CALIFORNIA
AIR RESOURCES BOARD

Standard Operating Procedure for Performance Audits of Ozone Analyzers Using a Portable Ozone Transfer Standard

Volume V
Audit Procedures Manual for Air Quality Monitoring

QMB SOP Appendix C
Version 6.0

Quality Assurance Section
Quality Management Branch
Monitoring and Laboratory Division

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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 Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

PERFORMANCE AUDITS OF OZONE ANALYZERS
USING A PORTABLE OZONE TRANSFER STANDARD

TABLE OF CONTENTS

FIGURES

C.1.0 INTRODUCTION

Ozone audits are used to validate ambient air data collected at air monitoring stations. The Quality Assurance Section (QAS) of the California Air Resources Board (CARB) currently employs two possible methods of conducting ozone performance audits.

In the first method (see Volume V, Appendix E), a gas dilution calibrator and an ozone analyzer housed in an audit van are used to audit the ozone analyzer in the air monitoring station (station). The gas dilution calibrator is used to generate a known amount of ozone in the United States Environmental Protection Agency's (U.S. EPA's) required audit ranges, and this ozone concentration is then introduced into the station's inlet probe via the audit van's presentation line. The response of the station's ozone analyzer is compared to the concentration levels measured by the audit van's ozone analyzer and a percent difference is calculated.

In the event that the audit van cannot be used to perform the audit, a second method is employed utilizing a portable ozone transfer standard (transfer standard). This second method is the subject of this SOP.

C.1.0.1 SUMMARY OF METHOD

In this method, the transfer standard serves as both the generation and measurement device for ozone, and can be used in various configurations to audit the station's ozone analyzer. The use of different tubing configurations allows audits to be conducted through-the-probe, through the station's sample manifold, or direct to the back of the ozone analyzer as conditions at the station permit.

During the audit the transfer standard delivers the test gas to the station analyzer in one of the three configurations mentioned above. The output from the transfer standard is compared to the response of the station's ozone analyzer and a percent difference is calculated. An Air Quality Data Action (AQDA) or Corrective Action Notification (CAN) could result if data quality is determined to be impacted by deviations from control criteria.

The transfer standards are certified quarterly by CARB's Standards Laboratory using a U.S. EPA verified Standard Reference Photometer (SRP).

This standard operating procedure addresses the set-up and operation of the portable ozone transfer standard during performance audits of ozone analyzers.

C.1.0.2 ACRONYMS AND DEFINITIONS

Acronym	Definition
AQDA	Air Quality Data Action
CAN	Corrective Action Notification
CARB	California Air Resources Board
LPM	Liters per minute
NPAP	National Performance Audit Program
OD	Outside diameter
PPB	Parts per billion
PPM	Parts per million
PTFE	Polytetrafluoroethylene
QAS	Quality Assurance Section
QMB	Quality Management Branch
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
UV	Ultraviolet
U.S. EPA	United States Environmental Protection Agency
VAC	Volts Alternating Current
VOC	Volatile organic compounds

C.1.0.3 INTERFERENCES

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 photometer in the transfer standard has been successfully tested for its ability to reject interference from most of these contaminants, and contains filters to assist in this process.

C.1.0.4 PERSONNEL QUALIFICATIONS

The Quality Assurance Section (QAS) auditor should be familiar with the regulations and guidance cited in the references section (C.1.5) prior to conducting any ozone audits. The auditor is expected to have a minimum level of on the job training and familiarity with the audit equipment prior to conducting the audit.

C.1.0.5 HEALTH AND SAFETY

All personnel must follow any general health and safety guidelines as described by the facility where the audit is conducted.

The transfer standard should be used only for the purpose and in the manner described in this standard operating procedure (SOP) and in the instrument manual. Gas from the transfer standard's vent and exhaust ports may contain ozone, which is known to cause health effects. Care should be taken to vent excess test gas outside of enclosed spaces or buildings whenever possible.

C.1.1 EQUIPMENT AND SUPPLIES

The performance audit, utilizing the portable ozone transfer standard, requires the following equipment:

1. Currently certified ozone transfer standard (Teledyne T703U)
2. Varying lengths of Polytetrafluoroethylene (PTFE) Teflon tubing and fittings
3. Extension cord
4. Ozone transfer standard worksheet
5. Computer or tablet and related audit software
6. Rotometer, 0-5 liters per minute (LPM)
7. Multi-plug surge protector

C.1.2 PROCEDURES

C.1.2.1 OZONE TRANSFER STANDARD AUDIT PROCEDURE

1. Connect the transfer standard to a 110 volts alternative current (VAC) outlet. A surge protector should be used when possible.

2. Turn on the instrument and clear the SYSTEM RESET warning message. Leave the instrument in STANDBY mode.

3. Assess the conditions at the air monitoring station and determine the method of presentation to the site's ozone analyzer (through-the-probe, to the sample manifold, or to the back of the instrument).

