



COLORADO
Department of Public
Health & Environment

Air Pollution Control Division

Technical Services Program

APPENDIX GM6

Standard Operating Procedure for the Determination of
Ozone in Ambient Air

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Standard Operating Procedure for the Determination of Ozone in Ambient Air

1 SCOPE AND APPLICABILITY

This standard operating procedure (SOP) document describes the procedures used by members of the Air Pollution Control Division (APCD) Technical Services Program (TSP) to operate continuous monitoring ozone (O₃) analyzers at state of Colorado, Department of Public Health and Environment (CDPHE) air quality monitoring sites. This includes analyzers at State and Local Air Monitoring Stations (SLAMS), special purpose monitoring (SPM) and NCore monitoring stations. The CDPHE uses the Teledyne Air Pollution Instruments (TAPI) 400A, 400E and T400 analyzers in its air monitoring network and this SOP covers all these analyzers. These procedures are a supplement to APCD's Quality Assurance Project Plan (QAPP), the latest information published in the Code of Federal Regulations CFR), and the Operator's manual for TAPI 400A, 400E and T400 analyzers.

1.1 Introduction

Ozone, a colorless gas, has both beneficial and harmful effects on human health and the environment. Ozone naturally occurring in the upper atmosphere protects humans against skin cancer caused by ultraviolet radiation from the sun. But ozone resulting from human activity at or near ground level is the principal constituent of smog, which adversely affects respiratory health, agricultural crops, and forests.

Ozone in smog is formed by sunlight reacting with oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) discharged into the air from gasoline vapors, solvents, and fuel combustion products. The many sources of NO_x and VOCs include large industrial plants, gas stations, and motor vehicles. Atmospheric conditions frequently transport precursor gases emitted in one area to another where the ozone-producing reactions actually occur.

1.2 Method Overview

The method for the determination of ozone by ultraviolet (UV) analysis has been widely used for several decades. The lower detection limit (LDL) is defined in [Table B-1](#) of the Code of Federal Regulations, Title 40, Subpart B, Section 53.20, or, in the shorthand format used hereafter, 40 CFR 53.20. For ozone analyzers the LDL is 0.010 parts per million (ppm). For reference, the ozone standard established in 2008 is the three-year average of the fourth-highest 8-hour average not to exceed 0.075 ppm (40 CFR 50.9).

1.3 Format and Purpose

The sequence of topics covered in this ozone method follows 2007 EPA guidance on preparing standard operating procedures (SOPs). This method was also written to help field operators understand why (not just how) key procedures are performed.(US EPA, 2007)

2 SUMMARY OF METHOD

2.1 Historical Review

The ozone reference measurement principle and calibration procedure, promulgated in 1971 and amended in 1979, is based on detection of chemiluminescence resulting from the reaction of ozone with ethylene gas. Later, Rhodamine B, an organic dye embedded in a disc, was approved for use in place of ethylene to detect chemiluminescence. But neither method was problem-free. The flammability of ethylene was a constant concern, especially when monitoring was conducted in or near a public facility. The Rhodamine B analytical system did not regain a stable baseline rapidly enough after exposure to ozone. Thus, when UV analyzers were first approved as equivalent methods in 1977, they gained rapid, almost universal acceptance. Today, users have their choice of many approved UV instruments from several manufacturers.

2.2 Ultraviolet Absorption by Ozone

The analytical principle is based on absorption of UV light by the ozone molecule and subsequent use of photometry to measure reduction of the quanta of light reaching the detector at 254 nm. The degree of reduction depends on the path length of the UV sample cell, the ozone concentration introduced into the sample cell, and the wavelength of the UV light, as expressed by the Beer-Lambert law shown below:

Equation 1. Beer-Lambert Law

$$T = \frac{I}{I_0} = e^{(-axC)} \quad (1)$$

where:

- T = Transmittance of light through the gas to the detector
- I = light intensity after absorption by ozone
- I₀ = light intensity at zero ozone concentration
- a = specific ozone molar absorption coefficient
- x = path length, and
- C = ozone concentration

The air sample is drawn into an optical absorption cell where it is irradiated by a low pressure, cold cathode mercury vapor lamp fitted with a Vycor® sheath to filter out radiation with a wavelength of less than 254 nm. A photodetector, located at the opposite end of the sample cell, measures the reduction in UV intensity at 254 nm caused by the presence of ozone in the sample cell. To compensate for possible irregularities in output, another photodetector is used in some instruments to monitor the intensity of the mercury vapor lamp.

Although some ozone analyzers measure reference and sample air simultaneously using two absorption cells, many analyzers alternate these measurements, using only one cell. In the first part of the cycle, sample air is passed through a scrubber with manganese dioxide to remove ozone. The scrubbed sample air then enters the sample absorption cell to establish a reference light intensity at zero ozone concentration (I₀). In the second part of the cycle, sample air is re-directed to bypass the scrubber and enter the sample cell directly for measurement of the attenuated light intensity (I). The difference is related to the ozone concentration according to the Beer-Lambert law shown above. Thus, ozone in a sample stream can be measured continuously by alternately measuring the light level at the sample detector, first with ozone removed and then with ozone present.

Any ozone analyzer used for routine ambient air monitoring must be calibrated against a suitable ozone standard that is directly traceable to a primary standard. An ozone primary standard is a photometer similar to a UV analyzer that meets the specifications in 40 CFR 50, Appendix D.

Potential interferences to the UV detection of ozone, including water, aromatic hydrocarbons, and mercury, are discussed in Section 6.

3 DEFINITIONS

The CDPHE/APCD/TSP QAPP contains an appendix of acronyms and definitions. Any commonly used shorthand designations for items such as the sponsoring organization, monitoring site, and the geographical area will be defined and included in this SOP or in the QAPP Appendix P2.

4 HEALTH AND SAFETY WARNINGS

To prevent personal injury, the following warnings should be heeded:

Chemical Hazards: Ozone is a very strong oxidant. Vent any ozone or calibration span gas to the atmosphere rather than into the shelter or other immediate sampling area. If this is not possible, limit exposure to ozone by getting fresh air every 10 to 15 minutes. If chest tightening occurs, leave the area immediately.

Ultraviolet light can cause burns to the cornea of the eye. Avoid looking at the UV lamp when it is on. Use protective glasses if the lamp must be checked when it is energized.

Electrical Hazards

1. Always use a third ground wire on all instruments.
2. If it is necessary to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltage inside the analyzer. The analyzer has high voltages in certain parts of the circuitry, including a 110 volt AC power supply. Refer to the manufacturer's instruction manual and know the precise locations of these components before working on the instrument
3. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.
4. Always unplug the analyzer whenever possible when servicing or replacing parts.

5 CAUTIONS

To prevent damage to the equipment, the following precautions should be taken:

1. Clean the optical tubes carefully to avoid damaging the interior of the tubes. Use cleaning procedures outlined in the manufacturer's instruction manual.
2. Keep the interior of the analyzer clean.
3. Inspect the system regularly for structural integrity.
4. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site.
5. Inspect tubing for cracks and leaks. Sample and vacuum lines may rest upon parts that vibrate, such as the air pump. Check all lines where they come into contact with other parts.
6. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts.
7. Sample gas should be delivered to the instrument at atmospheric pressure.

6 INTERFERENCES

Preventing interferences is crucial to the accurate measurement of ozone. This section describes the three most common interferences—water vapor, aromatic hydrocarbons, and mercury—and recommends procedures to minimize these interferences.

6.1 Overview

UV ozone analyzers measure ozone concentration by absorption of electromagnetic radiation at a wavelength of 254 nm. Any other gas in the air sample that also absorbs at that wavelength could present interference. The UV analyzer operates by comparing absorption measurements of the sample air with measurements of the same sample air after removal of only the ozone by an ozone scrubber.

