Through-the-Probe Criteria Pollutant Performance Audit Procedures

Volume V
Audit Procedures Manual for Air Quality Monitoring
QMB SOP Appendix E
Revision 9

Quality Assurance Section
Quality Management Branch
Monitoring and Laboratory Division

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<tr>
<td>Ranjit Bhullar, Manager</td>
<td>May 6, 2019</td>
</tr>
<tr>
<td>Quality Assurance Section</td>
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| Manisha Singh, Ph.D.     | May 6, 2019   |
| Chief, Quality Management Branch |           |

Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the California Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the California Air Resources Board’s Quality Assurance Section. Any functionally equivalent instrumentation is acceptable.
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THROUGH-THE-PROBE CRITERIA POLLUTANT PERFORMANCE AUDIT PROCEDURES

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E.1.0 INTRODUCTION

The California Air Resources Board (CARB) Quality Assurance Section (QAS) is responsible for conducting through-the-probe (TTP) performance audits. These audits are required annually on all continuous gaseous analyzers in the ambient air monitoring network measuring for criteria pollutants. TTP audits of gaseous analyzers monitoring for ozone (O3), carbon monoxide (CO), nitrogen dioxide (NO2), hydrogen sulfide (H2S) and sulfur dioxide (SO2) are conducted in accordance with U.S. Environmental Protection Agency (U.S. EPA) requirements (Title 40 Code of Federal Regulations, Part 58, Appendix A). These audits verify the accuracy of the gaseous analyzers and ensure the integrity of the entire sampling system.

E.1.0.1 SUMMARY OF METHOD

For TTP audits, an audit van is driven by QAS staff to the ambient air monitoring station. Audit vans contain the necessary instrumentation and equipment to allow the audit to be conducted under the same conditions as the station instruments. As depicted in Figure 1, various concentrations of pollutant gases are delivered from the van, through a presentation line, into the station sampling probe. QAS compares the results obtained from the station analyzer to the known values generated in the van to determine accuracy.

![Figure 1: Simplified depiction of an audit van and connection (through-the-probe) to an air monitoring station.](image-url)
The TTP audit methodology exposes deficiencies due to poor analyzer response, pollutant scavenging contaminants, and sampling system leaks. Deficiencies like these can cause the gaseous analyzers to fail an audit and possibly affect the quality of the ambient air data.

Figure 2 (below) shows an overview of the audit process including decision making and a simplified order of operations.

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**Figure 2**: Flowchart describing gaseous audit process.
### E.1.0.2 ACRONYMS AND DEFINITIONS

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<th>Definition</th>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>AIS</td>
<td>Audit Information System</td>
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<td>AQDA</td>
<td>Air Quality Data Action</td>
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<td>CAN</td>
<td>Corrective Action Notification</td>
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<tr>
<td>CARB</td>
<td>California Air Resources Board</td>
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<td>CE</td>
<td>Converter Efficiency</td>
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<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>H2S</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>ID</td>
<td>Inside Diameter</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LPM</td>
<td>Liters Per Minute</td>
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<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<td>NO2</td>
<td>Nitrogen Dioxide</td>
</tr>
<tr>
<td>NOX</td>
<td>Oxides of Nitrogen</td>
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<tr>
<td>NPAP</td>
<td>National Performance Audit Program</td>
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<tr>
<td>O3</td>
<td>Ozone</td>
</tr>
<tr>
<td>OD</td>
<td>Outside Diameter</td>
</tr>
<tr>
<td>PPB</td>
<td>Parts Per Billion</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts Per Million</td>
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<tr>
<td>PSI</td>
<td>Pounds per Square Inch</td>
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<td>QAS</td>
<td>Quality Assurance Section</td>
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<tr>
<td>SB #1</td>
<td>Superblend cylinder #1</td>
</tr>
<tr>
<td>SB #2</td>
<td>Superblend cylinder #2</td>
</tr>
<tr>
<td>SO2</td>
<td>Sulfur Dioxide</td>
</tr>
<tr>
<td>SOP</td>
<td>Standard Operating Procedure</td>
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<td>TTP</td>
<td>Through-The-Probe</td>
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<tr>
<td>U.P.</td>
<td>Ultra Pure air</td>
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<tr>
<td>UPS</td>
<td>Uninterruptible Power Supply</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>U.S. EPA</td>
<td>United States Environmental Protection Agency</td>
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<tr>
<td>VAC</td>
<td>Volts Alternating Current</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
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E.1.0.3 **INTERFERENCES**

The interferences associated with this method include factors that can alter the concentration of audit gases. Such changes can be the result of loss (through leak or reactivity) or contamination. Interferences can be minimized by following these guidelines:

- Take precautions to prevent the introduction of dirt or debris into the gas flow path. Ensure that the flow path’s interior surfaces are clean, including manifolds, tubing, fittings, presentation line connections, etc. Use leak checks as required to identify and correct any leaks found within the flow system.

- Do not jeopardize the integrity of the flow path by opening connections unnecessarily or leaving fittings open and uncapped.

- Take all steps to minimize sampling and analysis residence times, including tubing and other flow path component lengths and diameters, dead spaces, leaks, unnecessary path resistance (due to sharp bends, kinks, etc.).

- Follow procedures for purging the cylinder pressure gauges to remove interference caused by either bleeding from the regulators or reaction of the gases in the gauges and lines.

- Water vapor can result in false positive analyzer readings and inaccurate dynamic dilution concentrations. To minimize this interference, use only well-dried zero air.

