installed to prevent downstream oil contamination. Worse than expected precision estimates for the Wösthoff 5KA37 system prompted its inspection and repair by its manufacturer. A minor leak was discovered and the system was reevaluated at RTI after it was repaired.

Results

Several caveats concerning the evaluation should be considered as the results are reviewed. The evaluation studied only a limited range of experimental conditions. The evaluation did not attempt to obtain optimum performance (e.g., better precision estimates) from the gas dilution systems due to time constraints on the number of measurements that could be made during a single day. Not all of the gas dilution systems were evaluated in the same dilution region. The gas dilution systems that were evaluated were selected based only on their availability and their dilution principles. The evaluation did not assess the corresponding accuracy and precision of undiluted gas mixtures which might be used in multipoint calibrations.

The results of the evaluation are given in Table IV for the EnviroNics and Milton

Roy systems at the higher-concentration dilution range (i.e., 10 to 90 percent of the standard concentration). The results for the SO₂ and CO multipoint calibrations are given for both straight-line and quadratic regressions. The SO₂ analyzer is slightly nonlinear and the CO analyzer is quite nonlinear. Accuracy estimates were not calculated for the quadratic regressions. The Milton Roy 821S system was not evaluated beyond the NO and SO₂ calibrations because of the plugged capillary.

The results of the evaluation are given in Table V for the Environics and Wösthoff systems at the lower-concentration dilution range (i.e., 1 to 9 percent of the standard concentration).

Table IV. Results for higher concentration dilution range (10 to 90 percent of standard concentration).

Gas Mixture	Analyzer Range (PPM)	Gas Dilution System	Slope Accuracy (Percent)	Precision at Dilution of 50% of Std. Conc.
NO/N ₂	250	Environics 2020	1.60	0.97
		Milton Roy 821S	0.25	0.85
SO ₂ /N ₂	500	Environics 2020	2.50 ^a	1.24
		Milton Roy 821S	0.74	2.38
SO ₂ /N ₂ ^b	500	Environics 2020	—	0.76
		Milton Roy 821S	—	2.12
CO/N ₂	1000	Environics 2020	-4.53 ^a	10.90
CO ₂ /N ₂ ^b	1000	Environics 2020	—	0.47

^aStatistically significant difference between diluted and undiluted slopes

^bQuadratic regression

Table V. Results for lower concentration dilution range (1 to 9 percent of standard concentration).

Gas Mixture	Analyzer Range (PPM)	Gas Dilution System	Slope Accuracy (Percent)	Precision at Dilution of 5% of Std. Conc.
NO/N ₂	100	Environics 2020	-0.72	1.01
		Wösthoff 1KM67	-0.53	1.05
		Wösthoff 5KA37	-0.43	14.48
NO/N ₂ (after repair)	100	Wösthoff 5KA37	1.25 ^a	1.52
		Wösthoff 5KA37	0.98 ^a	1.39
		Wösthoff 5KA37	1.08 ^a	2.13
		Wösthoff 5KA37	2.17 ^a	1.38
		Wösthoff 5KA37	2.11 ^a	1.59
NO/N ₂ ^b	5	Environics 2020	1.39 ^a	0.31
		Wösthoff 1KM67	0.11	0.59
		Wösthoff 5KA37	0.34	12.64
SO ₂ /N ₂	50	Environics 2020	2.62 ^a	3.13
		Wösthoff 1KM67 ^c	9.87 ^a	3.81
		Wösthoff 5KA37	0.51	14.91
SO ₂ /N ₂	50	Environics 2020	-1.97 ^a	2.08
		Wösthoff 1KM67 ^c	10.04 ^a	5.22
		Wösthoff 5KA37	-1.52	12.28
CO/N ₂	50	Environics 2020	-3.33 ^a	0.74
		Wösthoff 1KM67 ^c	-0.90 ^a	1.11
		Wösthoff 5KA37	1.09	9.75

^aStatistically significant difference between diluted and undiluted slopes

^bReference standard was diluted for those measurements

^cPossible interference effect from silicone oil

Results are given for the Wösthoff 5KA37 system both before and after its repair. The last two after-repair accuracy estimates may be biased due to a concentration shift in the SRM associated with low cylinder pressure. The SO₂ calibration was replicated to verify the slope accuracy estimate for the Wösthoff 1KM67 system.

Conclusions

The number of experiments conducted in the evaluation is too small to allow one to draw any definitive conclusions concerning the accuracy of the gas dilution systems. For 12 of the 25 accuracy estimates, there was no statistically significant difference

between the slopes of the regression lines for the undiluted and diluted gas mixtures. The values of the remaining 13 accuracy estimates ranged from -4.5 to 10.0 percent although the extreme values are associated with a nonlinear calibration curve and a possible interference effect. The accuracy estimates exhibit some variations from one day to the next and from one experimental condition to the next. In general, the accuracy estimates for the four gas dilution systems were similar.

The precision estimates for the four gas dilution systems were also generally similar. The values range from 0.3 to 14.9 percent for predicted concentrations in the middle portion of the regression line. The largest values are associated with a leaking system. The precision estimates exhibited some variations from one day to the next and from one experimental condition to the next. The precision estimates were significantly different in different portions of the regression line. Better precision can be obtained by making more measurements during multipoint calibrations and sample measurements.

Disclaimer

Although the research described in this paper has been funded wholly by the U.S. EPA through Contract No. 68-D1-009 to RTI, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

1. M.G. Natrella, *Experimental Statistics*, National Bureau of Standards Handbook No. 91, U.S. Government Printing Office, Washington, D.C., 1963, pp. 5-1 to 5-46.

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Accuracy Assessment of EPA Protocol Gases in 1988

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The U.S. Environmental Protection Agency has established quality assurance procedures for air pollution measurement systems. These procedures are intended to reduce the uncertainty of environmental measurements. Among the areas of EPA's concern is the accuracy of compressed gas standards and liquid permeation standards used for calibration and audits of continuous emission monitoring systems and ambient air quality analyzers. EPA's regulations specify that the certified values for these standards be traceable to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or to NIST/EPA-approved Certified Reference Materials via two traceability protocols.¹⁻⁵ These protocols were published originally in 1978 and were revised in 1987. The revisions include the following items:

- Provision for analysis of compressed gas standards using dilution and ambient air quality analyzers;
- Provision for referencing liquid permeation devices to compressed gas standards;
- Extension of the certification period for the standards from 6 to 18 months in most cases;
- Additional documentation requirements for the standards' written certification reports; and
- Provision for periodic accuracy assessments of compressed gas standards and liquid permeation standards that are prepared and analyzed according to the protocols.