Ideally, a gas that absorbs at 254 nm will do so equally in both measurements, and the effect will cancel. The scrubber must remove 100% of the ozone while quantitatively passing other gases that absorb at 254 nm. Some gases, however, may be partially or temporarily absorbed by the scrubber, such that their concentration is not equal in both measurements. An interference can occur when a gas absorbs at 254 nm or produces some other physical effect (such as water condensing on scratches in the cell window), and does not pass freely through the ozone scrubber. Hence, proper scrubber performance is critical to minimizing interferences.

Negative interferences result from incomplete removal of ozone by the scrubber and from loss of ozone by reaction or absorption in dirty inlet lines, filters, analyzer plumbing components, and the measurement cells, particularly with long residence times. Condition all sample lines and filters by exposing them to high concentrations of ozone (0.4 ppm) for at least 30 minutes. New tubing and filters that are not conditioned will absorb ozone for some time.

Ozone breakthrough has been shown to be a transient problem occurring primarily under humid conditions. Before use in high humidity environments, new scrubbers may need to be pre-treated by proprietary methods recommended by the manufacturer to saturate ozone absorption or reaction sites. Ozone breakthrough can also occur in dry conditions if the scrubber is not replaced according to the manufacturer's recommended schedule.

Three common positive interferences for UV ozone analyzers are discussed below. Specific data on some interferences are substantially incomplete. The guidance provided here is the current best judgment based on available information and is subject to modification pending availability of further data.

Operators are encouraged to report any observations or anecdotal data that might add to the understanding or awareness of interferences or other anomalies in ozone measurements with UV analyzers. Observations can be noted on the analyzer log sheet.

6.2 Water Vapor

Water vapor can affect UV-based ozone measurements under some conditions. When the humidity of the sample air is high enough to approach saturation, condensation of water may occur at various points in the sampling system or analyzer. Further, the scrubber may absorb water vapor such that some point of time is required before the air leaving the scrubber is at the same humidity as the sample air. At high humidity, condensation can also occur on scratches in the cell windows. During transition periods when the humidity of the sample air is increasing, such condensation may even occur during the sample air measurement, but not during the zero ozone measurement, resulting in a positive interference.

High humidity or condensation in the sample air may also affect the ability of the scrubber to pass other potentially interfering gases, such as aromatic hydrocarbons, discussed in Section 6.3. Although condensed water did not affect ozone measurements in clean air tests, condensation in a dirty inlet line and other inlet components—especially particulate filters—is notorious for reducing measured ozone concentrations. Large amounts of liquid water can reduce or prevent sample airflow in inlet lines and filters and may cause damage to the analyzer cells or windows if it enters the analyzer.

Geography can influence the time of day of peak dew point temperatures. For example, in the eastern United States, dew point temperatures peak on hot summer afternoons, particularly with rain showers in the area, just at the time when peak ozone concentrations are likely to occur and when measurement accuracy is critically important. In the western United States, especially in southern California coastal basins, dew point temperatures are highest in the pre-dawn to mid-morning hours, but ozone concentrations are highest in the early afternoon. In the dry Southwest, however, water vapor interference is rarely a problem.

Data quality will be enhanced by following the recommendations.

Operate UV ozone analyzers to avoid condensation of moisture anywhere in the analyzer, sample inlet line, or filter. Condensation may first occur in the particulate filter because the slight pressure drop there favors it. The best way to avoid condensation in the inlet sample air is to assure that the temperatures of all locations in the analyzer and sample inlet line remain above the dew point temperature of ambient air.

In sample line condensation can be reduced by maintaining a monitoring shelter at temperatures no lower than 26-27°C (79-81°F), if possible, in areas where dew point temperatures are high. Outdoor ambient air dew point temperatures can exceed 27°C (80°F) on hot, summer days, particularly in coastal areas or following rain.

Make sure that air conditioners or cool air ducts do not blow directly on the analyzer or on the inlet line. Use a thermograph to monitor the shelter temperature near the analyzer for several days under a variety of weather conditions to ensure that the temperature does not get too low or too high when the air conditioner cycles on and off.

Check the particulate filter and lines frequently for condensation, especially at times when the outdoor dew point temperatures are likely to be the highest (afternoons or hot, rainy days). Today's condensation may be gone by tomorrow.

Record the ozone analyzer output using a data logger with graphics capability, or similar method, to plot 1-minute digital data for several days during humid weather. Look for abnormal characteristics such as cyclic patterns, long periods with little or no change in concentration, or unusually low readings when higher readings would be expected. These patterns are easily detectable on a graphical plot, but may not be recognizable in raw digital data. Cyclic patterns for instance, are frequently synchronized with the on-off cycles of the shelter air conditioner. All abnormal patterns should be investigated to see if they also represent errors in the ozone measurements.

Wrap the inlet line and sampling manifold with thermal insulation if condensation is observed in the inlet line or particulate filter, and if the shelter temperature cannot be increased. In extreme cases, the inlet lines may be heated slightly above ambient temperature with heating tape, but finding a heater of low enough wattage to do so may be difficult. Heating must be done very cautiously, because the lines should be heated no more than 3 or 4° C (5-7° F) above ambient temperature. Use a Variac© or similar device to control the temperature. Such heating may transfer condensation into the analyzer unless the analyzer is also heated internally about the same amount. How best to effect such a small temperature increase may be equipment-dependent and some experimentation may be necessary. Avoid excessive temperatures to prevent ozone loss.

6.3 Aromatic Hydrocarbons

Many aromatic hydrocarbons are known both to absorb light at 254 nm and to be “sticky”—readily absorbed or adsorbed on surfaces exposed to air samples. Smog chamber studies producing ozone by irradiation of toluene/NO_x mixtures showed that benzaldehyde and other aromatic photo oxidation products such as *o*-cresol and *o*-nitrotoluene were almost completely removed by ozone scrubbers used in ozone UV analyzers. Although scrubber retention of aromatic hydrocarbons produces a positive interference initially, the retained compounds may be released later when conditions change, giving rise to a negative interference. Under humid conditions, compounds may be desorbed from the scrubber.

Generally, aromatic hydrocarbons cannot be significantly removed from air samples without also altering the ozone concentration. Therefore, the only practical way to avoid interference from these compounds is to avoid sitting a UV analyzer in an area that may have significant concentrations of aromatic hydrocarbons.

Problems with hydrocarbon interferences can be minimized by taking the following precautions:

- Avoid sites near or downwind from asphalt plants, asphalt paving operations, chemical plants, and similar sources.
- Avoid large asphalt areas such as roadways and parking lots that can outgas significant aromatic hydrocarbon concentrations on hot, sunny days.
- Avoid local influence from hydrocarbons near motor pools, diesel fueling tanks, gas stations, thruways, tunnels, airports, and other areas of heavy motor vehicle traffic.

- Avoid highly urban or heavily polluted areas, if possible, to prevent interference from toluene, an aromatic hydrocarbon normally found in high concentrations in urban atmospheres.
- Avoid applying herbicide and pesticide formulations near the monitoring shelter, to prevent interferences from outgas of hydrocarbons used in the formulations.
- Use a non-UV type analyzer when an ozone monitoring site must be located in an area where aromatic hydrocarbon concentrations are high. Chemiluminescence ozone analyzers are not affected by interference from aromatic hydrocarbons and are recommended for such sites, but they are difficult to obtain because few manufacturers make them. Chemiluminescence analyzers requiring a supply of the flammable gas ethylene were in widespread use but were replaced by UV analyzers that have no such limitations. Current chemiluminescence ozone analyzers require a continuous supply of nitric oxide.

Another alternative is to use an open-path differential optical absorption spectrometer analyzer, which is not affected by interference from aromatic hydrocarbons. An open-path monitor provides measurements of a more integrated nature and may have more difficult siting requirements than a conventional point monitor. Nevertheless, it can be a good, though expensive, choice.

6.4 Mercury

Interference from mercury is generally not a problem at most sites because atmospheric concentrations are usually very low, but the possibility of locally high mercury concentrations in the vicinity of a monitoring site does exist. Local atmospheric contamination from mercury has been attributed to a wide variety of sources, ranging from dental fillings to herbicides used near a monitoring shelter. Anecdotal reports also suggest that field operators must be alert to the possibility of abnormal ozone readings caused by mercury vapor from broken equipment such as mercury thermometers. In one case, high ozone readings for nearly a year were attributed to a broken thermometer found on the roof near the sampling intake. In another, low readings were obtained for a week due to a broken thermometer found in a wastebasket inside a shelter where inside air was used to generate zero air. In both cases, ozone readings returned to normal range after the spilled mercury was removed.

