

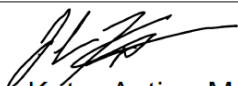



Standard Operating Procedure for
Performance Audits of Ozone Analyzers
Using a Portable Ozone Transfer Standard

Volume V
Audit Procedures Manual for Air Quality Monitoring

QMB SOP Appendix C
Revision 7.0

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 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.

Performance Audits of Ozone Analyzers Using a Portable Ozone Transfer Standard

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Performance Audits of Ozone Analyzers Using a Portable Ozone Transfer Standard

Acronyms and Definitions

Acronym	Definition
AIS	Audit Information System
AQDA	Air Quality Data Action
AQS	Air Quality System (U.S. EPA database)
CAN	Corrective Action Notification
CARB	California Air Resources Board
CFR	Code of Federal Regulations
LPM	Liters per minute
NAAQS	National Ambient Air Quality Standard
NIST	National Institute of Standards and Technology
O ₃	Ozone
PPB	Parts per billion
PQAO	Primary Quality Assurance Organization
PSIG	Pounds per square inch gauge
QA	Quality Assurance
QAS	Quality Assurance Section
QC	Quality Control
QMB	Quality Management Branch
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
Volume V	Air Monitoring Quality Assurance Manual (CARB)
ZAG	Zero Air Generator

C.1.0 **Introduction**

Ozone (O₃) 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 (refer to the Air Monitoring Quality Assurance Manual (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) 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 measured by the audit van's ozone analyzer and a percent difference is calculated.

In the event 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 Standard Operating Procedure (SOP).

C.2.0 **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 directly 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. While the transfer standard contains a filtration system to generate zero air from ambient air surrounding the instrument, a portable zero air generator (ZAG) should be used whenever possible as the source of zero air during ozone audits.

To compute the results of the multi-point audit, the output ozone concentration 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.

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

C.3.0 Interferences

The ultraviolet absorption method for detecting ozone is subject to interference from environmental contaminants such as sulfur dioxide, nitrogen dioxide, nitric oxide, water (high relative humidity), and volatile organic compounds (VOC). 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. Interferences by these contaminants can be further mitigated by using a portable ZAG as the source of zero air during audits.

Additional precautions against interferences should be taken as outlined in Volume V, Appendix E: *Through-the-Probe Criteria Pollutant Performance Audit Procedures* (Refer to References, Section E.3.0).

C.4.0 Personnel Qualifications

All new CARB auditors undertake a one-year training period. The training includes in-office reading and coursework, hands-on field experience conducting audits, and shadowing an experienced auditor for one year along with 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 of this SOP 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(s).

The U.S. EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Quality Monitoring Program (January 2017) is considered required reading prior to conducting audits. Additionally, auditors should be familiar with the Field Operation Manual for all audit equipment and analyzers being audited.

NOTE: A station operator familiar with the equipment must be present during the entire audit to perform the required manipulations of the equipment, data loggers, and sensors, as needed. Auditors should check for proper operating conditions before modifying equipment or accessing instrument software in any way.

C.5.0 Health, Safety, and Cautions

All personnel must follow any general health and safety guidelines as described by the facility where the audit is conducted. Audit equipment, including the ozone transfer standard and portable ZAG should be used only for the purpose and in the manner described in this SOP and in the instrument manual.

Gas from the transfer standard's vent and exhaust ports may contain ozone, which is known to cause adverse health effects. Care should be taken to vent excess test gas outside of enclosed spaces or buildings whenever possible.

Falls from portable ladders are one of the leading causes of occupational fatalities and injuries. Appropriate safety precautions must be taken and auditors should be familiar with, and trained on, proper ladder usage. Care must be taken when accessing probes on station rooftops or towers. All equipment being audited should be easily and safely accessible.