   NOTE: If through-the-probe presentation will not be possible due to inaccessibility or some other reason, the reason and the method of presentation to the station's ozone analyzer must be noted on the audit report general site survey.

4. For presentation through-the-probe, make the following connections to the ports on the back of the transfer standard, see Figure 1 (for presentation to the sample manifold or to the back of the analyzer, proceed to step 5):

    a. Uncap the Dry Air In port.

    b. Connect one end of a Teflon presentation line of an appropriate length and diameter to the Vent port labeled “To Station” (bottom port on the back of the transfer standard). This will be the presentation line to the station’s probe inlet.

    c. Connect a separate piece of Teflon tubing to the Exhaust port and direct the other end outside the building if possible.

    d. Leave the Cal Gas Out port labeled “Vent” capped.

    e. Proceed to step 6.

Figure 1: Example tubing configuration for presentation through-the-probe using a length of 3/8” outside diameter (OD) tubing. In this example, venting of bypass flow will be accomplished at the connection to the station’s sample probe, so the “Vent” port is left capped.

5. For presentation to the station's sample manifold or to the back of the station's ozone analyzer, make the following connections to the ports on the back of the transfer standard, see Figure 2:

    a. Uncap the Dry Air In port.

    b. Connect one end of a Teflon presentation line of an appropriate length and diameter to the Vent port labeled "To Station" (bottom port on the back of the transfer standard). This will be the presentation line to the station's manifold or ozone analyzer.

    c. Connect a separate piece of Teflon tubing to the Exhaust port and direct the other end outside the building if possible.

    d. Connect a third piece of Teflon tubing to the Cal Gas Out port labeled "Vent" and direct the other end outside the building if possible. (If sufficient bypass will be vented from the station manifold or the connection to the station's analyzer, the vent tubing connection is not necessary and the port may remain capped.)

    WARNING: Incorrect venting of bypass flow will affect the total flow presented to the station and may introduce ambient air into the test path when the final connection to the station is made.

Figure 2: Example tubing configuration for presentation to the station's sample manifold using a length of ¼" OD Teflon tube. In this example, venting of bypass flow is accomplished through a second length of ¼" OD Teflon tubing connected to the "Vent" port of the transfer standard.

6. Generate 500 parts per billion (PPB) ozone to condition the audit tubing while the instrument is warming up. Generate ozone in the following manner (see Figure 3):