Minimize the effect of mercury interference by taking the following precautions:

- Keep the monitoring station free of spilled mercury for measurement as well as health reasons.
- Inspect the area around a monitoring site for possible contamination from spilled mercury, application or disposal of mercury-containing chemicals, or other sources of possible mercury contamination.
- Never use a vacuum cleaner to pick up spilled mercury. More contamination can result if mercury vapor is spread through the area and liquid mercury remains in the bag. Instead, use a commercially available mercury clean-up kit that employs sponges and a bulb-type suction device.
- Examine ozone measurement data for unusual patterns or verify data with a non-UV ozone analyzer because the evidence of mercury contamination in the area may not be obvious.

7 PERSONNEL QUALIFICATIONS

General Personnel Qualifications are discussed in the CDPHE/APCD/TSP QAPP.

8 APPARATUS AND MATERIALS

Because of the complexity of ozone monitoring equipment and procedures, this section includes much more information than the customary list of equipment and supplies. The intent is to give field operators an in-depth understanding of their task and tools.

8.1 Monitoring Equipment

8.1.1 Analyzers

8.1.1.1 Teledyne 400E

Continuous air monitoring analyzers are commercially available from a number of vendors. An ozone analyzer uses a special internal scrubber that removes ozone, but not other gases, to provide a zero-concentration ozone reference for the analyzer's zero reference. Maintaining the distinction between an analyzer and a photometer is very important. The term analyzer is reserved for the air monitoring instrument, the term photometer for the calibration standard instrument. For use in State and Local Air Monitoring Stations (SLAMS) networks, an analyzer must be designated by EPA as an equivalent method under 40 CFR 53, Appendix C, Section 2.1.

Ozone analyzers have three major systems: the optical system (or optic bench, as frequently used by the instrument manufacturers), the pneumatic system, and the electronic hardware. Each is described below:

Optical System: Generally consists of the measurement cell or cells, a UV lamp, and a UV detector. The cells are usually made of aluminum, glass, or stainless steel tubes that can be sealed against leakage; the ends are either open or made of glass. The internal cell coating can vary, including Kynar, Teflon, glass, or stainless steel. The system should be easily accessible for preventive maintenance because particulate matter can collect in the cells and affect transmittance of light.

Pneumatic System: Consists of sample probe, sample inlet line, particulate filter, solenoid valves, scrubber, internal tubing, flow meter, and pump, all used to bring ambient air samples to the analyzer inlet.

Electronic Hardware: The part of the analyzer that generally requires little or no maintenance. If the instrument is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

8.1.2 Instrument Shelter

A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature, and provide security and electrical power. The following are operational shelter temperature requirements for the SLAMS (US EPA, 2013) and NCore networks (US EPA, 2005).

SLAMs: 5-40 °C (20-30 °C preferred) at $\leq \pm 2$ °C Standard Deviation over 24 hours.

SLAMs: 41-104 °F (68-86 °F preferred) at $\leq \pm 3.6$ °F Standard Deviation over 24 hours

NCore: 20-30 °C, daily changes in hourly temperature should not exceed ± 5 °C over a 24-hour period.

NCore: 68-86 °F, daily changes in hourly temperature should not exceed ± 9 °F over a 24-hour period.

8.1.3 Test Gas System

The APCD uses a span and precision system for ozone that generates concentrations, 0.240 ppm for span and 0.060 ppm for precision level, from a NIST-traceable ozone source which is delivered under controlled flow at atmospheric pressure to the analyzer. This system is enhanced by the use of the station data logger that is capable of controlling the quality control test gas processes and data collection in a repeatable manner. This standardizes reduces process errors. Data logger control of the tests and data averaging allows the test results to be reported by the data logger to a central computer.

8.1.4 Data Acquisition System

The APCD employs three different models of onsite data acquisition system equipment (DAS) in the operations of its air monitoring network. These are the ESC 8816 data logger, the ESC 8832 data logger, and the Agilaire 8872

data logger. The 8816 data logger is the oldest type of data logger in the network and is a predecessor to the 8832 and 8872 data loggers. The following are descriptions of these data loggers.

ESC 8816 Data Logger

The ESC Model 8816 Data System Controller is a microprocessor-based data acquisition system designed to acquire, process, store, report, and telemeter data in a multi-tasking environment. The 8816 is designed around an expansion bus that gives the user great flexibility in configuring the unit with a combination of analog and serial input and output (I/O) types.

For more details, refer to APCD's Data logger SOP or the individual operator manuals (Environmental Systems Corporation, 2001).

ESC 8832 Data Logger

The ESC Model 8832 Data System Controller is a microprocessor-based data acquisition system designed to acquire, process, store, report, and telemeter data in a multi-tasking environment. The 8832 is designed around an expansion bus that gives the user great flexibility in configuring the unit with almost any combination of input and output types. It is the successor to the 8816 data logger and is more robust in numerous areas. Of significance is expanded memory, faster processing speeds, faster communication speeds, remote Ethernet communications, and polling and Modbus enabled communications with peripheral devices.

For more details, refer to APCD's Data logger SOP or the individual operator manuals (Environmental Systems Corporation, 2006).

Agilaire 8872 Data Logger

The Model 8872 is a Windows-based data logger, a departure from the earlier 8816 / 8832 embedded systems designs. The 8872 includes a number of hardware and software features to ensure that the device matches the field reliability of the 8832, while offering the convenience of a Windows-based platform and integration with Agilaire's AirVision software.

The core of the 8872 is a fan-less PC, typically 2 GB of RAM. The device can be equipped with a 160 GB standard hard drive or, more commonly, a 64 GB solid state flash drive (SSD). For all digital versions of the 8872, the remainder of the enclosure simply provides convenient universal serial bus (USB), serial, and VGA I/O connections in a standard 3U rack mount enclosure, a form factor similar to the 8816 / 8832 family. However, the 8872 also supports traditional analog/discrete I/O via a variety of internal I/O modules and a protection / connector board to provide familiar detachable terminal block connections to the back. The layout of the connections is designed to make the unit easy to use as a 'drop in' replacement for an 8816 or 8832. (Agilaire, 2013)

For more details, refer to APCD's Datalogger SOP or the individual operator manuals.

8.1.5 Wiring, Tubing and Fittings

Teflon™ and borosilicate glass are inert materials that should be used exclusively throughout the ambient air intake system. It is recommended that Polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), or Fluoroethylpropylene (FEP) Teflon™ tubing be used. FEP Teflon is the best choice for sample lines and the connection between an intake manifold and the bulkhead fitting because of its inertness and lower costs. All fittings and ferrules should be made of Teflon™. Connection wiring to the DAS should be shielded two-strand wire for analog communications and properly shielded RS-232 serial cable or Cat5 or higher Ethernet cable for digital communications.

8.1.6 Reagents and Standards

Ozone analyzers used by the CDPHE do not require any reagents. All transfer standard calibration and quality control concentrations are obtained by calibration against sources whose operation must be traceable to NIST Standard Reference Material (SRM) gases via EPA Protocol procedures.

8.1.7 Spare Parts and Incidental Supplies

Replacements should be available for the ozone scrubber, UV lamp, particulate filters, cell cleaning supplies, etc. See the analyzer's operating manual for specific maintenance and replacement requirements.

8.2 Calibration Equipment

8.2.1 Calibration System

The following equipment is required for calibration of an ozone analyzer:

Ozone Transfer Standard: An ozone transfer standard is a transportable device or apparatus which, together with associated operating procedures, is capable of accurately measuring and producing (if an ozone generator is installed) ozone concentrations which are quantitatively related to a higher level and more authoritative standard. The transfer standard's purpose is to transfer the authority of a Level 1 ozone standard to a remote point where it is used to verify or calibrate an air monitoring analyzer (US EPA, 2013).