C.6.0 Equipment and Supplies

A performance audit utilizing the transfer standard requires the following equipment:

- Currently certified ozone transfer standard (Teledyne T703U)
- Portable ZAG (Teledyne 751H)

- Glass or Teflon® tee with varying lengths of pre-conditioned Teflon® tubing, fittings, and appropriately-sized wrenches
- Ozone audit worksheet
- Computer or tablet and related audit software
- Rotometer, 0-5 or 0-10 liters per minute (LPM)
- Extension cord and multi-plug surge protector

C.6.1 Maintenance and Certifications

The ozone transfer standards used by QAS are submitted to the CARB Standards Laboratory on a quarterly basis for recertification against a U.S. EPA Standard Reference Photometer (SRP). This includes a verification that the new certification slope does not differ by more than $\pm 1\%$ from the previous certification and that the standard deviation of the slope of the last six certification equations is less than 1.5%. The slope and intercept derived from the recertification are used in the calculation of the audit "True" O₃ values.

Operational and diagnostic values are checked regularly for deviations from manufacturer's specifications. Troubleshooting is performed as needed and maintenance is performed in accordance with the procedures outlined in Volume V, Appendix AL: *Maintenance Procedures for Audit Equipment*.

C.7.0 General Audit Procedures

The targeted ozone points used in audits conducted by QAS must fall within ranges set by the criteria outlined below and are also defined in the United States Code of Federal Regulations (CFR), specifically 40 CFR Part 58, Appendix A. Using these criteria, the audit point targets for auditing within the CARB Primary Quality Assurance Organization (PQAO) were identified. Auditing at additional levels is encouraged and is performed by QAS during ozone audits.

- One point must be within two to three times the method detection limit of the instruments within the PQAO network.

- The second point will be less than or equal to the 99th percentile of the data at the site or the network of sites in the PQAO or the next highest audit concentration level.
- The third point can be around the primary National Ambient Air Quality Standard (NAAQS) or the highest 3-year concentration at the site or the network of sites in the PQAO.

Additional details on the selection of audit ranges and how audit target levels are determined can be found in Volume V, Appendix E, Section E.8.0. The current audit point targets can be found on the most recent Quality Assurance (QA) Audit Worksheet for Ozone Audits (see Figure C-1).

**QA AUDIT WORKSHEET
OZONE AUDIT**

Site Name: _____ Audit Date: _____ POC: _____

Operator: _____ Audit Standard Model: _____ ID: _____

Auditors: _____ Van: _____ Backpressure Compensation Value: _____
(Transfer Standard) PPE/Std/Hg

Audit done: Thru the Probe Direct to Instrument Thru Manifold

Station data adjusted/corrected for zero? No Yes

Magnahelic reading (station)

Pre: _____ Shelter Temp: _____ °C
 During: _____ Controlled? No Yes
 Post: _____ Last Verif Date: _____

Ozone Responses (ppm)

Audit Point	Pre-Zero	AP 1	AP 2	AP 3	AP 4	AP 5	Post-Zero
Audit Ozone Target	0.000	0.130	0.080	0.055	0.015	0.005	0.000
Audit Display Reading							
Station Response							

Station Instrument Information

Manufacturer & Model: _____ Calibration Date: _____
* Daily ZS: 1yr
 * Weekly ZS: 18 mo.

Serial / ID Number: _____

Instrument Range: _____ Calibration Standard Model & ID: _____

Slope / Intercept: _____ / _____ Calibration Standard Certification Date: _____
Level 1: 18 mo.
 Level 1-2: 1yr

Indicated Flow (lpm): _____

In-line Filter Change Date: _____

Span & 1-pt QC Targets: Span 1-pt QC

Internal Zero/Span (IZS) **OR**

Auto Calibrator (for QC and zero/span checks):

Zero/Span frequency: _____

1-pt QC check frequency: _____

Last Zero- Air check date: _____

Data recorded and verified by: _____

California Air Resources BoardMLD/QAS-028 (Rev. 12-04-2020)

Figure C-1: Quality Assurance Audit Worksheet for Ozone Audits

In addition to evaluating the performance of the ozone analyzer at the air monitoring station, the audit should include an assessment of the following items:

1. Station maintenance records and logbooks for completeness.
2. Calibration and instrument information, which must be documented on the audit worksheet and in the Audit Information System (AIS). Refer to Section C.7.1 for more information.
3. Siting and residence time. Procedures for assessing siting and residence time can be found in Volume V, Appendix AE: Performance Audit Procedures for Conducting a Site Survey.