**Ozone:** The ultraviolet (UV) absorption method for detecting ozone is subject to interference from environmental contaminants such as sulfur dioxide, nitrogen dioxide, nitric oxide, water, and volatile organic compounds (VOCs). The photometers in both the ozone standard and gas calibrator have been successfully tested for their ability to reject interference from most of these contaminants, and contain filters to assist in this process.

**Carbon Monoxide:** The carbon monoxide (CO) analyzer utilizes a 4.7µm band pass filter just before the infrared (IR) sensor which allows the instrument to react only to IR absorption in the wavelength affected by CO. An analysis and comparison of the measure and reference signals and extraction of the ratio between them is performed to reject the effects of interfering gases. More information regarding the theory of operation
for gas filter correlation analyzers can be found in the manufacturer’s operations manual.

E.1.0.4 PERSONNEL QUALIFICATIONS

All new CARB auditors undertake a one year training program that is documented and monitored by the Quality Assurance Section (QAS) manager. The training includes in-office reading and coursework, hands-on field experience conducting audits, and shadowing an experienced auditor for one year along with several in-field evaluations by the QAS manager.

U.S. EPA reviews CARB’s training program regularly for approval as an equivalent to U.S. EPA’s national certification and recertification courses. Auditors should be familiar with the regulations and guidance cited in the references section (E.8.0) prior to conducting any audits without supervision. Each auditor is expected to have a minimum level of on the job training and familiarity with the audit equipment prior to conducting the audit.

E.1.0.5 HEALTH, SAFETY, AND CAUTIONS

All personnel must follow any general health and safety guidelines as described by the facility where the audit is conducted. All audit equipment, including audit vehicles, should be used only for the purpose and in the manner described in this standard operating procedure (SOP) and in the appropriate operator’s manual. Gases from the equipment’s vent and exhaust ports may contain ozone or other harmful compounds, which are known to cause health effects. Care should be taken to vent excess test gas outside of enclosed spaces or buildings whenever possible. Vehicles should be parked away from the air monitoring station when possible, taking note of wind direction and vehicle exhaust. Vehicles and generators should be left running only when necessary.
E.1.0.6 EQUIPMENT AND SUPPLIES

The current TTP audit system uses the following equipment:

1. Audit van with 240 VAC land-line and AC generator(s).
2. Voltage stabilized line conditioner, with battery backup.
3. Compressed gas cylinders traceable to National Institute of Standards and Technology (NIST).
   a. High CO (approximately 80-90% of the audit van’s CO analyzer range).
   b. Low CO (approximately 10-20% of the audit van’s CO analyzer range).
   c. Ultra Pure (UP) zero air.
   d. Superblend #1 (SB #1): CO, NO, NOX, and SO2.
   e. Superblend #2 (SB #2): CO and H2S.
4. Zero air generator.
5. Gas calibrator with an O3 generator and photometer.
6. Ozone analyzer.
7. Carbon monoxide analyzer.
8. Oxides of Nitrogen analyzer (optional).

   **NOTE:** The Oxides of Nitrogen analyzer is used for trouble-shooting and diagnostic purposes only. Therefore, it is not calibrated on a regular basis.

9. Presentation line is 150 feet of 3/8 inch inside diameter (ID) Teflon® line with stainless steel over-braiding and rubber casing with one to two feet of Teflon® line attached to the end.
10. Rotameter and glass tee for bypass flow.
11. Electronic barometer and temperature sensors.

12. Electronic chart recorder to document audit van temperature and audit van gaseous concentrations.

13. Audit software to record and store audit data, calculate results, and generate a report upon completion of the audit.

E.2.0 START-UP PROCEDURES

E.2.0.1 AUDIT VAN EXTERIOR

Open the generator compartment door(s) and verify that the oil is in the "safe" operating range for each generator. Park the vehicle on level ground and shut off generator before checking generator engine oil. Unscrew the fill cap and wipe oil off the dip-stick. Screw the cap back on, remove it and check the oil level on the dip-stick. The oil level should be in the "safe" operation range between the FULL and ADD marks on the dip stick. Add the correct type of oil, as necessary.

E.2.0.2 AUDIT VAN INTERIOR

If additional warm-up of instruments is required prior to starting the generator(s), turn on equipment, in the following order: the voltage stabilized line conditioner with battery backup, the O3 analyzer, the CO analyzer, and the gas dilution calibrator. The voltage stabilized line conditioner with battery backup should operate these instruments for up to one and a half hours. It is not necessary to have zero air flow through the system during the warm-up period.

1. Make certain that the generator/land-line power source selector is in the appropriate position (see generator operations manual located in the vehicle or online).

2. Check that all circuit breakers are in "on" position.

3. Start generator(s) and warm up for five minutes prior to placing electrical load on generator(s). If 240 VAC is available, use land-line power source in place of generator(s). After power source is stabilized place the power control switch in appropriate position (See specific procedures in audit van.)
4. Turn "on" the power to the voltage stabilized line conditioner with battery backup (if not already on).

5. Turn "on" the power to the zero air generator (if not already on).

6. Turn "on" the power to the gas calibrator dilution unit (if not already on).

7. The following analyzers are used for audit(s) of the indicated gases:
   b. CO, H2S, and SO2: CO analyzer.
   c. NO2: O3, CO, and NO/NOX (optional) analyzers.