Ozone Generator: A generator providing stable ozone concentrations that can be varied manually or by automatic electronic feedback circuitry. If the transfer standard is or has an ozone generator, no other ozone generator is needed.

Zero Air Generator: Zero air is required for the calibration of ozone instruments. This air must be ozone-free to 0.001 ppm, and also free of nitric oxide (NO), nitrogen dioxide (NO₂), particulates, and hydrocarbons. Although there are many commercially available zero-air systems, zero air can also be generated by using a series of canisters that contain thermally cracked carbon, Purafil®, and desiccant. Because NO may be difficult to remove, frequent changing of the carbon or use of an NO-to-NO₂ converter may be necessary. When such a converter is used, test the output with a NO/NO_x analyzer to ensure that the residence time in the system is long enough for complete conversion of NO to NO₂.

The desiccant used with the zero-air system should be changed regularly. A canister system set up with a pump and surge tank can provide a cost-effective zero-air system. If a zero-air system is created, the moisture content must remain constant. Changing humidity can affect the response of UV photometers. Very dry zero air may also be a problem. The scrubber needs time to adjust if the zero air is much drier than the ambient air.

Output Manifold/Sample Lines: Although the output manifold can be constructed of borosilicate glass or Teflon, Teflon is recommended. The manifold must have an opening that vents excess air to the atmosphere such that the pressure in the manifold is as close to atmospheric pressure as possible. If ozonated air is delivered under too high a pressure, the ozone readings obtained will not be representative. Manifolds collect particulate matter on the internal walls because neither zero air nor sample air is totally particulate-free. Because Teflon manifolds are opaque, it can be difficult to determine whether they are collecting particulates.

8.2.2 Accessories and Incidental Supplies

- Digital voltmeter (DVM) with a 0 - 1 volt range. It is periodically referenced against the in-house voltage standard, which has NIST traceability.
- Connecting lines made of 1/4" OD Teflon.

- Teflon™ is an inert material that should be used exclusively throughout the calibration system. It is recommended that Polytetrafluoroethylene (PTFE), Fluoroethylpropylene (FEP) Teflon™ or Perfluoroalkoxy (PFA) tubing be used.
- Calibration sheet (Figure 2).
- Ozone analyzer manual (ref. 9). Each ozone sampling station must have a permanent copy.

8.2.3 Reagents and Standards

Ozone Transfer Standards used by the CDPHE do not require any reagents. All transfer standard calibration and quality control concentrations are obtained by calibration against sources whose operation must be traceable to NIST Standard Reference Material (SRM) gases via EPA Protocol procedures.

9 CALIBRATION

9.1 Introduction and Summary

The calibration of a gaseous analyzer centers on introducing known concentrations of a pollutant to the analyzer and adjusting the analyzer so that its readings accurately represent those concentrations (US EPA, 2013) (US EPA, 1979). An overview of the calibration process is given below.

1. Site Inspection Summary (section 9.2):
 - a. General inspection of the station shelter.
 - b. General inspection of all measurement and recording instruments, along with the O₃ analyzer, to see if they are working properly.
 - c. Minor maintenance on the shelter or instruments if required and within the scope of the cal worker's resources. If any of the analyzer operational parameters are out of specification or nearing being out of specification from the station log sheet target values, the calibration should be halted so repairs and/or major maintenance can be performed prior to calibration.
2. Calibration Procedure Summary (section **Error! Reference source not found.**):
 - a. A pre-calibration station span, precision and zero routine is run (section 9.3.2).
 - b. A pre-calibration audit point at the precision level using the calibration equipment is introduced, plus calibration zero, to the ozone analyzer (section 9.3.3.1, Pre-Calibration Audit Procedure).
 - c. Performance of any minor maintenance on the analyzer if required and within the scope of the calibration specialist's resources. If major repairs are needed, the calibration should be halted so that this can be done before any calibration.
 - d. Adjustment of the analyzer's responses so that they accurately reflect introduced known concentrations of O₃ (section 9.3.3.2, Calibration Adjustment).
 - e. Introduction of five ozone concentrations plus zero air in order to characterize the calibrated ozone analyzer's response curve (section 9.3.3.3, Post-Calibration Assessment).
 - f. Determination of the automated zero, span, and precision values (in Post-Calibration Assessment).
3. Calculation, recording, and reporting of results. A detailed description of this procedure is presented below in Sections **Error! Reference source not found.** and 9.4.

9.2 Site Inspection

A site inspection is conducted every time a calibration specialist goes to a monitoring station to calibrate, audit, or perform any other kind of calibration unit operation.

The inspection routine includes the following actions:

1. Check that any water drop (if present), and sample lines are not dirty or show condensation.

2. Check that all monitors' operational parameters such as pressure, temperature, and sample flow look normal compared to the values recorded on their calibration stickers and station log sheets. Refer to an analyzer's manual and analyzer log sheet for allowable ranges for each of its diagnostic parameters. If any parameter on any analyzer is out of bounds then the monitoring technician should be notified that day. Maintenance should be performed by the calibration specialist if possible, and a calibration on the analyzer may be necessary afterwards.
3. Check that the station temperature high/low readings are within a range of 20 - 30 °C (68-86°F).
4. Check the station logs for non-routine actions.
5. Check that all gaseous analyzers and meteorological (met) sensors appear to be reading ambient values that are reasonable given outside conditions and past readings for that individual station. This is done by looking at the real time data logger readings. For the gaseous analyzers, make sure their front panel readings match those on the data logger. For specifics on using the data logger refer to data logger SOP appendix in this QAPP document.
6. If you need to access the data logger functions through one or more login codes (codes are required) and aren't sure if you're authorized for access, call either the supervisor or the monitoring technician to see if you are. If you know that you are authorized, but have forgotten the login codes, call key contact personnel within the GMM unit for the codes. Key contact people within the GMM unit are posted within every monitoring station.
7. If present, visually check that the meteorological tower's instrument crossbar is properly aligned. Check that the meteorological sensors aren't damaged and are moving without binding.
8. Check that the station structure is not damaged.
9. Check that all analyzer clocks and digital chart recorder clocks agree with the data logger and that they are showing the proper time (**Error! Reference source not found.**). If any change is made to a device then log the action, date and calibration specialist's initials in the relevant log. For changes to the data logger clock consult first with GMM supervisory or data management staff.
10. Check that all pumps are running smoothly and are not overly hot to the touch. Check also that exhaust lines between the pump and the analyzer are not rubbing on the pump, which can lead to a hole being worn in the line.
11. Perform a leak check on the analyzer that is to be calibrated (10.6.6).

If anything is found out of the ordinary it is to be recorded in the relevant log, along with the date and the calibration specialist's initials. The station's monitoring technician is notified that day (or another monitoring technician of the GMM unit if that person is not available). Maintenance should be performed if appropriate and within the scope of the calibration specialist's resources.

9.3 Calibration Procedure

9.3.1 Calibration Train Setup

A level 3 ozone transfer standard is used to calibrate the ozone analyzer. The transfer standard calibrator is equipped with an internal zero air pump, but may also use an external zero air source (TAPI 701(H) zero air pack). The transfer standard calibrator internally generates, and its photometer measures, ozone concentrations that are then used to challenge the analyzer under calibration. See the Standards SOP Appendix GA3 and the transfer standard calibrator's operational manual for more information.

1. Connect the zero air supply output to the zero air port on the calibration transfer standard (Figure 1), if the calibrator's internal zero air pump isn't being used.
2. Turn on and allow the zero air supply and transfer standard calibrator to warm up, during which the pre-calibration Zero, Span, and Precision routine can be performed (9.3.2).
3. After the station pre-calibration Zero, Span, and Precision routine has been completed, disconnect the test gas supply line from the station calibrator at its external valve output.
4. Connect the open end of the station's calibrator test gas supply line to the output port of the transfer standard calibrator to introduce calibration ozone concentrations to the analyzer. The station calibrator's gas supply line leads outside of the shelter and up to the analyzer's sample line inlet at the probe.