Research Triangle Institute (RTI) conducted an accuracy assessment of compressed gas standards in 1985 under contract to EPA.⁶ Fifty standards were purchased from eleven specialty gas producers. These standards were specified to be prepared and analyzed according to the protocols. They were one of the following gas mixtures: sulfur dioxide (SO₂) in nitrogen (N₂) at 70 or 300 parts per million by volume (ppm), nitric oxide (NO) in N₂ at 70 or 400 ppm or carbon monoxide (CO) in air at 30 ppm. They were analyzed at RTI using SRMs as reference standards. Seventy percent of the producers' certified concentrations were found to be accurate to within plus or minus 2 percent and 94 percent of the concentrations were found to be accurate to within plus or minus 5 percent.

Following publication of the revised traceability protocols, EPA conducted an accuracy assessment of compressed gas standards in 1988. These standards were to be prepared and analyzed by specialty gas producers according to the revised protocols. The purposes of the assessment were: (1)

to document the accuracy of the standards' certified concentrations; and (2) to check that the standards' written certification reports met the new documentation requirements. EPA directed RTI to purchase from all available sources and to analyze the following gas mixtures: 300 ppm SO₂ in N₂; 400 ppm NO in N₂; and 30 ppm CO in air.

Purchase of Compressed Gas Standards

A telephone survey indicated that eleven specialty gas producers market standards that are prepared and analyzed according to the protocols. These producers are as listed below:

- AGA Gas, Inc.;
- Airco Industrial Gases;
- Alphagaz Liquid Air;
- Big Three Industrial Gas, Inc.;
- Cryodyne Specialty Gases, Inc.;
- Linde (Union Carbide Corporation);
- Matheson Gas Products;
- MG Industries;
- National Specialty Gases;
- Scott-Marrin, Inc.; and
- Scott Specialty Gases.

Two anonymous third-party buyers purchased the standards to help ensure that gases of typical quality were obtained for the assessment. Standards were purchased from ten producers during January 1988. Standards were not purchased from AGA Gas because of procurement difficulties. The prices of the standards ranged from \$253 to \$480 with a mean price of \$342. The buyers subsequently shipped the standards to RTI to be analyzed.

Upon receipt of the standards, the following irregularities were discovered:

- One buyer had ordered standards containing 30 ppm CO in N₂ rather than 30 ppm CO in air;
- Alphagaz had shipped a double order;
- The written certification reports indicated that only one of three Linde standards had been prepared and analyzed according to the protocols;
- The standards purchased from Cryodyne Specialty Gases and Matheson Gas Products had been prepared and

Table I. Percent differences^a between producer-certified concentrations and auditor-measured concentrations.

Specialty gas producer	300 ppm SO ₂	400 ppm NO	30 ppm CO
Airco Special Gases	9.0%	-0.6%	0.8% ^d
Alphagaz (No. 1) ^b	5.7%	1.6%	0.4%
(No. 2) ^b	5.7%	2.0%	0.7%
Big Three Industrial Gas	2.5%	0.4%	1.1%
Cryodyne Specialty Gases ^c	2.5%	-0.4%	1.8% ^d
Linde (Union Carbide)	5.3%	0.2% ^e	-0.6% ^e
Matheson Gas Products ^c	3.9%	0.1%	4.3% ^d
MG Industries	6.4%	2.7%	0.9% ^d
National Specialty Gases	2.6%	1.0%	1.9% ^d
Scott-Marrin	1.2%	0.8%	-0.3%
Scott Specialty Gases	4.3%	-0.4%	-0.2%

^a Percent Difference = 100 $\left[\frac{\text{certified conc.} - \text{measured conc.}}{\text{measured conc.}} \right]$

^b Prepared and analyzed by MG Industries.

^c Prepared and analyzed by National Specialty Gases.

^d Balance gas for this standard is air. The balance gas for the remaining standards is nitrogen.

^e This standard was not an EPA Protocol Gas.

analyzed by National Specialty Gases. However, their written certification reports did not indicate that National Specialty Gases produced these standards; and

- The standards purchased from Alphagaz had been prepared and analyzed by MG Industries. However, their written certification reports did not indicate that MG Industries produced these standards.

The revised protocols specify that the written certification reports must be signed by the analyst. They also specify that the reports must contain the identification of the laboratory where the standard was certified and the analyst who performed the certification.

MG Industries and National Specialty Gases may have inferred that an accuracy assessment was being conducted because of preparing and analyzing identical orders. They may have given special attention to the analysis of these standards.

RTI Analytical Procedures

Upon receipt of the standards, RTI measured the standards' pollutant concentrations with instruments using the following analytical principles: ultraviolet fluorescence for SO₂; chemiluminescence for NO; and nondispersive infrared photometry for CO. The standards were sampled without dilution through a stainless steel and Teflon[™] sampling manifold. Sample flow through the manifold was controlled by stainless steel solenoid valves, a needle valve, and a digital

timer. The voltage outputs from the instruments were recorded by a data logger with data averaging capabilities.

The reference standards for each set of measurements were two SRMs whose concentrations bracketed the concentrations of the standards that were being analyzed. For example, 100 and 500 ppm SO₂ SRMs were used in the analysis of the 300 ppm SO₂ standards. The linearity of the instruments' calibration curves was investigated by measurement of a zero gas and additional SRMs. The SO₂ data were corrected for the nonlinearity of the SO₂ instrument. The NO and CO instruments' calibration curves were found to be sufficiently linear such that the NO and CO data did not have to be corrected. The reference standards for the CO measurements contained the same balance gas as the standards being analyzed. The slope of the CO in air calibration curve was 1.4 percent greater than the CO in N₂ slope because of pressure broadening effects in the nondispersive infrared analyzer. This difference in the slopes was the motivation for the use of two different sets of carbon monoxide reference standards.

The pollutant concentration of each standard was measured at least three times. The mean measured concentration was compared with the producer's certified concentration. The relative standard deviation (RSD) for the replicate measurements was used as an index of measurement precision. The following mean RSDs were obtained for the instruments used in the assessment: 0.2 percent for SO₂; 0.4 percent for NO; and less than 0.1 percent for CO.

Results of Accuracy Assessment

The results of RTI's 1988 accuracy assessment are summarized in Table I. The accuracy of a producer's certified concentration is defined as the percent difference between the producer's certified concentration and RTI's corresponding mean measured concentration. A frequency distribution for these results is given in Table II. In general, 64 percent of the results fell within the 0 to 2 percent range and 85 percent of the results fell within the 0 to 5 percent range. These 1988 results indicate a decline in accuracy in comparison with the results of the 1985 accuracy assessment of EPA Protocol Gases.⁶ When only the standards containing 300 ppm SO₂, 400 ppm NO and 30 ppm CO are considered, 83 percent of the 1985 accuracies fell within the 0 to 2 percent range and 97 percent fell within the 0 to 5 percent range. The cause of this overall accuracy decline is the change in the accuracy of the 300 ppm SO₂ standards. Nine of ten 300 ppm SO₂ standards were accurate to within 5 percent in 1985. However, only six of eleven 300 ppm SO₂ standards were accurate to within 5 percent in 1988.