   **NOTE:** While the analyzers are in operation, the inside temperature of the van laboratory area should be maintained at 20-30 degrees Celsius (Quality Assurance Handbook Volume 2, Section 7.2.2). Check temperature routinely and adjust climate controls as necessary to minimize fluctuations. U.S. EPA suggests maintaining temperatures within a standard deviation of ±2 °C over a 24-hour period, in order to provide a stable temperature environment for the analyzer.

8. Turn "on" the power to the electronic chart recorder.

9. Allow a minimum warm-up time of one hour for the O3 analyzer and three hours for the CO and NOX analyzers.

10. For ozone audits, condition the van’s presentation line by running a high level of ozone thru the system prior to arriving at the station. H2S audits should also include pre-conditioning by flooding the system with H2S before arrival.
E.2.0.3 INITIAL AUDIT SET-UP

1. Place safety cones around van as necessary to ensure public and worker safety.

2. Verify that the zero air generator and all instruments required for the audit are operating properly and warmed up.

3. Ensure that the Superblend cylinder concentrations for the current quarter have been correctly entered into the gas dilution calibrator.

4. Have the station operator place the station’s data logger into audit or maintenance mode, or flag channels as appropriate.

4. Set the gas dilution calibrator to flow zero air through the van’s presentation line. Be sure the amount of zero air is sufficient based on the flow requirements for all analyzers in the sampling train and the station’s manifold configuration. Adjust the van’s bypass rotameter to 0.3-0.4 liters per minute (lpm), if necessary.

5. Attach the presentation line to the station’s gaseous probe inlet such that there is no entrainment of ambient air and bypass of at least one lpm of excess flow from the audit van. Use a rotameter to verify excess flow, as necessary.

   NOTE: Connections will vary from station to station. Common connections are: (1) through the calibration port on the station’s glass inlet and (2) using the glass tee available in the audit van. Whatever the connection, be sure there is at least one lpm of bypass, and that ambient air is not entrained into the system, causing dilution of audit gases. A maneghelic can be used to ensure that the system’s pressure has not changed.

6. Secure the presentation line to prevent movement during the audit.
E.2.0.4 VAN INSTRUMENT OPERATIONAL CHECK

If any of the analyzers fail to meet operational standards, consult the operator’s manual to review the analyzer’s test parameters and look up the troubleshooting guidelines. The operator’s manual, instrument operation manuals, and standard operating procedures are located on the van’s laptop and tablets in electronic form.

E.3.0 THROUGH-THE-PROBE AUDIT

E.3.0.1 OVERVIEW

To challenge the continuous gaseous analyzers measuring criteria pollutants, QAS conducts TTP audits by diluting known quantities of NIST traceable gases with up to 16 lpm of pure air to achieve concentrations of pollutants recorded at various levels. The TTP technique also serves to test the integrity of the entire sampling system. This is accomplished by introducing the diluted gas mixture into the monitoring station’s probe inlet, where it is drawn through the sampling system by the gaseous analyzers.

A gas calibrator with an O3 generator is used to control the dilution of O3 and high concentration gases from U.S. EPA protocol compressed gas cylinders containing the following pollutants: CO, NO, NOX, and SO2 (SB #1); or CO and H2S (SB #2). An ozone standard is used to determine a true O3 concentration which is used for auditing the station O3 analyzer. A CO analyzer is calibrated at a known high level (approximately 80-90% of the range) and checked for linearity at a lower level (approximately 10-20% of the range). The Zero response is calibrated using zero air generator, and a cylinder of Ultra Pure zero air is used to verify the purity of the zero air generator. The switching of calibration cylinders may be achieved by manually moving the quick connect fitting to each cylinder or through the use of solenoids, depending on the configuration of the audit van. After calibration, the CO analyzer is used to track the level of CO present in diluted gas samples. The CO analyzer response to the level of CO present in the diluted gas samples is used for auditing CO analyzers. The CO analyzer response also determines the true concentrations of all other pollutants present in the diluted sample, based on the ratios in the cylinder, which is used for auditing the respective analyzers.
E.3.0.2 DATA RETRIEVAL / RECORDING

The station instrument response for each sample gas delivered from the audit van (audit point) is noted from the data acquisition system used for collecting and storing the data-for-record. This data acquisition system may be a chart recorder, data logger, or computer.

NOTE: For each audit point, the station instrument response and van instrument display are both recorded on the Gaseous Audit Worksheet (Figure 3) and entered into the Audit Information System (AIS) software program. AIS references calibration information (such as the O3 line loss factor, O3 standard slope and intercept, and gas cylinder certification data) to calculate the van’s true response at each audit point. AIS then calculates the percent difference between the two responses for each audit point and compares it with the acceptance criteria to indicate results. At lower audit levels, the actual difference is also calculated for comparison.

Figure 3: QA Gaseous Audit Worksheet
With current technology, many monitoring stations are using electronic data loggers that store data at the site until collected on a set schedule. The data from the electronic data logger is handled in the same manner as the strip chart data, except that it is read directly from an electronic display at each audit level. The responses are recorded by the auditor on the audit worksheet and entered into the audit software program. Station meta-data, such as calibration information, flows, and manifold pressure (if applicable), are also recorded onto the audit worksheet.

**E.3.0.3 OZONE AUDIT PROCEDURE**

1. **Pre-Audit Zero Air:** Introduce zero air from the audit van to the station through the presentation line. When the van and station readings are stable (at least ten minute chart trace and stability at or below 0.5 parts per billion [ppb]), record the responses on the Gaseous Audit Worksheet and in AIS with the laptop. This will be the first zero audit point. Consult the CARB Audit Ranges document (Figure 4) for the currently targeted O3 audit points.