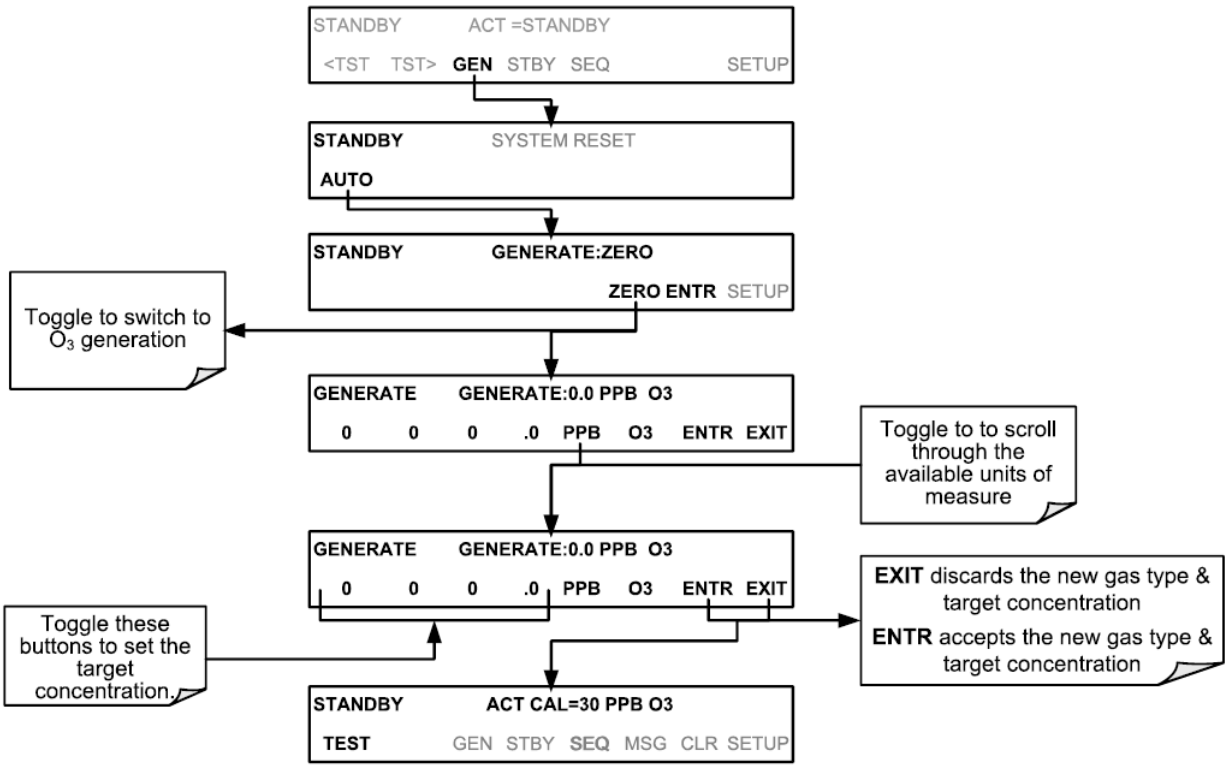

Figure 3: Generating test gas using the T703U.

NOTE: The transfer standard requires a minimum of 30 minutes of warmup and conditioning time before connecting to the station instrumentation and beginning the audit.

7. While the transfer standard is warming up and conditioning, complete the applicable fields of the portable ozone transfer standard audit worksheet (See Figure 5).

8. After a minimum of 30 minutes of warmup and conditioning time, generate 0 PPB ozone using the procedure outlined in step 6.

9. Connect the other end of the presentation tubing to the station's probe inlet, sample manifold, or to the back of the station analyzer.

NOTE: Proper venting of bypass flow should ensure that the station analyzer is not pressurized by the presentation of test gas, and that ambient air is not being entrained into the test path. The transfer standard generates test gas at approximately five LPM, so the excess bypass flow should be equal to the total flow minus the flow required by the station's analyzer(s). A 0-5 LPM rotometer can be used to measure bypass flow when all connections have been made.

10. When all necessary tubing connections have been made, perform an automated backpressure compensation calibration on the transfer standard in the following manner (See Figure 4):

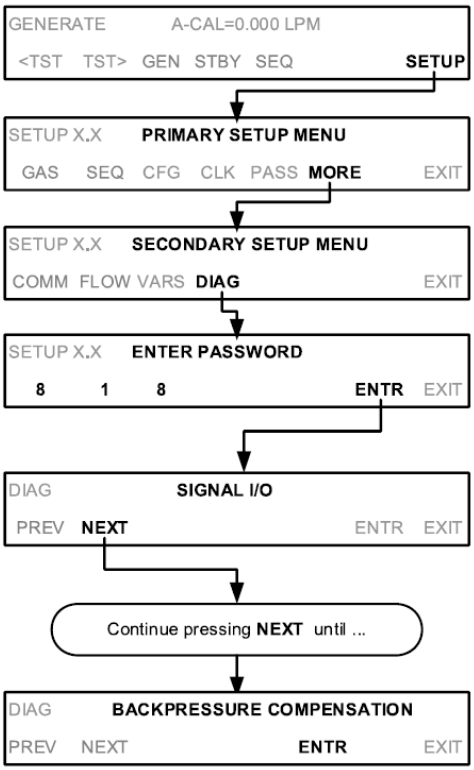

Figure 4: Performing a backpressure compensation calibration on the T703U.

NOTE: The backpressure compensation calibration accounts for any influence that the tubing configuration may have on the transfer standard's ozone photometer. Since the tubing configuration is likely to be different at each air monitoring station, the backpressure compensation calibration should be performed each time an audit is conducted.

11. When the backpressure compensation calibration is complete, the pump will stop and the screen will show PRESSURE COMP PASSED/FAILED: value (XXX.XX). Record this value on the audit worksheet (see Figure 5) before returning to the main menu and proceeding with the audit.

    NOTE: A passing value (between -200.00 and 200.00) indicates a successful compensation was completed and the value will be integrated into the transfer standard's calculation of ozone concentrations. If the backpressure compensation failed, there was not enough backpressure exerted on the photometer to warrant compensation. Proceed with the audit.

12. Generate 0 PPB ozone again using the procedure outlined in step 6.

13. Allow the zero to stabilize for at least 10-15 minutes.

14. After both the transfer standard and the station analyzer are stable, record the zero response for both instruments on the audit worksheet under "Pre-0". The transfer standard's reading must be converted from PPB to PPM by multiplying by 10^{-3}.

15. Move through the audit target concentration points using the same procedure outlined in step 6, leaving enough time between points for both instruments to stabilize. Record values on the audit worksheet under "AP1" through "Post-0".

    NOTE: QAS audit points are designed to fulfill requirements for the National Performance Audit Program (NPAP) and/or Annual Performance Evaluations as required in 40 CFR Part 58 Appendix A and current guidance documents.