Any accuracy assessment is an instantaneous snapshot of the process being measured. These results should not be regarded as a final statement concerning the accuracy of EPA Protocol Gases. They can be used as an indicator of the current status of the accuracy of EPA Protocol Gases as a whole. However, individual results should not be taken as definitive indicators of the analytical capabilities of individual producers.

Table II. Frequency distribution for percent differences between producer-certified concentrations and auditor-measured concentrations.

Gas composition	Nominal concentration	Number of cylinders falling within a given range of absolute values of percent differences			
		0-2%	2-5%	5-10%	>10%
SO ₂ /N ₂	300 ppm	1	5	5	0
NO/N ₂	400 ppm	10	1	0	0
CO/N ₂	30 ppm	6	0	0	0
CO/Air	30 ppm	4	1	0	0
Total		21	7	5	0

Table III. Required documentation for EPA protocol gases appearing on the producers' written certification reports.

Required documentation	Airco	Alphagaz	Big Three	Cryodyne	Linde	Matheson	MG Indust.	Nat. Spec.	Scott Mar.	Scott Spec.
Std. ID number	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Certified conc.	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Balance gas	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Cylinder pressure ^a	N	Y	Y	N	N	N	Y	N	Y	Y
Certification date	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Expiration date	Y	Y	Y	Y	b	Y	Y	Y	Y	Y
Ref. standard data ^a	Y	c	Y	c	b	c	c	c	Y	Y
Protocol statement ^a	d	Y	c	c	b	Y	Y	c	Y	c
Lab and analyst ID ^a	Y	e	Y	e	f	e	Y	Y	Y	Y
Gas analyzer ID ^a	c	Y	Y	c	c	c	Y	c	Y	c
All analyzer readings ^a	N	g	g	g	h	g	g	g	g	Y
Chronological record ^a	i	i	i	i	i	i	i	i	i	i
3 Significant digits ^a	Y	Y	Y	N	Y	N	Y	N	Y	Y
Cert. period (months) ^a	18	18	18	6	6 ^b	6 ^l	18	6	18	18

Y = Yes, N = No

^a New documentation requirement.

^b Only one of three Linde certificates listed this information.

^c Incomplete information was given in the report.

^d 1978 protocol was cited.

^e Incorrect information was given in the report.

^f Supervisory personnel, rather than the analyst, signed the report.

^g Calculated concentrations, rather than analyzer readings, were given.

^h Only one of three Linde cylinders were reassayed on a later date.

ⁱ Not applicable for the original certification of the standard.

^l One of the three Matheson certificates listed an 18-month certification period.

NIST Confirmatory Analyses

Both RTI and EPA were concerned that the SO₂ results may have been biased because of some unknown error in RTI's analyses. As a result of this concern, one of the producers' SO₂ standards was sent to NIST for confirmatory analyses. NIST found that the SO₂ standard contained 326.0 ppm using an ultraviolet fluorescence instrument and 326.8 ppm using an electrochemical method. These values agreed to within 0.7 percent with RTI's measured value of 324.4 ppm. The good agreement between RTI's and NIST's analyses for this SO₂ standard suggests that RTI's other SO₂ concentration measurements were also accurate.

Documentation

An important part of the revised protocols is the requirement for additional information in the written certification reports. The producers' reports were reviewed to determine if the new documentation requirements were being followed. The results of this review are summarized in Table III. In general, all the reports met the 1978 documentation requirements. However, none of the reports met all the new 1987 documentation requirements. Some of the reports indicated that some producers were not aware of the revised protocol or had not implemented them yet.

Acknowledgments

This work was funded by the EPA under contract number 68-02-4550. The information contained in this article does not necessarily reflect U.S. Environmental Protection Agency's policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The authors gratefully appreciate the confirmatory analyses that were performed by Gerald D. Mitchell of NIST. The technical assistance provided by the two third-party buyers is also appreciated.

References

1. "Procedure 1. Quality Assurance Requirements for Gas Continuous Emission Monitoring Systems Used for Compliance Determination," U.S. Environmental Protection Agency, *Code of Federal Regulations*, Title 40, Part 60, Appendix F, 1987.
2. "Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS)," U.S. Environmental Protection Agency, *Code of Federal Regulations*, Title 40, Part 58, Appendix A, 1987.
3. "Quality Assurance Requirements for Prevention of Significant Deterioration (PSD) Air Monitoring," U.S. Environmental Protection Agency, *Code of Federal Regulations*, Title 40, Part 58, Appendix B, 1987.
4. "Procedure for NBS-Traceable Certification of Compressed Gas Working Standards Used for Calibration and Audit of Continuous Source Emission Monitors (Revised Traceability Protocol No. 1)," June 1987 in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods*, Section 3.0.4, U.S. EPA, EPA-600/4-77-027b.
5. "Procedures for NBS-Traceable Certification of Compressed Gas and Permeation Device Working Standards Used for Calibration and Audit of Air Pollution Analyzers (Revised Traceability Protocol No. 2)," May 1987 in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods*, Section 2.0.7, U.S. EPA, EPA-600/4-77-027a.
6. R. S. Wright, E. L. Tew, C. E. Decker, D. J. von Lehmden, W. F. Barnard, "Performance audits of EPA protocol gases and inspection and maintenance gases," *JAPCA*, 37: 284 (1987).

R. S. Wright and C. E. Decker are with RTI's Center for Environmental Measurements, P.O. Box 12194, Research Triangle Park, NC 27709. C. V. Wall is with RTI's Center for Environmental Quality Assurance at the same address. D. J. von Lehmden is with EPA's Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Mail Drop 77, Research Triangle Park, NC 27711. This note manuscript was peer reviewed.

APCA NOTE-BOOK

Performance Audits of EPA Protocol Gases and Inspection and Maintenance Calibration Gases

Robert S. Wright, Edward L. Tew, and Clifford E. Decker

Research Triangle Institute
Research Triangle Park, North Carolina

Darryl J. von Lehmden and William F. Barnard

U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

One of the assumptions used in quality assurance programs for air pollution measurement systems is that the uncertainty of each step in the measurement process is quantifiable and is controllable to some degree. One of these uncertainties is associated with the certified concentrations of compressed gas mixtures used in calibration. The U.S. Environmental Protection Agency (EPA) seeks to limit this uncertainty by requiring that the certified concentrations be traceable to National Bureau of Standards' (NBS) gaseous Standard Reference Materials (SRMs) or NBS/EPA-Certified Reference Materials and that certain traceability procedures be followed. Two such procedures are EPA Traceability Protocol No. 1¹ and the EPA Recommended Practice for Naming Inspection and Maintenance (I/M) Calibration Gases.² Even if specialty gas producers follow these procedures, users may ask, "How accurate are the certified concentrations?"