![ARB Audit Ranges, Revised 09-05-2018](image-url)

*Additional points added for 2017 based on EPA Technical Note: Guidance on using filtering Annual PE audit levels using Method Detection Limits, dated 05-03-2016.
Annual Performance Evaluations are as operational checks, and numbers (especially at lower levels) do not automatically validate the data.

![Trace Level Audit Points (ppm)](image-url)

*Audit points are designed only for reference for the Attachment requirements and do not reflect annual performance information in this CARB Audit Program. Always review guidance documents.

**Figure 4: CARB Audit Ranges and Audit Points**
2. Audit Points: Beginning with the highest O3 audit point, use the gas dilution calibrator to generate ozone quantities within the desired audit ranges (based on the U.S. EPA Audit Levels). When the van and station readings are stable, record the responses on the Gaseous Audit Worksheet and in AIS with the laptop or tablet. Continue to introduce new ozone audit points as listed in Figure 4, ensuring that the audit is completed within prescribed U.S. EPA audit levels.

3. Verify that all data entered into AIS matches the values on the Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.

4. Inform operator of preliminary audit results. In the event AIS identifies a “fail” result, refer to Section E.3.0.7 PERFORMANCE AUDIT FAILURES.

5. Proceed with the audit of other gaseous analyzers. If no further audits are to be conducted, follow Sections E.4.0 POST-AUDIT PROCEDURES and E.5.0 SHUT DOWN PROCEDURES – AUDIT VAN.

E.3.0.4 CARBON MONOXIDE ANALYZER VERIFICATION PROCEDURE

The audit van CO analyzer is used during a performance audit to analyze the amount of CO present in a diluted gas sample. Before and after each audit (of a gas other than O3), the CO analyzer is verified using a zero air generator, Ultra Pure air, and NIST-traceable CO gases at high and low concentrations. The pre-audit and post-audit CO analyzer responses are used in calculations to obtain true CO concentrations.

NOTE: If the CO analyzer response exceeds 0.25 ppm from the expected CO cylinder concentration for any of the verification points, the analyzer may require calibration or adjustment. Before calibration, be sure to troubleshoot, taking note of temperatures, pressures, flows, and warm-up conditions that may affect drift. Refer to the instrument specific operations manual for troubleshooting and calibration procedures.

Two multi-port glass manifolds in the audit van are used during a performance audit. One manifold is used to supply the van instruments with zero air, Ultra Pure zero air, and CO calibration gases, or diluted Superblend #1 gases. The additional manifold supplies the station with
zero air or diluted Superblend gases. A three-way valve is used to isolate the manifolds during verification of the van's CO analyzer.

1. The CO analyzer should be warmed-up based on the manufacturer's required warm-up period prior to calibration. The three-way valve should be in the “Sample” position prior to the audit.

2. If an O3 audit was conducted prior to the CO analyzer calibration, the O3 analyzer may either remain on or be turned off. If the O3 analyzer is turned off, readjust the flow to the bypass rotameter to 0.3-0.4 lpm.

3. Once the CO analyzer response to the zero air is stable, record the result on the Gaseous Audit Worksheet under “CO Calibration.” If the response to zero air is not within ± 0.25 ppm of zero, the CO analyzer may need to be calibrated or adjusted (refer to the “NOTE” above).

**NOTE:** Stability determination for CO analyzers can vary depending on model and settings defined in the analyzer's software. Stability values below 0.1 ppm are typical and auditors should record results when the stability reading is as low as possible, with a straight-line chart trace of ten minutes or more. Refer to the instrument specific operations manual (located on the QA laptops) for troubleshooting procedures and more details.

4. Attach the quick connect on the “Span” line to the High CO cylinder, or if equipped, switch the High CO solenoid switch to the “on” position. Switch the 3-way valve to the “Span” position. Open the valve on the High CO gas cylinder and adjust the pressure regulator on the cylinder to 25 psi. Readjust the bypass to 0.3 to 0.4 lpm, using the appropriate needle valve.

5. Once the CO response is stable, record the result on the Gaseous Audit Worksheet under “CO Calibration.” If the CO response is not within ± 0.25 ppm of the certified values listed on the High CO cylinder, the CO analyzer may need to be calibrated (refer to the CO analyzer operator's manual).

6. Disconnect the “Span” line from the High CO and connect the quick connect to the Low CO cylinder. Close the valve on the High CO cylinder. If the van is equipped with a solenoid, switch off the CO High, and then switch on the CO Low.
7. Open the valve on the Low CO gas cylinder and adjust the pressure regulator to 25 psi. Readjust the bypass flow to 0.3 to 0.4 lpm, if necessary.

8. When the “Low CO” response is stable, record the result on the Gaseous Audit Worksheet under “CO Calibration.”

9. Disconnect the “Span” line from the Low CO cylinder and connect the quick connect to the Ultra Pure air cylinder. Close the valve on the Low CO cylinder. If the van is equipped with a solenoid, switch off the CO Low then switch on the Ultra Pure. Open the valve on the Ultra Pure air cylinder and adjust the pressure regulator to 25 psi. Readjust the bypass to 0.3 to 0.4 lpm, if necessary.