9.3.2 Station Pre-calibration Zero, Span, and Precision Routine

This routine is done prior to adjusting the analyzer to help correlate the preceding automatic zeros and spans (z/s) and precisions (p) with the pre-calibration audit responses. It is also done at the end of the calibration procedure to generate new official z/s/p values for the following sampling period until the next calibration. In practice these routines are started just before and after any calibration or audit and can be performed while the calibration or auditing staff is performing set up or take down of their equipment.

1. Take the O₃ analyzer channel offline (10.6.1).
2. Start an automatic precision/zero routine. This is done by a command through the data logger (10.6.10). Allow this routine to run fully until its automatic ending. During the run make sure that all readings from the front panels of the station calibrator and ozone analyzer match the numbers seen in the data logger. Record the final reported numbers on the calibration sheet. A precision is done before a span because the ozone analyzer is more sensitive to conditioning effects at this level, and the purpose of the pre-cal precision is to emulate the midnight precisions as closely as possible.
3. Start an automatic span/zero routine as done with Step 2.
4. Zero-correct the data logger precision and span test level (t) results.

$$t - \text{zero value} = \text{zero corrected test level (zct)}$$

5. Calculate the percentage relative error (%RE) of the precision and span zct's and record on the calibration sheet.

Equation 2. Percent Relative Error

$$\frac{zct - \text{Actual Concentration}^*}{\text{Actual Concentration}^*} * 100\% = \%RE$$

*Actual Concentration is the concentration of the test gas as reported by the station calibrator through the data logger.

The pre-calibration span and precision plus station zero can also be run manually through the data logger. The calibration specialist must be careful to emulate automatic phase times so that conditioning effect differences between previous midnight auto spans and precisions and this pre-calibration span and precision can be minimized. For some diagnostic purposes a manual running of the precision and span is sometimes more useful and practical

than using the automatic routines. The manually triggering of relays through the data logger is non-routine and the procedure to perform this task is not included in this SOP. Contact the Data Manager to attain information on how to perform this task.

9.3.3 Pre-Calibration Audit, Calibration Adjustment, and Post-Calibration Assessment

9.3.3.1 Pre-Calibration Audit Procedure

Introduction

From the transfer standard calibrator introduce to the analyzer zero and precision levels. Calculate %RE for the zero corrected precision level results. If this equals or exceeds +/- 7%RE, follow with a full five point plus zero calibration assessment before any adjustment is made to the analyzer. This assessment is the same as described below in section 9.3.3.3 Post-Calibration Assessment. This is to characterize the out-of-spec condition over the full measurement range of the analyzer, and the information will be used during data validation.

If the analyzer fails the assessment audit then repairs, when necessary, and calibration of the instrument are done as soon as possible after the check. If the repairs required are beyond the scope of the calibration specialist then the site operator is notified immediately. Failed pre-calibration assessment audits require an electronic message in the data logger that will be use for data validation purposes. The procedure for performing the pre-calibration assessment is given below.

Procedure

1. If not already done, connect the transfer standard calibrator to the station's nightly check line. Please see Section 9.3.1 Step 5 for how to connect the transfer standard to the station inlet.
2. Introduce zero air from the transfer standard calibrator to the analyzer. If the transfer standard calibrator is certified at the zero level by keying in 0.000 ppm (as opposed to just pressing "ZERO-ENTER") at the time of its test, then follow this method during an actual calibration. Be sure that excess supply flow at the probe inlet is 25 to 50% greater than analyzer flow (compare total flow readings on the analyzer and transfer standard calibrator).
3. Let the zero readings on the transfer standard calibrator and the analyzer stabilize and then wait an additional five minutes to confirm stabilization (this will be done with all transfer standard calibrator test points). Record the results on the calibration sheet. This is the pre-calibration zero air concentration reading.
4. Generate a precision level and introduce to the analyzer. This is the pre-calibration precision concentration reading.
5. Zero correct the precision levels from the transfer standard calibrator and analyzer. Calculate the % relative error (%RE) of the analyzer's responses.

Equation 3. Percent Relative Error

$$\frac{zc\ DAS - true[O_3]}{true[O_3]} * 100\% = \%RE$$

Where: zc DAS = zero corrected analyzer reading as read through the data logger.

True[O₃] = zero corrected transfer standard calibrator reading.

5. If the precision level error is $< +/- 7.1\%$ RE a full assessment audit is not required. If it equals or exceeds $+/-7.1\%$ RE, the assessment fails and is followed with a full five point plus zero calibration assessment audit (the same as a post-calibration assessment in section 9.3.3.3 below) before any adjustment or repairs are made to the analyzer. This is to characterize the out-of-spec condition fully, and the information will be used during data validation. Additionally, if the assessment fails, documentation of this failure in a Message to Central is required as described in Section 9.3.3.3 Step 10.

9.3.3.2 Calibration Adjustment

Introduction

After the pre-calibration audit, the analyzer is adjusted (calibrated) at the zero and precision level so that they most closely match the known concentrations put out by the transfer standard calibration system. After this is done, a five level plus zero multipoint test is reintroduced to characterize the analyzer response over the entire measurement range.

The recommended ranges for the multi-point calibration points are detailed in Table 1. As each calibration point is generated, the responses shown by the data logger should be compared to the calibrator value.

Table 1. Calibration Range Ozone Analyzers

Units	Parts per billion (ppb)
Calibration Scale	0 to 250 ppb
<u>Approximate Calibration Points</u>	
Level 1	240 ppb
Level 2	200 ppb
Level 3	150 ppb
Level 4	100 ppb
Level 5	60 ppb
Zero Level	0 ppb

Level 5 is the accepted precision level that is used to adjust the calibration of the analyzer with as little error as possible, along with the Zero Level. The procedure for performing the calibration is given below.

Procedure

1. To start the analyzer calibration adjustment, introduce zero air again to the analyzer and let the chart trace stabilize.

If the analyzer does not display zero for the concentration reading, on the analyzer's front panel press CAL. ZERO will appear. Press this. Display concentration will go to 0.000. This is the calibration adjustment of the zero level.

2. Generate another precision level and introduce to the analyzer again. Let the analyzer stabilize.

3. Press Cal. CONC will appear. Press this. O₃ SPAN CONC: XXX.X CONC will appear. Using buttons, input zero corrected O₃ precision concentration as displayed by the transfer standard calibrator. Press ENTER. This is the calibration adjustment of the precision level. The analyzer readings must be made as accurately as possible at the zero and precision levels.
4. Steps 1 thru 3 can be repeated if the calibration settings from the initial calibration or subsequent calibrations are not sufficiently accurate. This is accomplished by independently sending zero air and known test gas concentrations (10 to 20% of calibration full scale) to the analyzer to assess the accuracy of the calibration. If the results are not optimal, repeat steps 1 thru 6. Several attempts between the zero air and the test gas, along with calibration adjustments, may be required. Record the calibration results on the calibration sheet.
5. If any analog readings from the analyzer are taken by the data logger, press SETUP-MISC-D/A-CAL and use a DVM to calibrate the analog-to-digital converter. Adjust the D/A potentiometer R31 on the V/F card so that the DVM and the data logger readings match the front panel reading. If all readings are digital then this step may be skipped.

9.3.3.3 Post-Calibration Assessment

Introduction

The post-calibration assessment challenges the analyzer with five different test gas concentrations levels plus a zero to evaluate the accuracy of the new calibration. The assessment begins with a zero point followed by points at <20% (Level 4 - precision), >80% (Level 1 - span), ~60% (Level 2), and ~40% (Level 3). Results for these tests are used to evaluate the relative error at full scale. Concentration levels are generated as described in the pre-calibration assessment (**Error! Reference source not found.**). The procedure for performing the post-calibration assessment is given below.