The EPA has a continuing interest in assessing the accuracy of calibration standards for air pollution measurement systems. Between 1978 and 1981, Research Triangle Institute (RTI) conducted five performance audits of such calibration standards for EPA.³ These standards were purchased from specialty gas producers and contained nitric oxide, sulfur dioxide, and carbon monoxide at source concentrations. The EPA plans to conduct additional performance audits in the future.

Two performance audits of calibration gas mixtures were conducted by RTI in 1985 to assess the accuracy of certified concentrations assigned by specialty gas producers. The first audit

involved the purchase and analysis of EPA Protocol No. 1 gases from 11 specialty gas producers.⁴ These mixtures contained sulfur dioxide in nitrogen, nitric oxide in nitrogen, and carbon monoxide in air. Such mixtures are used for the calibration and auditing of ambient air quality analyzers and continuous emission monitoring systems. The second audit involved the purchase and analysis of I/M calibration gases from 13 specialty gas producers.⁵ These mixtures contained carbon monoxide and propane in nitrogen. Such mixtures are used for the calibration and auditing of motor vehicle emission analyzers. This note summarizes the analytical results from these two audits.

Purchase of Audit Samples

The first step in both audits was a telephone poll of specialty gas producers to determine whether they produce and sell the gas mixtures of interest. Eleven producers indicated that they could supply EPA Protocol No. 1 gases, and 13 indicated that they could supply I/M calibration gases. Either RTI or an anonymous third-party buyer then purchased one cylinder of each of the following gas mixtures from the 11 producers: 70 and 300 parts per million (ppm) sulfur dioxide in nitrogen; 70 and 400 ppm nitric oxide in nitrogen; and 30 ppm carbon monoxide in air. These gas mixtures were specified to be prepared and analyzed according to EPA Traceability Protocol No. 1. The third-party buyer was used to ensure that the gas mixtures were of typical quality. The third-party buyer also purchased I/M calibration gas containing 640 ppm propane and 1.6 percent

carbon monoxide in nitrogen from the 13 producers. This gas mixture was specified to be prepared and analyzed according to the EPA Recommended Practice in the three cases in which the producers could provide such a gas mixture. The highest available accuracy was specified in the 10 remaining cases.

RTI Analytical Procedures

When the gas mixtures were delivered to RTI, their pollutant concentrations were measured with instruments using the following analytical principles: ultraviolet fluorescence for sulfur dioxide; chemiluminescence for nitric oxide; nondispersive infrared photometry for low-concentration carbon monoxide; gas chromatography with thermal conductivity detection for high-concentration carbon monoxide; and gas chromatography with flame ionization detection for propane. The gas mixtures were sampled without dilution through a stainless steel and Teflon® sampling manifold controlled by a digital timer. Data were recorded by an averaging data logger or a digital integrator. The reference standards were gaseous SRMs.

The concentration of each gas mixture was measured at least three times. These measurements yielded a mean concentration that was compared with the producer's certified concentration and a coefficient of variation ($CV = 100$ [standard deviation/mean]), which is used as an index of measurement precision. The following mean CVs are for the instruments used in the audits: sulfur dioxide—0.3 percent relative; nitric oxide—0.4 percent relative; low-concentration carbon monoxide—0.2 per-

Table I. Percent differences^a between producer-certified concentrations and auditor-measured concentrations.

Specialty gas producer	EPA protocol gases					I/M cal. gases	
	70 ppm SO ₂	300 ppm SO ₂	70 ppm NO	400 ppm NO	30 ppm CO	1.6% CO	640 ppm C ₃ H ₈
AGA Burdox	—	—	—	—	—	1.0 ^b	6.5 ^b
Airco	-1.3	-1.9	-3.2	0.6	0.2	-11.2 ^c	3.9 ^c
Air Products	9.8	-0.8	2.3	-1.6	—	1.0	1.5
Air Quality Prod.	—	—	—	—	—	-1.1	-0.6
Big Three Ind.	-2.8	-2.7	4.3	-0.9	2.5	0.1	6.7
Ideal Gas Prod.	—	—	—	—	—	1.3	-4.3
Liquid Carbonic	2.0	-1.9	0.7	-2.1	-0.3	-0.1 ^c	-1.8 ^c
Matheson Gas Prod.	—	—	4.2	2.3	—	-0.1	-1.9
MG Industries	-3.1	0.8	0.6	0.0	0.3	0.0 ^b	1.6 ^b
National Specialty	3.2	1.9	1.1	0.9	0.7	—	—
Sci. Gas Products	-7.0	20.4	-0.2	0.6	-0.3	-0.7	0.8
Scott-Marrin	-1.1	-0.3	-0.2	0.3	-0.6	-1.0 ^c	0.1 ^c
Scott Specialty	-3.6	-0.3	2.0	-0.7	0.4	-0.5 ^b	0.4 ^b
Union Carbide	—	-0.7	-0.3	-0.4	-1.6	-0.6	-0.5

^a Percent difference = 100 × (certified conc. - measured conc.)/measured conc.

^b Prepared and analyzed according to EPA Recommended Practice for Naming I/M Calibration Gases.

^c Prepared and analyzed according to EPA Traceability Protocol No. 1.

cent relative; high-concentration carbon monoxide—0.3 percent relative; and propane—0.1 percent relative.

Performance Audit Results

The results of the performance audits of EPA Protocol No. 1 gases and I/M calibration gases are summarized in Table I. The accuracy of a producer's certified concentration is defined as the absolute value of the percent difference between the certified concentration and RTI's corresponding measured concentration. A frequency distribution for these results is given in Table II. In general, the accuracies of the producers' certified concentrations are good with 74 percent of the values falling within the 0-2 percent relative range. Ninety-two percent of the values fell within the 0-5 percent relative range. The 70-ppm sulfur dioxide values and the propane values, as a group, are less accurate than the other values.

The values for the EPA Protocol No. 1 gases are significantly better than those from RTI's 1981 performance au-

dit of commercial cylinder gases containing sulfur dioxide, nitric oxide, and carbon monoxide.⁶ In that audit, only 45 percent of the values fell within the 0-2 percent relative range, and 65 percent fell within the 0-5 percent relative range. No comparable audit data exist for I/M calibration gases.

Following both audits, selected cylinders were sent for confirmatory analyses to EPA laboratories in Ann Arbor, Michigan, and/or Research Triangle Park, North Carolina. The confirmatory analyses, in general, showed good to excellent agreement with RTI's analyses. However, the agreement for the 300-ppm sulfur dioxide measurements was approximately 2.6 percent relative, which was larger than expected.

Acknowledgments

This work was funded by the EPA under Contract No. 68-02-4125. The information contained in this article does not necessarily reflect U.S. Environmental Protection Agency policy. Mention of trade names or commercial

products does not constitute endorsement or recommendation for use. The authors appreciate the confirmatory analyses of Avis Hines and Gordon Becker. Technical assistance provided by the third-party buyer is also appreciated.