10. When the CO response is stable, record the result on the Gaseous Audit Worksheet under “CO Calibration.”

11. Close the valve on the Ultra Pure and disconnect the span line. If the van is equipped with a solenoid, put the switch for the Ultra Pure in the “off” position.

12. Switch the 3-way valve back to the “Sample” position. Zero air should be flowing thru the system, to the station. Readjust the bypass to 0.3 to 0.4 lpm, if necessary.

13. Enter all values into the Audit Information System software, if not already done.

14. To continue with other gaseous performance audits, refer to the next Section.

E.3.0.5 FULL AUDIT PROCEDURE

NOTE: This procedure can be modified depending on the suite of analyzers present at the monitoring station. This procedure is designed for CO, NO2, and SO2 analyzers, or H2S analyzers, in operation at ambient air monitoring stations. If any of these analyzers are not present, corresponding audit points should be skipped. Consult Figure 4 for the targeted audit points.

NOTE: H2S audits must be conducted separately from NO2 and/or SO2 audits due to the use of different Superblend cylinders and the
interaction of the various gases. Use Superblend #2, which contains CO and H2S concentrations. The van’s presentation line should be conditioned by sampling H2S immediately prior to arriving at the station.

Consult with the station operator on their manifold setup and disconnect any analyzers that may be adversely affected by the introduction of H2S at higher levels.

1. The van gas calibrator should be introducing zero air thru the presentation line, to the station. Once stable, record the van and station readings into AIS.

2. Verification of the CO analyzer should have been performed as outlined in Section E.3.0.4. Consult Figure 4 for the targeted audit points.

3. Pressure regulator bleeding procedures: To bleed the Superblend pressure regulator, open the valve located at the gas dilution calibrator inlet for at least ten seconds prior to the audit. This procedure will evacuate any NO2 that has accumulated in the regulator and lines. After bleeding, adjust the regulator pressure to 25 psi.

4. Audit Points: Starting with the highest value audit point, introduce gas to the station by adjusting the target concentration and total flow on the gas dilution calibrator. Refer to the current CARB Audit Ranges document for the targeted audit points (Figure 4).

NOTE: Depending on the Superblend cylinder concentrations and mass flow controller (MFC) sizes, multiple parameters can be audited using a single CO value, based on the ratios in the cylinder. Adjustments may be needed to stay within the desired U.S. EPA audit level ranges. Approximate concentrations can be found on Figure 4, depending on the audit range.

NOTE: Depending on the Superblend cylinder concentration ratios, higher CO values may generate concentrations that may “over-range” analyzers in the station. Auditors should always be aware of the concentrations being generated and take precautions to avoid over-ranging station instruments when possible.
When the van and station analyzer readings are stable, record the responses from the van’s CO analyzer and the station’s analyzer(s) (or data logger) on the Gaseous Audit Worksheet and in AIS. The station’s instrument response for all audit points should be stable for a minimum of 10 minutes.

For ozone titration steps during an NO2 audit, refer to the gas dilution calibrator’s operating manual.

5. Audit Points (continued): Repeat Step 4 for the remaining audit points, ending with the lowest value audit point. When the station readings are stable for a minimum of 10 minutes, record the responses on the Gaseous Audit Worksheet and in AIS with the laptop.

6. Post-audit zero air: After all audit points are completed and results are checked, set the gas dilution calibrator to introduce zero air to the station. Zero air should continue to flow to the station throughout the post-audit CO verification procedure.

7. Post-audit CO verification procedure: Switch the 3-way valve to the “Span” position. Open the High CO calibration cylinder. Connect the “Span” line to the High CO regulator using the quick connect or switch the High CO to the “on” position. Readjust the bypass to 0.3-0.4 lpm, if necessary. When the High CO reading is stable, record the response on the Gaseous Audit Worksheet under “CO Calibration,” “Post-Audit CO Van Reading,” and in AIS with the laptop.

8. Repeat step 7 using the Low CO cylinder to obtain a post-audit Low CO value.

9. Repeat step 7 using the Ultra Pure cylinder to obtain a post-audit Ultra Pure value.

10. Close the valves on all of the cylinders.

11. Switch the 3-way valve back to the “Sample” position. After the CO value has been stable for approximately 10 minutes, record the station and audit zero air value in AIS.
12. Verify that all data entered into AIS match the values on the Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.

13. Inform the station operator of preliminary audit results. In the event AIS identifies a “fail” result, follow Section E.3.0.7 PERFORMANCE AUDIT FAILURES.

14. Continue to Sections E.4.0 POST – AUDIT PROCEDURES and E.5.0 SHUT DOWN PROCEDURES – AUDIT VAN.

E.3.0.6 ACTUAL AUDIT CONCENTRATION / CONVERTER EFFICIENCY DETERMINATION

1. Ozone: True O3 value for each audit point, for comparison with the station response, is calculated by applying a slope and intercept (derived from the quarterly CARB Standards Laboratory certification) to the audit van O3 analyzer’s net display reading, and multiplying by one minus the O3 quarterly line loss correction factor (see Section E.6.0.2).

\[
\text{True O3 (ppm)} = \left[ \left( \text{Display} - \text{Zero Response} \right) \times \text{Slope} + \text{Intercept} \right] \times \left( 1 - \text{Line Loss} \right)
\]

where

- Display = O3 analyzer’s display response (ppm)
- Zero Response = O3 analyzer’s zero response (ppm)
- Slope = O3 analyzer’s slope
- Intercept = O3 analyzer’s intercept
- Line Loss = O3 analyzer’s line loss correction factor