C.7.1 Station Data Retrieval / Recording

The station instrument response for each ozone concentration (audit point) delivered from the transfer standard should be noted from the data acquisition system used for collecting and storing the station's data-for-record. This data acquisition system may be a chart recorder, data logger, or computer. With current technology, many monitoring stations are using electronic data loggers that store data at the station, 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 are 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.

For each audit point, the station instrument response and transfer standard instrument display are both recorded on the QA Audit Worksheet for Ozone Audits (Figure C-1) and entered into the AIS software program. AIS references calibration information (such as the ozone transfer standard's slope and intercept) to calculate the true response of the transfer standard at each audit point. AIS then calculates the percent difference between the true and station 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.

C.7.2 Ozone Audit Procedures

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

NOTE: Through-the-probe is the desired method. 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.

2. Connect a short piece of tubing to the "DRAIN" port of the ZAG and direct this tubing to a receptacle that can catch any moisture that may be expelled during the instrument's use.
3. Connect a piece of tubing from the output port of the ZAG to the ZERO AIR IN port on the transfer standard. The transfer standard's DRY AIR IN port should be capped. Power on the ZAG.
4. Wait for the dewpoint light to turn green, indicating that it is producing clean dry air.

NOTE: When connecting an external source of zero air to a T703U with an internal zero air pump installed, the zero air pump should be disabled. In the QAS audit default configuration, the "ZA_PUMP_ENABLE" variable should be set to OFF (refer to the User Manual for the T703U: Pneumatic Connections, Zero Air In Section).

5. Adjust the output pressure of the ZAG to 30 pounds per square inch gauge (PSIG). This is the normal operating pressure. The ZAG should not be operated with an unrestricted flow.
6. For presentation through-the-probe, make the following connections to the ports on the back of the transfer standard; see Figure C-2 for an example of these connections (note: for presentation to the sample manifold or to the back of the analyzer, skip to step 9):
 - a. Connect one end of a 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.

- b. Connect a separate piece of tubing to the EXHAUST port and direct the other end outside the building if possible.
- c. In most cases, leave the CAL GAS OUT ports capped, maximizing output pressure to the station. In this configuration, venting of excess presentation gas, or bypass flow, can be accomplished at the connection to the station's sample probe.
- d. Proceed to step 8.



Figure C-2: Example tubing configuration for presentation through-the-probe using a length of 3/8" outside diameter tubing

7. 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 C-3 for an example of these connections:
 - a. Connect one end of a 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.

- b. Connect a separate piece of tubing to the EXHAUST port and direct the other end outside the building if possible.
- c. Connect a third piece of tubing (less than 2 meters long) to the CAL GAS OUT port labeled "Cap or <2m 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.