Procedure:

1. Generate zero air with the transfer standard calibrator and deliver to the analyzer. Record zero air results and all following test points on the calibration sheet.
2. Introduce a Level 1 concentration (greater than 80% full scale to the analyzer). Let it stabilize for at least five minutes. Record results on the calibration sheet.
3. Measure and generate three more O₃ concentrations that come in at approximately 70, 50, and 30% of full range. Introduce to the analyzer as above. Record the results on the calibration sheet.
4. Generate a final zero air to the analyzer and record the results. Calculate a least-squares linear regression between the known O₃ concentrations (including the zero point) as the ordinate and the zero corrected analyzer responses as the abscissa. Record slope, intercept, and correlation coefficient on the calibration sheet. Also calculate, using this response curve, a %REFS (Equation 4) for a calibrated analyzer response given a known introduced concentration of exactly 90% of the full measurement range of the analyzer.
5. The criteria for a successful calibration is where all non-zero test points after the calibration adjustment show a <+/-2% full scale error from the final best fit regression calibration line. The precision level should be as close to 0% error as possible. If the post-calibration assessment begins to show a failure at any point, and repeating previous analyzer adjustments do not solve the problem, then maintenance is probably needed for the analyzer.

Equation 4. Relative Error at Full Scale

$$\frac{[(90\% \text{ full scale} * m) + i] - 90\% \text{ full scale}}{90\% \text{ full scale}} * 100 = \%REFS$$

where:

m = slope of response curve.

i = intercept of response curve.

90% full scale = 225 ppb

%REFS = Relative Error at Full Scale

6. Reattach the station calibrator supply line back to its external valve output.
7. Do another zero, span and precision routine like the one done before the calibration (Section 9.3.2). Record results on the calibration sheet and on the calibration sticker. These are the z/s/p values at time of calibration.
8. Record analyzer parameters, especially the new analyzer calibration settings, from the front panel display, on the calibration sticker and sheet.
9. Enable the analyzer (**Error! Reference source not found.**). Record the MST time the instrument was brought back on line on the calibration sheet and on the station O₃ log. Put the calibration sticker on a surface near the analyzer so that it is easily read.
10. Enter the calibration results in a “message to central” (10.6.8). On the data logger message window to Central type and send:

O₃ cal, z=xxx, s=yyy, p=zzz, aaa

Where:

xxx= zero reading of the station calibrator through the data logger.

yyy= span reading of the station calibrator through the data logger.

zzz=precision reading of the station calibrator through the data logger.

aaa=initials of calibration specialist.

This is a message through the data logger to the GMM unit worker responsible for tracking calibrations in the ZSPTracking database. This message is permanently stored in the AirVision system and information from this message is manually inputted into the ZSPTracking database.

In the event of a failed precalibration audit or assessment, a separate message is sent to Central in the form of

O₃ CAL FAILED AUDIT,

(in all CAPS) followed by a general description in regular text and the calibrator’s initials. This is to highlight important cal/audit information for the purposes of data validation.

11. Record analyzer parameters and calibration and maintenance actions on the station O₃ log.

9.4 Reporting and Filing of Calibration Results

The results of a calibration or assessment audit are recorded and reported by the calibration specialist as follows (this is a summary; some of these actions have already been mentioned):

1. Record analyzer parameters, calibration and maintenance actions, cal date, beginning/ending disabled time and calibration specialist's initials on the station logs.
2. Record the calibration points, linear regression results, cal date and calibration specialist's initials on the calibration report form (Figure 2) and in the Calibrations database (Figure 3), along with relevant comments. If possible and if the required computer and software are available download the data stored in the analyzer's own internal data logger.
3. IF anything unusual is observed at the station, even if rectified by the calibration specialist, is reported that day to the monitoring technician and recorded in the station logs
4. Record uncorrected data logger and chart (if in use) z/s/p results, analyzer calibration settings, cal date and calibration specialist's initials on the station sticker.
5. File data logger z/s/p results into the data logger. These can be accessed at any time by the home office.
6. Put the calibration sheet with all of the calibration information, beginning/ending disabled time, cal date and calibration specialist's initials into the designated ring binder at the home office. Each year of calibrations and assessment has its own binder. The most recent four to five years of calibration and assessment audit sheets are kept at the home office. Older binders are put into permanent storage.
7. When the calibration specialist is at the home office, the Calibrations database forms on their field PCs will be uploaded to the Technical Services' J:Drive Master Calibration database monthly or more frequently if needed.

10 OPERATION AND MAINTENANCE

10.1 Introduction and Description of Monitoring

The APCD Technical Support Program (TSP) uses exclusively TAPI model 400A, 400E and T400 ozone instruments. Three manuals give the operational details and requirements for the three systems. The manufacturer's instruction manuals are complete and cover all necessary procedures and controls for successful operations. These manual is available at each ozone site and at the TSP central offices. For the data logger, the manufacturer's technical manual provides all operating instructions and system keyboard command descriptions. This manual is also available at each site and at the TSP central offices. Refer to these manuals regarding any aspect of operation of these systems.

Each continuous O₃ monitoring site is assigned to a specific TSP GMM employee (electronic specialist) qualified by formal training, experience, on the job training, and courses offered by EPA. The assigned employee is responsible for all aspects of site monitoring operation, including but not limited to maintenance, repair, documentation updates, logs, etc. In addition to keeping sites operational with a minimum of downtime, any of the senior level electronic specialists may be called upon to accept the responsibility for training of new TSP employees and/or contracted operators.

In the current monitoring network all of the ozone analyzers have some capacity to store data internally, which has been configured to serve as a backup. As a result TSP considers the data acquired by the site data logger system when properly validated to be the primary data source with the internal data storage on the analyzer as an emergency data backup and verification system for all ozone analyzers and one of several data validation and troubleshooting tools.

Data quality and validity determinations are based partly on quality control data produced from onsite test systems. An “Onsite Test System” is a system of control hardware, software and standards at the monitoring location that is capable of accurately generating and introducing known concentrations of test gas to a monitoring system. These onsite test systems are capable of performing “Performance Tests” and “QC Precision Tests”. The different tests are used to assess and document different aspects of system performance and data quality. A “Performance Test” is an automated or manual evaluation of a monitoring system’s performance and is achieved through the introduction of a known concentration of test gas, typically at the span or precision level, and is not intended to be submitted to EPA for determinations of bias. A “QC Precision Test” is a manual check initiated by APCD staff, who can attest to its validity, and is achieved through the introduction of a known concentration of test gas at the precision level and whose purpose is to be submitted to EPA for determination of bias. “Performance Tests” and “QC Precision Tests” are inherently different and are initiated by different sequences within the data logger. These sequences consist of phases that can vary in concentration, order, and duration.

For ozone, test concentrations are listed in Table 2 **Error! Reference source not found.**

Table 2. Ozone Test Targets

	Span	Precision
Non-diluted EPA protocol	0.240 ppm	0.060 ppm

The APCD uses three different types of onsite test systems within the air monitoring network. Ozone is only introduced by a NIST traceable gas generation system. Explanations of the onsite test systems are as follow.

Generated EPA test gas system

The test gas is generated in a NIST-traceable ozone generator, which then connects to the analyzer.

The onsite test system generates ozone from zero air that has been dried and scrubbed for ozone. The formation of ozone from oxygen is endothermic, that is it requires energy. When exposed to ultraviolet light an oxygen molecule in a ground state will absorb the light energy and dissociate to a degree dependent on the energy and the particular wavelength of the absorbed light. The oxygen atoms then react with other oxygen molecules to form ozone. An ozone generator is calibrated against an EPA transfer standard such that voltages appropriate to produce the desired amount of ozone are stored in the source and can be altered programmatically during a source calibration. Combining the use of drying agents and ozone scrubbers before the generator with the known voltage of the generating lamp provides adequate confidence in the concentration of ozone being produced and introduced to the analyzer. This system is ideal for ozone sampling test gas systems since ozone is very reactive and difficult to store. This system is enhanced by the use of the station data logger that is capable of controlling the quality control test gas processes and data collection in a repeatable manner. Data logger control of the tests and data averaging allows the tests results to be collected and reported by the central computer.