The percent difference between actual audit (true O3) concentration and the station response is determined by

\[
\text{Percent Difference} = \frac{\text{Station Response} - \text{Actual Audit}}{\text{Actual Audit}}
\]

For each audit point, this percent difference is compared against the control limit criteria. If the percent difference is greater than ±10 percent, the audit will result in a failure.
2. **Gases other than O3**: Actual concentrations for each gaseous pollutant except O3, at each audit point, are determined by multiplying a dilution ratio with the concentration value of the pollutant in the Superblend cylinder. The dilution ratio and audit level concentrations are determined using the following formulae:

Dilution Ratio =

\[
\frac{(\text{Van CO} - \text{Van Zero}) \times \text{CO Slope} + \text{CO Analyzer Intercept}}{\text{SB #1 or #2 CO Concentration Value}}
\]

Actual audit values for NO, NOX, SO2, H2S (in ppb) =

Dilution Ratio \times \text{SB #1 or SB #2 Concentration Value}

The percent difference between actual audit concentration and the station response is determined by:

\[
\text{Percent Difference} = \frac{\text{Station Response} - \text{Actual Audit}}{\text{Actual Audit}}
\]

For each audit point, this percent difference is compared against the control limit criteria. If the percent difference is greater than ±15 percent the audit will result in a failure.

3. **Converter Efficiency**: The converted NO2 concentration is used at each point to determine NO/NOX analyzer converter efficiency. The converter efficiency is calculated as follows:

\[
\text{Percent CE} = \frac{\Delta\text{NO} - \Delta\text{NOX}}{\Delta\text{NO}} \times 100
\]

where

\[
\text{CE} = \text{Converter Efficiency}
\]

\[
\Delta\text{NO} = ([\text{NO}] \text{ original} - [\text{NO}] \text{ remainder})/\text{NO Slope}
\]

\[
\Delta\text{NOX} = ([\text{NOX}] \text{ original} - [\text{NOX}] \text{ remainder})/\text{NOX Slope}
\]

Calculated converter efficiencies (for chemiluminescent analyzers) less than 96 percent or greater than 104 percent result in a failure.
4. **True NO2 Concentrations**: True ambient level concentrations for NO2 are calculated using the following formulae:

\[
\text{Van NO2} = \frac{\text{NO [O3 Off]} - \text{NO [O3 On]}}{\text{NO Slope}}
\]

\[
\text{Station NO2} = \left(\text{NOX [O3 On]} - \text{NOX Zero Average}\right) - \left(\text{NO [O3 On]} - \text{NO Zero Average}\right)
\]

### E.3.0.7 PERFORMANCE AUDIT FAILURES

1. In the event of a “fail” audit result, an investigation is necessary to determine the possible cause(s) of the failure. It may be necessary to inspect all aspects of the audit, beginning with the van operation and ending with the station operation.

   **NOTE:** If the cause for the failure is determined during any point in the investigation, resolve the problem (if possible) and resume the audit. If the source of the problem is from the station, the site operator should be notified of the “As Is” failure, and an “AUDIT ACTION ITEM NOTIFICATION” worksheet (Figure 5) should be filled out. If the cause of the failure is determined to be the audit van set-up, the problem should be resolved and the audit restarted. Delete the results of the first audit.

2. Beginning with the audit van, all instruments need to be checked to verify proper operation. This will include all of the following, unless the cause of the failure is discovered and resolved at any point during the investigation process.

   a. Is the airflow set correctly on the gas dilution calibrator? What values do the mass flow controllers indicate? Is the targeted gas value entered correctly for the appropriate audit point (including units)? Does the analyzer display correspond with the targeted level and range? Check the cylinder concentrations in AIS and the gas dilution calibrator. Are the appropriate valves and regulators open, with pressures sufficient for proper operation?

   b. Is the zero air generator operating correctly? Is there sufficient output pressure (40-45 psi) to maintain a constant pressure of 30-35 psi to the calibrator? Is the regulator pressure set at 30 psi? Is...
there sufficient pressure in the gas cylinder (at least 200 psi)? Is the by-pass rotameter set for a flow of 0.3-0.4 lpm? Is the correct gas port selected? Is the 3-way valve (SPAN/SAMPLE) in the correct position?

c. Are all lines correctly connected to the manifolds and/or probe line? Are the lines to the instruments connected? Are there any apparent leaks? Are the filters installed correctly and filter holders sealed? Is ambient air being entrained into the system and diluting the audit concentrations?

3. When these checks have been completed and all instruments checked for proper operation, the next step is to verify that the station is receiving enough flow to their inlet probe. This flow can be easily checked with a mass flow meter or rotameter. If there is not enough flow to the inlet probe, disconnect any booster pump that the station may be using. The van flow needs to be at least one lpm greater than the station flow requirement.

4. If the cause for the failure still cannot be determined, check the flow path of the audit gas from the station inlet probe to the back of the station instruments. Make certain to check all lines and in-line filters for leaks or breaks.

5. If the cause for the failure cannot be determined during this examination, remove the “Line” from the station inlet probe and connect it to the station’s instrument manifold (if present, otherwise proceed to step 6). Recheck the instruments for the proper response.

6. If the instrument still indicates a failure, remove the “Line” from the instrument manifold and check for the response at the back of the instrument using a glass tee and a bypass.