References

1. "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Sources Emission Monitors (Protocol No. 1)," June 1978, in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods*, Section 3.0.4, U.S. EPA, EPA-600/4-77-027b (August 1977).
2. "EPA Recommended Practice for Naming I/M Calibration Gas," U.S. EPA, EPA-AA-TSS-83-8-B, 1983.
3. C. E. Decker, M. L. Saeger, W. C. Eaton, D. J. von Lehmden, "Analysis of Commercial Cylinder Gases of Nitric Oxide, Sulfur Dioxide, and Carbon Monoxide at Source Concentrations," in *Proceedings of the APCA Specialty Conference on Continuous Emission Monitoring—Design, Operation, and Experience*, APCA, Pittsburgh, PA, SP-43, 1981.
4. R. S. Wright, E. L. Tew, C. E. Decker, D. J. von Lehmden, "Analysis of EPA Protocol Gases Used for Calibration and Audits of Continuous Emission Monitoring Systems and Ambient Air Analyzers—Results of Audit 6," U.S. EPA, EPA-600/D-85-268, 1985.
5. R. S. Wright, C. E. Decker, W. F. Barnard, "Performance Audit of Inspection and Maintenance Calibration Gases," U.S. EPA, EPA-600/D-86-101, 1986.
6. C. E. Decker, W. C. Eaton, R. C. Shores, C. V. Wall, "Analysis of Commercial Cylinder Gases of Nitric Oxide, Sulfur Dioxide, and Carbon Monoxide at Source Concentrations—Results of Audit 5," U.S. EPA, EPA-600/4-81-080, 1981.

Table II. Frequency distribution for percent differences between producer-certified concentrations and auditor-measured concentrations.

Gas composition	Nominal concentration	Number of cylinders falling within given range of absolute values of percent difference			
		0-2	2-5	5-10	>10
SO ₂ /N ₂	70 ppm	3	4	2	0
	300 ppm	8	1	0	1
NO/N ₂	70 ppm	7	4	0	0
	400 ppm	9	2	0	0
CO/Air	30 ppm	8	1	0	0
CO/N ₂	1.6%	12	0	0	1
C ₃ H ₈ /N ₂	640 ppm	9	2	2	0
Total		56	14	4	2

R. S. Wright, E. L. Tew, and C. E. Decker are with RTI's Center for Environmental Measurements, P.O. Box 12194, Research Triangle Park, NC 27709. D. J. von Lehmden and W. F. Barnard are with the EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Mail Drop 77, Research Triangle Park, NC 27711. This note manuscript is a condensed version of a technical paper which appeared in the peer-reviewed transactions *Continuous Emission Monitoring—Advances and Issues*, published by APCA in 1986.



Calibrated Instruments, Inc.

200 Saw Mill River Road, Hawthorne, NY 10532 TEL: (914) 741-5700 FAX: (914) 741-5711

September 24, 1996

96-7-2
9/26/96

STATE OF CALIFORNIA
AIR RESOURCES BOARD
RECEIVED 9/25/96
BY BOARD SECRETARY

Ms. Pat Hutchens
Board Secretary
California Air Resources Board
2020 "L" Street
Sacramento, CA 95814

XC: Board Members
JDD TAC
MPK Legal
MLD

SUBJECT: California Air Resources Board; Source Test Methods
Section 94114, Method 100
RE: Appendix 100.1; Verification of Gas Dilution Systems For Field Instrument Calibration

Dear Board Chairperson & Board Members - Ladies & Gentlemen;

GENERAL COMMENT

California Air Resources Board (CARB) Proposed Method 100; Appendix 100.1 (as above) continues the same flow controller technology bias (see paragraph 3.2) as that found in EPA Method 205; Verification of Gas Dilution Systems for Field Instrument Calibrations; CFR 40, Part 51, Appendix M.

Additionally, I respectfully submit that CARB Proposed Method 100; Appendix 100.1 exhibits an inadequate understanding of PDP technology, as is also unfortunately evidenced in EPA Method 205 from which it has been derived.

SPECIFIC COMMENTS

Paragraph 3.1 Gas Dilution System:

It is not necessary to have a certified gas standard to prove the field accuracy of a positive displacement pump (PDP). Linearity (predictability) of the PDP gas dilution system may be proven with any gas concentration (even uncertified) so long as: (1) the final diluted gas concentration is within the measuring range of the calibrated certifying analyzer; and (2) the gas to be diluted and measured remains stable for at least the duration of the verification test period. The accuracy evaluation procedure of a PDP system may be made independent and irrespective of the stated accuracy (certification) of the verification test gas being used.

Once the predictability of the PDP system has been proven during the verification test, Paragraph 3.4.2 Mid-Level Calibration Gas "independent check" is an unnecessary check if the user can rely upon the "1.0% stated accuracy" (certification) of the EPA Protocol Gases that are to be diluted by the PDP for system verification test purposes. It is questionable whether it is valid to "inter-compare" 2-different test gas standards in the same verification test procedure, if the "actual certified concentration" is deemed meaningful to the protocol.

DIGAMIX mixes all gases at: (1) ambient pressure(s); and (2) equal temperatures. The Wosthoff PDP system DIGAMIX is a primary gas dilution standard. Accordingly; the dimensionally fixed, variable stroking physical character of each controlled piston unit volumetrically proportions and delivers "same state" gases to create the final diluted concentration required. All final gas concentrations selected may be delivered to the test analyzer at the same flow rate. No gas-correction factors are required, as with flow controllers; nor is there any need to continually monitor temperature and pressure while the final dilution gas is being generated.

Paragraph 3.2 Annual Certification Procedure:

Unlike flow controller based units, Wosthoff PDP systems do not require calibration to a NIST-traceable primary flow standard. A symmetry test may be performed by setting two gases (100% oxygen and 100% nitrogen) to a 50%-50% dilution ratio. Once having taken the analyzer readings for oxygen, reverse the gas inlets and repeat the readings. Any difference between the two readings for oxygen and the predicted 50% oxygen reading should result in an instrument accuracy equal to or better than the manufacturer's stated accuracy.

Paragraph 3.3 Mass Flow Controller Systems:

DIGAMIX PDP gas dilution systems do not have a "no fly" zone as cautioned in this paragraph. PDP units provide variable gas dilutions at the same standard flow rate. PDP units may be used with the same manufacturers stated accuracy at any dilution increment (ratio) throughout an instrument's entire dilution range (0-100%).

VERY IMPORTANT: Wosthoff PDP dilution system accuracy is stated as a "percentage (%) of the final gas concentration (dilution ratio) selected" not a "percentage (%) of full scale" as with flow controllers. This is a major consideration when evaluating accuracy. For example; if a Wosthoff unit has a (+/-) 1.0% stated accuracy and the user wishes to make a 1.0% final dilution the accuracy of the final mixture will be (+/-) 1.0% of the 1.0% concentration desired or (+/-) 0.01%.