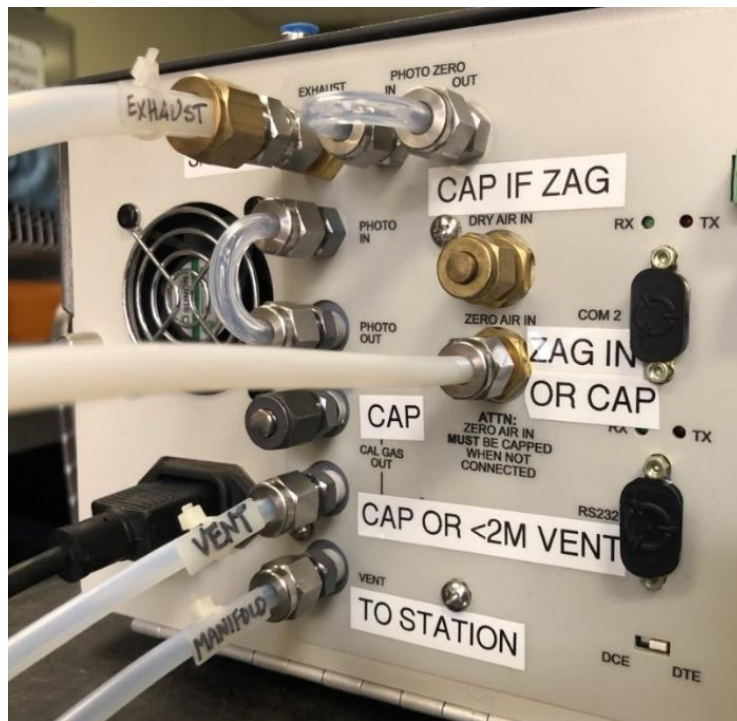


Figure C-3: Example tubing configuration for presentation to the station's sample manifold using a length of ¼" tubing. In this example, venting of bypass flow is accomplished through a second length of ¼" tubing connected to the "VENT" port.

8. Connect the T703U to a 110 Volts, Alternating Current outlet. A surge protector should be used when possible.
9. Turn on the instrument and clear the SYSTEM RESET warning message.
10. Generate 400 parts per billion (PPB) ozone to condition the audit tubing while the instrument is warming up.

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.

11. While the transfer standard is warming up and conditioning, complete the applicable fields of the portable ozone audit worksheet (See Figure C-1).
12. After the warmup and conditioning time is completed, generate 0 PPB.
13. Connect 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 liters per minute (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.

14. When all necessary tubing connections have been made, perform an automated backpressure compensation calibration on the transfer standard: Ensure the instrument is in Standby Mode, then navigate to the Utilities > Diagnostics > Back Pressure Compensation Menu, and press the Calibrate button.

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.** 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 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, troubleshoot as needed to find and remedy the source of additional backpressure, and run the compensation again. Possible adjustments could include using a larger diameter presentation line, or a shorter piece of tubing.

15. Generate 0 PPB ozone again and allow time for stabilization (typically 10-15 minutes).
16. 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".
17. Move through the audit points from highest to lowest concentration, leaving enough time between points for both instruments to stabilize. Record values on the audit worksheet under "AP1" through "Post-0".
18. When the audit is complete, disconnect the presentation line from the station and turn off the transfer standard.
19. Turn off the ZAG. In preparation for transport, do the following:
 - a. Wait approximately 1 minute after turning off the ZAG.

- b. Turn on the ZAG. The water drain valve will switch into the open position and vent any accumulated water through the water drain. (Standing water will cause corrosion.)
- c. Turn the ZAG off.

20. Disconnect all lines and cap all open ports.

21. The information gathered on the worksheet must be entered into AIS on the computer or tablet to generate the preliminary results and audit report. Additional details on compiling results and creating reports can be found in Volume V, Appendix E: *Through-the-Probe Criteria Pollutant Performance Audit Procedures* (Refer to References, Section E.9.1).

C.7.3 Troubleshooting Performance Audit Failures

In the event of a “fail” audit result after assessing all audit points, an investigation should be made as time permits to determine the possible cause(s) of the failure. It may be necessary to inspect all aspects of the audit, beginning with the transfer standard operation and hookup, and ending with the station operation.

If the cause for the failure is determined during any point in the investigation, resolve the problem (if possible) and initiate another audit. If the source of the problem is from the station, the station operator should be notified of the failure. If the cause of the failure is determined to be the audit set-up, the problem should be resolved, and the audit restarted. More information on troubleshooting failing audit results can be found in Volume V, Appendix E: *Through-the-Probe Criteria Pollutant Performance Audit Procedures* (Refer to References, Section E.8.7).

C.8.0 Data Management and Records

Always use the most recent audit worksheets, which are available on QA audit laptops and online in the QAS SharePoint folder. Audit Worksheets must be filled out carefully, using ink (no pencil) with legible characters and numbers. There must be no erasures, alterations, or correction fluid. Errors must be crossed-out with a single line, dated and initialed. Notes are to be made on any exceptional events or conditions that may

influence the data, the equipment, or routine operation of the sampler during the audit. Audit Worksheets and Preliminary Audit Reports will be reviewed by a minimum of two people, including management, before finalization of the audit.