7. If the cause for the failed condition cannot be determined after a thorough investigation, take pictures of the audit set-up. The pictures should show how the “Line” is connected to the station’s inlet probe and the sampling system from the inlet probe to the instruments. Document all trouble shooting measures performed.

8. When the investigation is completed, proceed with an Air Quality Data Action (AQDA) Request or Corrective Action Notification (CAN) as described in Sections E.4.0.2 and E.4.0.3, if appropriate. If the cause
for the failed condition is determined and corrected, proceed with the scheduled gaseous audit.

9. An incomplete audit or audit failure may require rescheduling. Contact the QAS manager or audit scheduler as soon as possible to discuss options, make a determination, and initiate a re-scheduling process, if necessary.

Figure 5: Audit Action Item Notification Form
E.4.0 **POST-AUDIT PROCEDURES**

E.4.0.1 **COMPILING PRELIMINARY AUDIT RESULTS**

1. Auditors responsible for data entry and review should sign the completed Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.

2. Notify the operator of preliminary audit results. A copy of the report will be provided electronically after review, via email.

E.4.0.2 **AIR QUALITY DATA ACTION (AQDA) REQUEST**

AQDA Requests are issued when the audit reveals that the station’s analyzer(s) are not operating within federal critical criteria or CARB control limits. Refer to the SOP for Air Quality Data Action Requests (Volume V, Appendix AO) for guidance.

E.4.0.3 **CORRECTIVE ACTION NOTIFICATION (CAN)**

CANs are issued to document issues that may impact or may potentially impact data quality, completeness, storage, or reporting. Refer to the SOP for Corrective Action Notifications (Volume V, Appendix AN) for guidance.

E.5.0 **SHUT DOWN PROCEDURES – AUDIT VAN**

E.5.0.1 **INTERIOR**

1. After reviewing the audit report, log out of the AIS program and shut down the computer.

2. Turn off the power to the gas calibrator, zero air system, and applicable analyzers.

3. Turn off the power to the APC Smart Uninterruptible Power Supply (UPS) line conditioner.

4. Close the valves and regulators on all compressed gas cylinders.
5. After turning off all overhead lighting and climate controls, shut down the generator(s).

**E.5.0.2 EXTERIOR**

1. Disconnect the presentation line from the station inlet and inform the operator that the station's data logger can be put back on line.

2. Reel the "Line" into the audit van. Make certain the end of the "Line" is placed into the "Line" cradle, and lock the hose reel into position.

3. Secure the ladder and safety cones.

4. Remove the wheel chocks.

**E.6.0 AUDIT VAN CALIBRATION CHECKS AND PROCEDURES**

**E.6.0.1 QUARTERLY "O3 LINE LOSS" TEST START-UP**

The "O3 Line Loss" test is conducted quarterly to determine the actual O3 concentration being delivered to the station's inlet probe. By analyzing the O3 concentration before and after the "Line," it is possible to determine the actual amount of O3 loss attributed to the "Line." This loss percentage is used to correct for "true" O3, so as not to bias audit results.

1. Plug in the audit van land-line or start the generator.

2. Make certain the land-line/generator switch is in the correct position.

3. Turn on the power to the APC Smart UPS, zero-air generator, gas calibrator, O3 analyzer, and the chart recorder.

4. Make certain that the chart recorder is logging.

5. Record the date of the test, vehicle the test is being conducted in, and the name of the person conducting the test.

6. Make certain that all the above instruments are "ON" and operating properly.
E.6.0.2 QUARTERLY "O3 LINE LOSS" TEST

Two lines are used during the quarterly "O3 Line Loss" test. These are referred to as the "Inside" and "Outside" lines. For determination of the line loss, information is recorded on the O3 Line Loss Audit Worksheet (Figure 6).

![QA AUDIT WORKSHEET OZONE LINE LOSS](image)

Average % Difference = \[
\frac{\text{Ozone Loss } \%}{\text{at Each TP}} = \left(\frac{\text{Inside Line Ozone Response} - \text{Outside Line Ozone Response}}{\text{Inside Line Ozone Response}}\right) \times 100
\]

Average % Difference = \[
= \frac{\text{TP 1} + \text{TP 2} + \text{TP 3} + \text{TP 4} + \text{TP 5}}{5}
\]

Quarterly Line Loss = \[
\frac{\text{Current Quarter Line Loss} + \text{Previous Quarter Line Loss}}{2}
\]

Quarterly Line Loss % = 

Data recorded and verified by: __________________________

Manager’s Review: __________________________

Figure 6: O3 Line Loss Worksheet
INSIDE: Teflon® line (1/4 inch OD) from the instrument port of the rear manifold to the calibration port of the front manifold.

OUTSIDE: Stainless steel braided presentation line (150 feet long, 3/8 inch ID) with a needle valve, stainless steel tee, and one to two feet of Teflon® line (1/4 inch OD).

NOTE: The van also uses two glass manifolds for gas distribution to the van and station instruments. The "rear" manifold supplies audit gas concentrations to the station and a portion of the sample is supplied to the "front" manifold through a three-way valve which supplies the O3, NOX, and CO instruments.

1. Allow the zero-air generator, O3 analyzer, and the gas dilution calibrator (calibrator) to warm-up for at least one hour prior to conducting the "O3 Line Loss" test. The line should be conditioned by running a high concentration of O3 through the system. The length of conditioning time required varies, depending on line age/condition, humidity, the length of time passed since the last audit, etc., but should be no less than one hour. The calibrator should be configured to deliver 16 liters per minute of air flow.