Wosthoff DIGAMIX gas dilution system accuracies range from better than (+/-)1.0% to better than (+/-)0.25%, depending upon the system configuration selected.

CONCLUSION

I know many hours and much time have been devoted to this draft proposal.

I respectfully request that the California Air Resources Board Proposed Section 94114, Method 100; Appendix 100.1; Verification of Gas Dilution Systems For Field Instrument Calibration be amended to reflect a more balanced and equally weighted presentation of available gas dilution technologies. If "cautions" are issued, as they are in the proposed Method 100, then more desirable performance attributes and alternatives to flow controllers should also be acknowledged.

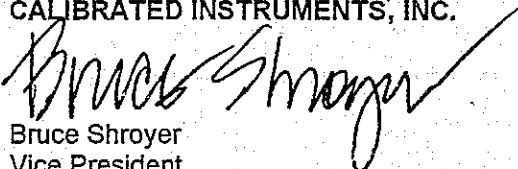
Since Appendix 100.1 will be read and followed by current gas dilution system users as well as those who are considering gas dilution technology for the first time, the presentation in Appendix 100.1 should be no different in scope or purpose than that provided in the greater documentation of the complete Test Method 100. It should provide information as well as guidance. It is only appropriate that readers be apprised fairly and adequately. CARB has a unique opportunity to rectify the technical deficiencies and "not so subtle" bias found in EPA Method 205.

I challenge your Board to do what EPA Method 205 does not do. Do it right !

Thank you for your consideration of my comments.

Sincerely,

CALIBRATED INSTRUMENTS, INC.



Bruce Shroyer
Vice President
Technical Services

JBS:sp

file: CARB



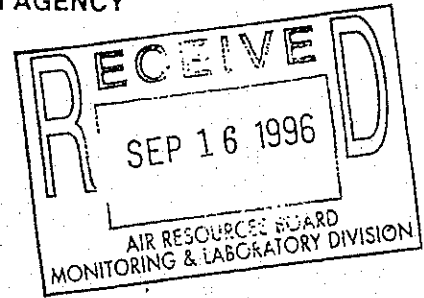
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IX

75 Hawthorne Street
San Francisco, CA 94105-3901

96-7-2
9/26/96

September 11, 1996



George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812-2815

STATE OF CALIFORNIA
AIR RESOURCES BOARD
RECEIVED 9/19/96
BY BOARD SECRETARY
XC: Board Members
JDD TAC
MPK Legal
MLD

Re: ARB Method 5
ARB Method 7
ARB Method 100
ARB Method 425
ARB Method 436

Dear Mr. Lew:

I am pleased to inform you that EPA has reviewed the latest revisions of the above listed test methods and has deemed them acceptable for compliance determinations. Upon adoption of these methods by your Board, they may be substituted for EPA methods in the following manner:

- ARB Method 5 for EPA Method 5
- ARB Method 7 for EPA Method 7
- ARB Method 100 for EPA Methods 3A, 6C, 7E, 10, 25A, and 25B
- ARB Method 425 for EPA Method 306
- ARB Method 436 for EPA Method 29

EPA welcomes the opportunity to review your test methods for consistency with EPA policy on test methods. If you have any questions on test methods, please do not hesitate to call Duane James of my staff at (415) 744-1191.

Sincerely,

Daniel A. Meer, Chief
Rulemaking Section

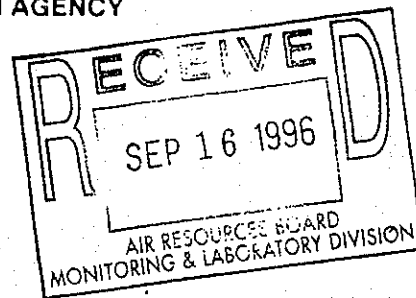


UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IX

75 Hawthorne Street
San Francisco, CA 94105-3901

96-7-2
9/26/96



September 11, 1996

George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812-2815

STATE OF CALIFORNIA
AIR RESOURCES BOARD
RECEIVED 9/19/96
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XC: Board Members
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- ARB Method 436 for EPA Method 29

EPA welcomes the opportunity to review your test methods for consistency with EPA policy on test methods. If you have any questions on test methods, please do not hesitate to call Duane James of my staff at (415) 744-1191.

Sincerely,

Daniel A. Meer, Chief
Rulemaking Section

96-7-2
9/26/96

STATE OF CALIFORNIA
AIR RESOURCES BOARD
RECEIVED 9/13/96
BY BOARD SECRETARY

September 6, 1996

XC: Board Members
JDD TAC
MPK Legal
MLD

Board Secretary
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Re: Comments For Existing And New Test Methods

Dear Secretary:

Please find comments for proposed Method 429 and the new Method 436:

Method 429 - PAHs

Section 4. SAMPLING APPARATUS, MATERIALS AND REAGENTS

4.1 SAMPLING APPARATUS

Sealing Materials - A number of testers or currently using "O" rings to seal the filter holder and the ball/socket joints as well as the "O" ring for sealing the impinger joints (45/50). Some testers elect to use a viton material "O" ring which in the measurement of PAHs could possibly contaminate the collected sample when rinsed with the solvents. To allow for flexibility, "O" rings should be addressed, however, with the stipulation that the material be of teflon which is inert.

Section 5. SAMPLE RECOVERY

5.1 SAMPLE RECOVERY APPARATUS

5.1.1 Probe Nozzle Brush

May want to insert teflon to replace inert bristle with stainless steel wire handle. Teflon brushes with teflon handles are now available and being widely used.

5.?? Should protective surgical gloves be addressed?

5.2 SAMPLE RECOVERY REAGENTS

5.2.1 Reagent Water

Most testers refer to this as HPLC water grade.

5.3 SAMPLE RECOVERY PROCEDURE

No smoking is allowed.

Smokers should not be allowed to recover the samples unless they have thoroughly washed their hands or are wearing non-contaminating gloves.

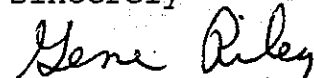
Method 436 - Multiple Metals

13. Bibliography

Several of the EPA/OSW Reference Methods have not been updated (see attached letter dated August 9, 1996).

Thank you for the opportunity to comment.

Sincerely



C.E. (Gene) Riley
2300 Southern Drive
Durham, NC 27703

(919) 544-5729 X 258

TRIANGLE LABS

August 9, 1996

Mr. William Grimley
USEPA
Mail Drop 19
Research Triangle Park, NC 27711

RE: EPA Reference Method 29 Bibliography References

Dear Mr. Grimley:

This is a summary of a telephone conversation that I had with Mr. Tom Ward on August 7, 1996. As you know, Mr. Ward recommended that we inform you of our situation regarding the EPA references listed in the Method 29 (M-29) Bibliography, Section 9.