10.2 Equipment and Supplies

For a complete listing of supplies and equipment please see Section 8 of this standard operating procedure.

10.3 Logs and Forms

All actions at the site, scheduled and non-scheduled, are logged on forms. These forms are collected monthly, reviewed and filed together in monthly folders in a maintenance files cabinet. Three complete calendar years of forms are readily available on site. The intent of these forms is to be able to recreate events and actions taken well after the fact. Examples of these forms can be found at the end of this subsection.

The forms in routine use are:

1. MONTHLY STATION ACTIVITIES LOG (Figure 4)
2. MONTHLY O3 ACTIVITIES LOG (Figure 5)
3. MONTHLY MAINTENANCE REPORT FORM (Figure 6)

10.4 General Operations

This section provides an overview of scheduled inspection and preventive maintenance procedures. To minimize downtime and ensure data quality, preventive maintenance is to be performed on all gaseous monitors in the network according to a schedule established by the TSP, using the inspection criteria documented in this chapter. Below is a general summary of the types of maintenance checks performed.

Data from each site is evaluated daily. There is a daily morning review of overnight performance tests results, data validity flags, data completeness, data representativeness, logger messages, and shelter environmental status to determine if an immediate site visit is needed. Data loggers are contacted as needed to evaluate and configure instrument systems.

The Weekly inspection is performed once each calendar week and as needed.

Performance tests and QC precision tests are performed at prescribed intervals. Performance tests are automatically performed every night and QC precision tests are manually performed once every two weeks and are to be reported as the regulatory required bi-weekly QC precision test.

The Monthly inspection is performed on or near the beginning of each calendar month.

Upon completion of an inspection, log entries onto the STATION/MET log, O₃ TAPI 400 log, and into a “message to central” are required. Enter all tasks performed, and note any malfunctions or other actions needed or discovered during the inspection.

All scheduled checks are minimum requirements. Individual site circumstances may dictate a more frequent preventative maintenance schedule. Monthly, quarterly, and semi-annual inspections are always conducted by TSP-approved staff that has the training or experience to reliably perform the required checks or maintenance.

By contract agreement, it is the responsibility of all contracted site operators to notify TSP of any unusual instrument/equipment performance, possible malfunction, or outright malfunction, and action taken, if any. TSP in turn will take the appropriate action as soon as workload and priorities permit. TSP monitoring technicians will summarize work performed in a “message to central” for all non-scheduled maintenance activities.

10.5 Routine Preventative Maintenance and Scheduled Activities

Preventive maintenance inspections and services should follow the recommended intervals by the EPA, the manufacturer, or as determined by actual experience. If preventive maintenance services are not being done according to the minimum guidelines of the manufacturer as set forth in this standard operating procedure, the TSP may jeopardize any claim to a manufacturer’s warranty and may jeopardize the validity of the data collected. The preventive maintenance inspections are scheduled to provide an opportunity to detect and repair damage or wear conditions before major repairs are necessary and the loss of data occurs. The documentation of these activities is essential for quality control tracking and for compliance with EPA’s Quality Systems methods. Site and analyzer log sheets along with “messages to central” are part of the official record and the documentation of maintenance or observations are to be written clearly and concisely and in accordance of good laboratory practices.

Table 3. Routine Preventative Maintenance and Schedule Activities

Procedure or Resource	Description
Every Onsite Visit	
	Check station for general condition and proper operation of heating, air conditioning, lighting, and sample pumps.
10.6.2	Check all analyzers for faults and operability. Verify that the data logger is working correctly and reported values match the analyzer display.
Error! Reference source not found.	If equipped, observe the operating condition of zero air pack. Check for faults and short cycling.
	Remove trash when waste receptacles are full. Remove from shelter all odorous trash, such as leftover food and food packaging.
10.6.8 Figure 4 Figure 5	Leave a “message to central” and a site log entry summarizing purpose of visit and a summary of all maintenance performed
Weekly Inspection / Maintenance	
	Perform Every Onsite Visit inspections as defined above.
	Perform general housekeeping as necessary. Includes sweeping station as necessary. Dispose of trash as necessary. Clean up trash and remove weeds/vegetation from surrounding property.
10.6.7	Check analyzer and Data Charts times against a National Institute of Standards and Technology traceable time piece (i.e. cell phone) and adjust if ($>\pm 1$ min) see analyzer manual or clock procedure. For changes to a data logger clock contact GMM supervisor or central computer staff first.
10.6.2 Figure 5	<p>Note analyzer operational and diagnostic parameters on analyzer log sheets.</p> <ul style="list-style-type: none"> • Check results from previous night’s Performance Test and record ppm levels on Analyzer Log Sheet • Using the log sheet as guidance, record the analyzer calibration factors and analyzer diagnostic test parameters on analyzer log sheet.
	Check analyzer readout, data chart trace (if equipped) and data logger readout for agreement. Verify agreement between devices is within ± 0.2 ppm
10.6.6	Inspect and empty water drop out system, (if equipped) – note on analyzer log sheet if water found. If flask is removed, perform a leak check after reassembling the system.
10.6.3	Inspect sample filter and replace once every 2 weeks at a minimum. If the sample filter is dirty, a change frequency of greater than once every 2 weeks is permissible. Leak check analyzer after filter change.
	Visually inspect the sample line inlet. Ensure the Teflon inlet shroud is in place and free from insects and debris. Clean if necessary.
Figure 4	Log all bottle gas supply pressures on station log sheet (if present).
Figure 4	Log station maximum & minimum temperatures on station log sheet and reset thermometer if available.
10.6.4	Check desiccant moisture content and replace if mostly pink.

Procedure or Resource	Description
Figure 4	Enter notes and initial both the analyzer log sheet and the station log sheet.
10.6.8	Leave a “message to central” summarizing purpose of visit and a summary of all maintenance performed.
Every Two Week Period	
10.6.10	Perform Manual Quality Control Precision Test – Performed by APCD staff
10.6.3	Inspect sample filter and replace once every 2 weeks at a minimum. If the sample filter is dirty, a change frequency of greater than once every 2 weeks is permissible. Leak check analyzer after filter change.
Monthly Inspection / Maintenance	
	Perform Weekly Inspection/Maintenance as defined above.
	Check associated wiring, power cables, and plumbing (lines and fittings) for wear, damage and proper installation.
	Inspect analyzer fan filters and clean as necessary (if equipped).
10.6.5	Check that the internal data acquisition program in the analyzer or the data chart is operational.
10.6.3	Replace sample filter. Leak check the analyzer.
10.6.6	Perform leak check of test gas manifold solenoid/s (if equipped)
Figure 4 Figure 5	Fill out new monthly station, analyzer, and calibrator (if equipped) log sheets for the upcoming month. Include the following key elements: <ul style="list-style-type: none"> • Analyzer log sheet – site name, month, year, analyzer range and analyzer firmware, analyzer SN and other appropriate info required by log sheet • Station log sheet - site name, month, year, bottle numbers, expiration date, concentration and pressure and other appropriate info required by log sheet • Calibrator log sheet - site name, month, year, model, firmware, SN and other appropriate info required by log sheet
	Upon completion of the Monthly Maintenance site visit, all previous months log sheets are collected and placed in the monthly forms data collection box within 2 business days of being collected.
Quarterly Inspections / Maintenance	
	None Required
Six Month Inspections / Maintenance	
	Inspect and clean the sample probe weather cap once every 6-months and when the sample line is replaced. Trim one foot off the end of the sample line six months after the annual line change or after the ozone season has ended (September 30). The trim should occur at the sample inlet, not the back of the analyzer.
Annual Inspections / Maintenance	

Procedure or Resource	Description
	Inspect and clean Heating, Ventilation and Air Conditioners (HVAC) units at site. Inspect for water access holes in the shelter, roof, and sides. Ensure AC unit is sealed against moisture on the shelter wall. <ul style="list-style-type: none"> • Perform maintenance in June or July • Replace or clean air conditioning and/or heater dust filters (if equipped) • Clean air conditioner coils
10.6.9	In March or April, replace all sample lines annually. Inspect and clean the sample probe weather cap once every 6-months and when the sample line is replaced. Through the probe (TTP) calibration lines are to be replaced once every three years (2015, 2018, 2021, ect...). On years when the TTP calibration lines are not replaced, trim 6” off the inlet side of the calibration line.