2. Prepare the audit van presentation line. Remove the two-foot Teflon® line at the end of the presentation line, and attach the test equipment to the end of the presentation line.

3. With the "Outside" line connected to the front manifold, adjust the flow to the rotameter until a by-pass flow of 0.3-0.4 lpm is indicated. When the O3 analyzer has a stable zero, begin the Line Loss test.

4. Generate O3 with the calibrator for Test Point 1 (as in Figure 6). Allow sufficient time for a stable trace and record the O3 analyzer response under the "Outside Line" column.

5. Disconnect the "Outside" line and connect the "Inside" line. Readjust the by-pass flow if necessary. Allow sufficient time for a stable trace and record the O3 analyzer response under the "Inside Line" column.

6. Repeat steps 3 and 4, alternating between "Outside" and "Inside" for each of the remaining O3 Test Points. Allow sufficient time for stable traces and record each of the responses from the O3 analyzer.
7. Calculate the Quarterly O3 Line Loss using the following formulae:

\[
O3 \text{ line loss percent for each Test Point} = \frac{(\text{Inside Line Response} - \text{Outside Line Response}) \times 100}{\text{Inside Line Response}}
\]

Average percent difference = \[
\frac{\text{Test Point 1} + \text{Test Point 2} + \text{Test Point 3} (\ldots \text{etc})}{\text{# of Test Points}}
\]

Quarterly Line Loss percent = \[
\frac{\text{Previous Quarter Loss} + \text{Current Quarter Loss}}{2}
\]

**WARNING:** If the current quarter line loss exceeds 2.5%, repeat the O3 line loss test. Check for leaks and pressure issues. Condition the presentation line by running 0.500 ppm O3 through the line, if necessary.

8. Remove the O3 line loss test equipment from the presentation line. Reconnect the two-foot Teflon® line, and wind the presentation line back on the hose reel. Place the end of the "Line" in the hose cradle, and lock the hose reel in place.

E.6.0.3 **INSTRUMENT AND GAS RECERTIFICATION**

1. O3 analyzer and transfer standard – The CARB Standards Laboratory re-certifies the UV Photometer against a Standard Reference Photometer quarterly. The slope and intercept derived from the recertification are used in the calculation of audit van "True" O3 values.

2. Compressed Gases – The High CO, Low CO, and SB #1 cylinders are certified on an annual basis in accordance with the U.S. EPA National Performance Audit Program requirements. SB #2 cylinders are certified in accordance with manufacturer recommendations.
E.6.0.4 PREVENTATIVE MAINTENANCE

1. At the end of each quarter perform 90-day maintenance on all audit vans.

2. Replace particulate filters on all gaseous analyzers quarterly or as needed. Follow all manufacturer’s recommended maintenance schedules as outlined in the operator’s manuals.

3. Document test parameter functions on all gaseous analyzers quarterly or as needed.

4. Leak check all analyzers annually or as needed.

E.7.0 ADDENDUM – TRACE-LEVEL THROUGH-THE-PROBE-AUDIT

E.7.0.1 OVERVIEW

Trace-level analyzers are ultra-sensitive and designed to measure lower levels of gases than ambient-level analyzers. For CO, a trace-level analyzer typically ranges from 0 to 5 ppm, while an ambient-level analyzer ranges from 0 to 20 (or 50) ppm. For SO2, trace-level analyzers are typically 0 to 100 ppb, while ambient-level analyzers can range up to 500 ppb. The audit van CO analyzer is used during a performance audit to analyze the amount of CO or SO2 present in a trace-level diluted gas sample.

The audit procedures for trace-level audits are similar to “regular” audits with the following points of note:

- Superblend #1 CO concentrations are lower
- High and Low CO cylinder concentrations are lower
- Instrument warm-up periods are longer
- Temperature and pressure fluctuations may affect analyzer drift
- Exceedances of audit criteria at low audit levels do not automatically invalidate data
- Audit data is entered on a separate worksheet (refer to Figure 7) designed specifically for trace-level audit points and levels.
E.7.0.2 TRACE-LEVEL CARBON MONOXIDE ANALYZER VERIFICATION PROCEDURE

Before and after each audit, the trace-level CO analyzer is verified using a zero air generator, Ultra Pure air, and NIST traceable CO gases at concentrations of approximately 4 (High CO) and 1 (Low CO) ppm. The pre-audit and post-audit CO analyzer responses are used in calculations to obtain true CO concentrations.

NOTE: If the CO analyzer drift exceeds 0.25 ppm for any of the verification points the analyzer may require calibration or adjustment. Before calibration, be sure to troubleshoot, taking note of temperatures, pressures, flows, and (especially) warm-up conditions that may affect drift. Refer to the instrument specific operations manual for troubleshooting, adjustment, and calibration procedures.
Refer to Figure 4 for CARB Audit Ranges and Trace-Level Audit Points.

Refer to Section E.3.0.4, steps 4 through 14, for the CO analyzer verification procedure using trace-level High and Low CO cylinders.

E.7.0.3 TRACE-LEVEL CO AND SO2 AUDIT PROCEDURE

Refer to Section E.3.0.5 for the Trace-Level CO and/or SO2 Audit Procedure using the trace-level Superblend #1 cylinder.

E.8.0 REFERENCES


E.9.0

REVISION HISTORY (REVISION 9 [2019] VS. REVISION 8 [2015])

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