Triangle Laboratories is currently conducting M-29 analyses on air emission samples from USEPA Region 2. Our M-29 analytical staff as well as procedures were being monitored by Mr. Don Wright of the USEPA Region 2 Office. Mr. Wright noticed that we were performing analytical procedures according to revised OSW promulgated methods and not per the OSW methods listed in the Bibliography references. Examples of these OSW methods are listed in the following:

M-29 OSW Methods/Dates Listed

M-6010 - September 88
M-6020 - September 88¹
M-7000 - September 88
M-7041 - September 88
M-7060 - September 88
M-7131 - September 88
M-7421 - September 88
M-7470 - September 88
M-7740 - September 88
M-7841 - September 88

OSW Revised Methods/Dates

M-6010A - July 92
M-6020 - September 94¹
M-7000A - July 92
M-7041 - September 86
M-7060A - September 94
M-7131A - September 94
M-7421 - September 86
M-7470A - September 94
M-7470 - September 86
M-7841 - September 86

¹ M-6020 is listed in Section 2 as being promulgated in September 1988, but is listed in the SW-846 manual as being promulgated in September 94.

As you can see, not one of the revised EPA/OSW promulgated inorganic methods was updated in the April 96 M-29 document.

Located in Section A. of the EPA SW-846 manual under "Instructions For New Subscribers" there is a statement that directs the analyst to use the latest revised final version of the SW-846 manual methods.

This is where Triangle Labs became confused and made their mistake by assuming that the current EPA/OSW promulgated methods (SW-846) superseded the EPA/OAQPS M-29 Section 2 References.

Upon discussing this problem with Mr. Ward and other inorganic laboratory staff, we believe that EPA/OAQPS should consider; 1) notifying the testing community that there is a potential problem, and 2) determining if the OSW promulgated analytical M-29 Referenced methods are equivalent and therefore, should supersede the current M-29 referenced OSW methods.

In the meantime, we would recommend that a notice be placed on the TNN bulletin board to forewarn M-29 users of this potential problem. Also there may be other M-29 Bibliography items that require possible updates.

In the case of the M-29 Reference Hg Method 7470 versus the "new, final" Method 7470A there is considerable increase in time and cost associated with performing the M-7470 as compared with M-7470A. Timewise, we estimate that it requires @ 2.5 hrs to analyze 12 samples by M-7470 vrs @ 2 hrs to analyze 30 samples by M-7470A. Sample preparation and analysis cost are estimated to be @ \$200/train for M-7470 vrs @ \$75/train for M-7470A.

We appreciate your situation in dealing with this problem and understand that reduced EPA budgets limit what you can accomplish in a short period of time.

Triangle Labs plans to conduct some comparison test for the Hg M-7470/M-7470A procedures and will gladly provide the comparison data to EPA for review. We would appreciate, if you could review our analytical performance plan as we would like to possibly include the QA/QC elements that would satisfy your DQO requirements.

Thank you for your time and attention in this matter and we look forward to hearing from you. Please contact Mr. C.E. (Gene) Riley @ (919) 544-5729 X 258 for additional information or if we can be of further assistance.

Sincerely,

C.E. (Gene) Riley

cc:

Larry Johnson
Gary McAlister
Tom Ward


Steiner Environmental, Inc.

Legal

96-7-2
9/26/96

September 5, 1996

Air Resources Board
P. O. Box 2815
Sacramento CA 95812

Attention: Board Secretary

Reference: September 26, 1996, 9:30 am Hearing
Public Hearing to Consider the Amendment and Adoption of
Regulations Regarding Stationary Source Test Methods

Subject: Written Comments on Methods 5, 100 and 436

Enclosed are 20 copies of my written comments pertaining to the proposed revisions to Methods 5 and 100 and the new Method 436, for your consideration. Thank you for the opportunity to provide these comments.

Yours truly,

Jim Steiner
(st)

Jim Steiner

JS/1st:C-4B:CARB.com
enclosures

Corporate Headquarters
4930 Boylan Street
Bakersfield, California 93308
(805) 334-1102 FAX (805) 334-1440

METHOD 5 COMMENTS

- 2.1.5 Other filter supports must be approved besides the glass frit. The pressure drop across a glass frit is much too high and a frit is very difficult to clean. Glass frits are not suitable for some test methods, such as fluorides. Section 4.1.4 of Method 429 allows the use of a Teflon coated wire support or a Teflon frit. CARB allows the filter holder itself to be made of other materials, such as stainless steel and Teflon, so why not the filter support? Specific language should be added here to allow the use of a glass frit, a 316 stainless steel screen, a Teflon coated 316 stainless steel screen, or a Teflon frit in the method without requiring the approval of the Executive Officer.
- 3.1.5 There is a new grease out on the market which is insoluble in acetone or methylene chloride. It is called Krytox (per-fluoroalkylether and polytetrafluoroethylene) and it is made by DuPont. This should be added to the list of acceptable greases without having to get the approval of the Executive Officer.
- A statement should be included here to indicate that silicone grease cannot be used when methylene chloride is used to clean the impinger train of Method 5 since methylene chloride will dissolve the silicone grease.
- 3.2 A statement should be added here to specify the use of reagent grade methylene chloride.
- 4.1.3 I would like to have graphite ferrules added to the list of acceptable ferrules. We used these in place of stainless steel ferrules at high temperatures to avoid breakage problems associated with the different expansion coefficients of glass and steel at elevated temperatures.
- 4.1.4.1 A pretest leak check is required. And, yet, Section 4.1.4.2 makes a leak check optional once a new component is put into a sampling train. A leak check should be required before and after a component is changed out.

COMMENTS METHOD 5 (CONCLUDED)

4.2 This section implies that sample recovery of the probe and nozzle cannot take place on the stack. Steiner Environmental, Inc. (and probably other testers) has devised a closed system for cleaning the probe on the stack without sample loss or contamination. The sample bottle is connected directly to the end of the probe and the probe is brushed and rinsed directly into the sample bottle.

On large stacks, the probe may have to be lowered 100 feet or more to the ground, perhaps in a wind. The chance of breaking a probe liner and losing a sample increases with every trip up and down a stack. An option should be allowed to clean the nozzle and probe on the stack provided a closed sample recovery system is used. All other sample recovery should take place in a clean, wind free environment, such as a monitoring trailer or lab on site.

4.3.1.2 The sample bottle description should be changed from "Mason jars" to a glass bottle with Teflon lined screw cap to be consistent with the description in 2.2.3.



Steiner Environmental, Inc.

Comments Method 100
Mr. Jim Steiner
Steiner Environmental, Inc.

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METHOD 100 COMMENTS

2.2.8 This item still concerns me because the output from the data recorder is the heart of the test result.

The strip chart recorder should be specified as 0 to 100 divisions with 0.5 divisions, 10 inches wide, with no more than two channels per recorder. Offset paper (-10 to 0 to 100) should be used to quantitate negative drift. This will provide a clear written record of the test results. It also will show what events took place over the test time (e.g., zero, span checks, bias checks, offscale spikes, etc.). This avoids the problems associated with trying to read a small recorder output with several channels of overlapping traces. Strip chart recorders should be mandatory.