16. When the audit is complete, disconnect the presentation line from the station and turn off the transfer standard.

17. Disconnect all Teflon lines and cap all open ports.

QA AUDIT WORKSHEET
PORTABLE OZONE TRANSFER STANDARD

Site Name: _____ Date: _____ POC: _____

Operator: _____ Audit Standard ID: _____

Auditors: _____ Inside Temp: _____ °C

Ozone Responses (ppm)							
Audit Point	Pre-0	AP 1	AP 2	AP 3	AP 4	AP 5	Post-0
Transfer Standard Ozone Target	.000	.130	.080	.055	.030	.015	.000
API T703U Display Reading							
Station Response							

Station data adjusted/corrected for zero? No ☐ Yes ☐

Station Instrument Information	
Manufacturer	
Model Number	
Serial/ID Number	
Instrument Range	
Calibration Date	* Daily 2/5: 1/yr * Bi-weekly 2/5: 1/6 mo.
Cal. Equip. Model & ID	
Cal. Equip. Cert. Date	Level 3: 1/6 mo. Level 1-2: 1/yr
Slope/Intercept	
Indicated Flow (lpm)	
In-line Filter Change Date	

Zero/Span performed:
☐ Daily
☐ Bi-weekly
☐ Other: _____

☐ Internal Zero/Span (IZS) **OR**
☐ Auto Calibrator (for zero/span checks):
Model: Serial/ID #:
Calibration Date: (1/yr.)

Audit done: ☐ Thru the Probe ☐ Direct to Instrument ☐ Thru Manifold

Backpressure Compensation Value: _____ PPB/dIn-Hg

Data recorded and verified by: _____ _____

California Air Resources Board

MLD/QAS-028 (Rev. 07-11-18)

Figure 5: Portable ozone transfer standard audit worksheet

C.1.2.2 FOLLOW UP AND CORRECTIVE ACTION

The information gathered on the audit worksheet can be entered into the laptop computer or tablet to generate the preliminary results and audit report (refer to Volume V, Appendix E). The report will include the percent difference between the audit transfer standard and the station analyzer. Based on U.S. EPA guidance, passing criteria for ozone analyzers is ± 10% at audit levels 3-5. However, audit levels 1 and 2 are subject to ±1.5 PPB difference or ±15% difference, whichever is greater. Annual performance audits are based on operational criteria, and exceedances (especially at lower levels) do not automatically invalidate the data. An AQDA or CAN could result if the analyzer is found to be operating outside of this criteria and data quality is determined to be impacted.

C.1.3 CERTIFICATION AND MAINTENANCE

The ozone transfer standards are submitted to the Standards Laboratory on a quarterly basis for recertification and are certified against a U.S. EPA SRP. This includes a verification that the new certification slope does not differ by more than ±1% from the previous certification and that the standard deviation of the slope of the last six certification equations is less than 1.5%.

Operational diagnostic values are checked regularly for deviations from manufacturer's specifications. Troubleshooting and maintenance are performed on an as-needed basis.

C.1.4 CHANGES FROM PREVIOUS SOP

Several new sections were added to the Version 6.0 of this SOP including Summary of Method, Acronyms and Definitions, Interferences, Personnel Qualifications, Health and Safety, Follow up and Corrective Action, and References. The audit procedure section was edited to include more details and to reflect the section's use of new audit equipment, the Teledyne API T703U. The Certification section was also edited to reflect changes in Standards Lab passing criteria for ozone transfer standards and to include information on equipment maintenance.

C.1.5 REFERENCES

EPA Quality Assurance Handbook for Air Pollution Measurement Systems: "Volume II: Ambient Air Quality Monitoring Program" EPA-454/B-17-001, (January 2017): https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/Final%20Handbook%20Document%201_17.pdf

40 CFR Appendix D to Part 50 – Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method): https://www.ecfr.gov/cgi-bin/retrieveECFR?gp=&SID=0f3bfa16342b3e5b858743bbbbdcfa4f&r=PART&n=40y2.0.1.1.1#ap40.2.50_119.d

Teledyne API User Manual: "Models T703 and T703U Photometric O_3 Calibrator" 07223E DCN7334, (August 2016): http://www.teledyne-api.com/prod/Downloads/07223E%20-%20MANUAL,%20T703-T703U.pdf

CARB Air Monitoring Quality Assurance Manual-Volume V: Audit Procedures for Air Quality Monitoring, "Appendix C: Performance Audit Procedures for Ozone Analyzers Using a Portable Ozone Transfer Standard" Version 5, (September 2008): https://www.arb.ca.gov/aaqm/qa/qa-manual/vol5/v5apxc.pdf

CARB Air Monitoring Quality Assurance Manual-Volume V: Audit Procedures for Air Quality Monitoring, "Appendix E: Performance Audit Procedures for Through-the-Probe Criteria Pollutant Audits" Version 8, (July 2017): https://www.arb.ca.gov/aaqm/qa/qa-manual/vol5/v5apxe.pdf