C.8.1 Audit Data

1. Review the Audit Worksheet for completeness and accuracy, then sign it. Verify that all audit steps are complete.
2. Input data from the Audit Worksheet into AIS to generate results and a preliminary report. Review AIS for any questions or data that is not on the Audit Worksheets (such as verification of the most recent AQS information). The second auditor (if present) should review and verify that the Audit Worksheet and AIS entries match.
3. Station maintenance records and logbooks should be reviewed for completeness.
4. Notify the operator of preliminary audit results and any necessary follow up actions. Forward a copy of the preliminary report to the operator and/or their supervisor upon returning from the field.

C.8.2 Audit Information System

AIS is used by QAS to manage data and site information collected during performance evaluations of air monitoring stations throughout the state. More information can be found in Volume V, Appendix AK: *Using the Audit Information System* (Refer to References; Section C.11.0).

C.8.3 Audit Data Calculations

After data is entered into AIS, actual audit concentrations and other values can be calculated. AIS performs these calculations using information from the selected standards file.

True O₃ concentration 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 transfer standard's display reading.

$$\text{True O}_3 \text{ (ppm)} = (\text{Display} * \text{Slope}) + \text{Intercept}$$

where:

- Display = transfer standard's display response (ppm).
- Slope = value provided on certification.
- Intercept = value provided by certification.

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

$$\text{Percent Difference (\%)} = \frac{[(\text{Station Response} - \text{Actual Audit}) / \text{Actual Audit}] * 100}{}$$

Refer to Section C.9.1 and C.9.2 for passing criteria, interpretation of results, and follow-up and corrective actions.

C.9.0 Quality Assurance and Quality Control

Quality control (QC) includes establishing specifications or acceptance criteria for quality characteristics of the monitoring/analytical process, assessing procedures used in the monitoring/analytical process to determine conformance to these specifications, and taking any necessary corrective actions to bring them into conformance.

This section describes the most important performance conditions that are required to determine the outcome of the audit. It includes criteria for QC results and actions required if QC results are not within limits/criteria (issuance of an AQDA request or CAN), and procedures for reporting QC data and results.

C.9.1 Limits and Criteria

The information gathered on the Audit Worksheet can be entered into the laptop computer or tablet to generate the preliminary results and Preliminary Audit Report. 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 $< \pm 10\%$ at audit levels 3 to 10. However, audit levels 1 and 2 are subject to ± 1.5 PPB difference or $\pm 15\%$ 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 these criteria and data quality is determined to be impacted.

C.9.2 Corrective Actions

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

AQDA requests are issued when the audit reveals that the station's monitor(s) are not operating within federal critical criteria or critical CARB control limits. Additional guidance on AQDA requests can be found in Volume V, Appendix AO: *Air Quality Data Action Request*.

C.10.0 **Revision History**

Subject	Revision 6.0 (2018)	Revision 7.0 (2022)
New or Revised Sections	<ul style="list-style-type: none"> • Summary of Method • Acronyms and Definitions • Interferences • Personnel Qualifications • Health and Safety • Follow up and Corrective Action • References 	<ul style="list-style-type: none"> • General Audit Procedures (edited and subsections added) • Data Management and Records (includes three new subsections) • Quality Assurance and Quality Control (includes information formerly in another section)
New Equipment	Reflects equipment change from Teledyne API 401 to the T703U	Incorporates the use of a portable ZAG (Teledyne API 751H)
Calibration and Audit Points	Revised figure of QA Audit Worksheet (new target values)	Revised figure of QA Audit Worksheet (new target values)
Audit Procedures	<ul style="list-style-type: none"> • Detail added to procedure including three possible presentation methods • Added figures to procedure section to show sequence of commands for audit equipment 	<ul style="list-style-type: none"> • Incorporates the use of a portable ZAG into setup and audit procedures • Removed figures which depict outdated audit equipment software • Expanded to include subsections: Station Data Retrieval/Recording, Ozone Audit Procedures, Troubleshooting Performance Audit Failures
Certification and Maintenance	Edited to reflect changes in Standards Laboratory passing criteria and to include equipment maintenance information	Edited and relocated as a subsection to Maintenance and Certifications
References	Added reference section	Updated reference section

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