An automatic data acquisition can be used to eliminate the need to integrate the traces off a strip chart recorder, but it should not eliminate the need for the recorder itself. There is one test consultant who has a computerized data acquisition system in a trailer complete with a color monitor, but no strip chart recorders. I had a chance to observe this system in use. When doing an O₂ bias check (or any other calibration check) the system operator would observe the screen and watch the different bias values flash by. It was clear to me that the system operator was selecting the bias check result because he would strike a key and record a favorable result at an appropriate time, rather than have the computer integrate the entire bias check attempt and record a true value. Since there was no strip chart recording to see how the bias check was progressing with time, the test reviewer at the regulatory agency could only accept or reject the bias check based on the number reported by the data acquisition system. There is no doubt that a computer can provide a more accurate integration of a strip chart trace than the human eye, but it would be a mistake to eliminate the strip chart recording requirement and go solely with a data acquisition system.



Steiner Environmental, Inc.

Comments Method 436
Mr. Jim Steiner
Steiner Environmental, Inc.

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METHOD 436 COMMENTS

- 5.1.8 The procedure for the field blank train is different from the other Air Toxic test method field blank trains. There is no reason to leave the field blank train in the test area for a length of time equivalent to an actual Method 436 sampling period. If the train is completely sealed after the leak check, nothing is going to happen to it sitting there for up to 6 hours. Nothing is going to get in or out of the train during that time because it is sealed. Any contamination present in the train is a result of poor cleaning in the lab, which is what the field blank is supposed to show, not whether or not contamination occurred during some variable sitting period. This procedure should be changed to eliminate the need to have the train sit there for hours. This will reduce the cost of testing because one less set of glassware will need to be cleaned for a Method 436 test.
- 5.2 This section implies that the nozzle and probe cannot be cleaned on the stack. Most stack testers have a closed system for recovering the probe catch to insure no sample loss or no sample contamination occurs. Sometimes the sampling platforms are high up on stacks (>100 feet). There is a great deal of risk raising and lowering a glass lined probe, especially if the wind is blowing. If the probe is broken, the sample is invalid. Please clarify this section to allow for nozzle and probe cleaning on the stack.
- 9.4.1 Five days is insufficient time between sampling and storage in pH 2 acid solutions. Almost all our Method 436 air toxics tests follow this schedule:



Steiner Environmental, Inc.

Comments Method 436
Mr. Jim Steiner
Steiner Environmental, Inc.

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COMMENTS ON METHOD 436 (concluded)

Monday	Pack test equipment. Travel to test site. Set up test equipment. Take blanks.
Tuesday	Conduct 6-hour Test #1.
Wednesday	Conduct 6-hour Test #2.
Thursday	Conduct 6-hour Test #3.
Friday	Pack test equipment and samples. Return travel to office.
Saturday	Off.
Sunday	Off.
Monday	Pack samples for shipment to analytical lab.
Tuesday	Samples arrive at analytical lab.

The best that can be hoped for is that the sample arrives at the analytical lab seven (7) days after it was acidified. Time must also be allowed for the sample to sit at the lab prior to analyses as well. Five days is unworkable.



9/26/96

Legal

CERTIFIED MAIL
Return Receipt Requested
(20 copies)

August 29, 1996

California Air Resources Board
Board Secretary
P.O. Box 2815
Sacramento, CA 95812

RE: Proposed Amendment of Title 17, CCR Section 94105, 94107, 94114, 94135, 94141, 94143 and Proposed Adoption of Title 17, CCR Section 94161.
California Regulatory Notice Register 96, Volume 32-Z, 8/9/96, pp. 1523-1526.

Dear Sir:

Red Star Yeast & Products, a division of the Universal Foods Corporation, herewith submits its comments concerning the proposed actions. Specifically, Red Star proposes changes to Section 94114, Method 100, Procedures for Continuous Gaseous Emission Stack Sampling to address unique monitoring situations.

In the last two years, Red Star has been required to install continuous monitoring systems to measure the VOC content in the exhaust from its fermenters. This happened at Red Star's facilities in Wisconsin and Maryland that are classified as major VOC sources. Red Star has also installed a system (though not a full continuous emission monitoring system) at our Oakland, CA facility even though it is not a major VOC source. Through these experiences, Red Star has learned that monitoring fermentation exhaust is very different from monitoring "typical" sources such as combustion equipment. Red Star has had to either develop its own sampling system or work with independent suppliers to significantly modify their standard installation. Examples of how our situation is different include:

- We cannot use a filter at the sample probe. Entrained liquid which may contain dilute molasses could be pulled from the stack, through the filter, and into the sample system. As the heated sample system evaporates the moisture, dried molasses results. If a sample probe filter was installed, we could not blow out the dried molasses since it could no longer pass through the filter. In addition, there is very little particulate matter in the exhaust that would require a sample probe filter. To protect the instrument, there is a filter located at the end of the sample line.

RED STAR® YEAST & PRODUCTS

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CARB Board Secretary
August 29, 1996
Page Two

- We cannot "condition" the sample by reducing the moisture content. The VOCs we measure are ethanol and acetaldehyde. Both of these materials are very water soluble and will be removed during any moisture removal. In order to accurately measure the exhaust gas, Red Star must keep the system heated. Thus, any condensation creates problems.
- We cannot heat the sample probe. If this was done, the molasses in the entrained exhaust-air moisture would immediately dry and quickly plug the probe. To operate continuously, the sample probe must be unheated and lead into a knock-out pot that will remove the entrained liquid. The knock-out pot can be designed to be heated and readily accessible so that any dried molasses can be removed.

As these short examples illustrate, Red Star's monitoring situation is very different from those for which this method was developed. In one state where the continuous monitoring requirements are very inflexible, Red Star and the agency have had difficulty addressing the yeast-specific problems while still meeting the requirements. Therefore, Red Star suggests that the District allow substantial flexibility in its continuous monitoring requirements. If Red Star's Oakland facility should someday become subject to these requirements, we could then work with the District to assure a system that can meet your expectations and operate reliably. This flexibility could be accomplished either by

1. not requiring Method 100 for all installations where it is not required by rule; or
2. modifying the Method 100 requirements as follows:

Section 1.2 Applicability

Continuous gaseous sampling methods that employ the principle stated in Section 1.1 above, but differ in details of equipment and operation may be used, provided that the criteria set below are met or provided that the system is approved by the District based on alternate criteria.

Red Star appreciates the opportunity to comment on these proposed actions. Please don't hesitate to contact me at (410)631-5876 to discuss this further.

Sincerely,



Alan Bahl
Environmental Engineer