10.6 Maintenance Procedures

10.6.1 Disable/Enable Analyzer in Data Logger

ESC 8816/ 8832

Disable analyzer data channel:

From the top level menu, to disable a data channel from reporting to the data logger, the user must:

1. Choose menu options **CDM (C Configuration Menu > D Configure (Data) Channels > M Disable/Mark Channel Offline)** to view the list of available channels.
2. From the keyboard, using the down arrow button, scroll to the target channel name and hit the **Enter** or **Return** key. A limited list of channels that could be encountered includes:

Channel Option	Instrument or Analyzer / Channel
O3	Ozone Analyzer
O3 Cal	Ozone Calibrator
CO	Carbon Monoxide Analyzer/Calibrator
CO_Trace	Carbon Monoxide Trace Level Analyzer/Calibrator
NO	Nitrogen Oxide Analyzer
NO2	Nitrogen Oxide Analyzer
NOX	Nitrogen Oxide Analyzer
NOY	NOY Analyzer
SO2	Sulfur Dioxide Analyzer

3. Next, hit the **Esc** (Escape) key twice to

get back to top level menu.

4. Select menu option **DF (D Real-Time Display Menu > F Display Readings w/flags)** to ensure the proper machine was disabled. You should see the letter “D” within parenthesis and adjacent to the targeted channel indicating it has been disabled.

Enable analyzer data channel:

From the top level menu to enable the data channel to resume reporting to the data logger, the user must:

1. Choose menu options **CDE (C Configuration Menu > D Configure (Data) Channels > E Enable /Mark Channel Online)** to view the list of available channels.

2. From the keyboard, using the down arrow button, scroll to the target channel name, and hit the **Enter** or **Return** key.
3. If all machines/instruments and/or channels are already on line, the user will receive a message stating “No channels are offline” at the bottom left screen. Otherwise a list of channel names will appear.
4. Next, hit the **Esc** key twice to get back to the top level menu.
5. Select menu option **DF (D Real-Time Display Menu > F Display Readings w/flags)** to ensure the proper channel was enabled. You should see parenthesis adjacent to the targeted channel without the letter “D” inside indicating the machine/instrument channel is enabled and reporting to the data logger. Note that enabling a channel may take a few moments to take effect.

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Disable analyzer data channel:

1. After logging in to AirVision™, if the Site Node Logger Toolbox is not open, from the top level menu select the **Home** tab > **Utilities** > **Site Node Logger Toolbox** > then select the **Channels** tab.
2. Identify the channel to be disabled. At the right side of the form, under the “Disabled” heading, click on the row with the target channel name. This action will change the channel state from “False” to “True” indicating that it is now disabled and not reporting to the data logger.

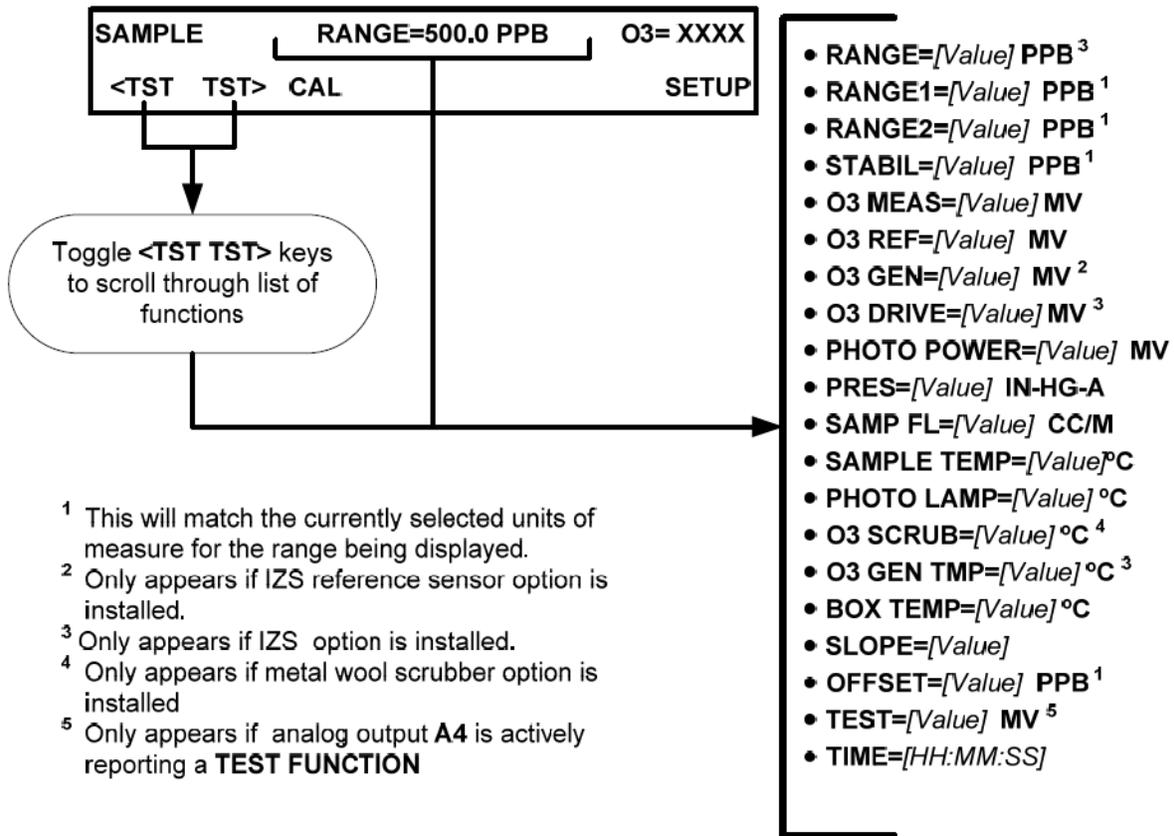
Enable analyzer data channel:

1. After logging in to AirVision™, if the Site Node Logger Toolbox is not open, from the top level menu select the **Home** tab > **Utilities** > **Site Node Logger Toolbox** > then select the **Channels** tab.
2. Identify the channel name to be enabled. At the right side of the form, under the “Disabled” heading, click on the row with the target channel name. This action will change the channel state from “True” to “False” indicating that it is now enabled and will now report to the data logger.

10.6.2 Check Analyzer Calibrations Factors and Diagnostic Test Parameters Procedure

Verify that the analyzer is in SAMPLE mode. It may be in another mode if left in such a state after an audit or calibration. If SAMPLE does not appear in the upper left of the analyzer display, contact senior staff or reference the manual for the appropriate solution. Use caution. Pressing an incorrect button without SAMPLE in the top left corner could recalibrate the instrument.

Use the <TST and TST> buttons on the display to scroll through the available diagnostic parameters and calibration factors. Make notes as appropriate on the analyzer log sheet. Below is a listing of available parameters for a 400E analyzer. Reference the site manual if another model is present.



10.6.3 Filter Change Procedure

1. Disable the analyte channel on the data logger (10.6.1)
2. Remove the old filter from the filter housing behind the front panel of the analyzer.
3. Place new 1µm filter into the filter housing using tweezers to handle the filter.
4. Tighten the filter holder closed by hand being careful to properly seat the o-ring and glass.
5. Inspect lines and fittings for seal.
6. Perform a leak check from the back of the analyzer (10.6.6).
7. Enable analyte channel on data logger (10.6.1).

10.6.4 Desiccant Regeneration

Desiccant changes from blue to pink as it absorbs water. When the desiccant container is mostly pink it should be swapped with dry desiccant. To regenerate desiccant (to dry it out) spread the granules thinly on a baking sheet and place in the oven in the laboratory for one hour at 210°C or 425°F. After one hour the desiccant should be stored in a sealed container at room temperature.

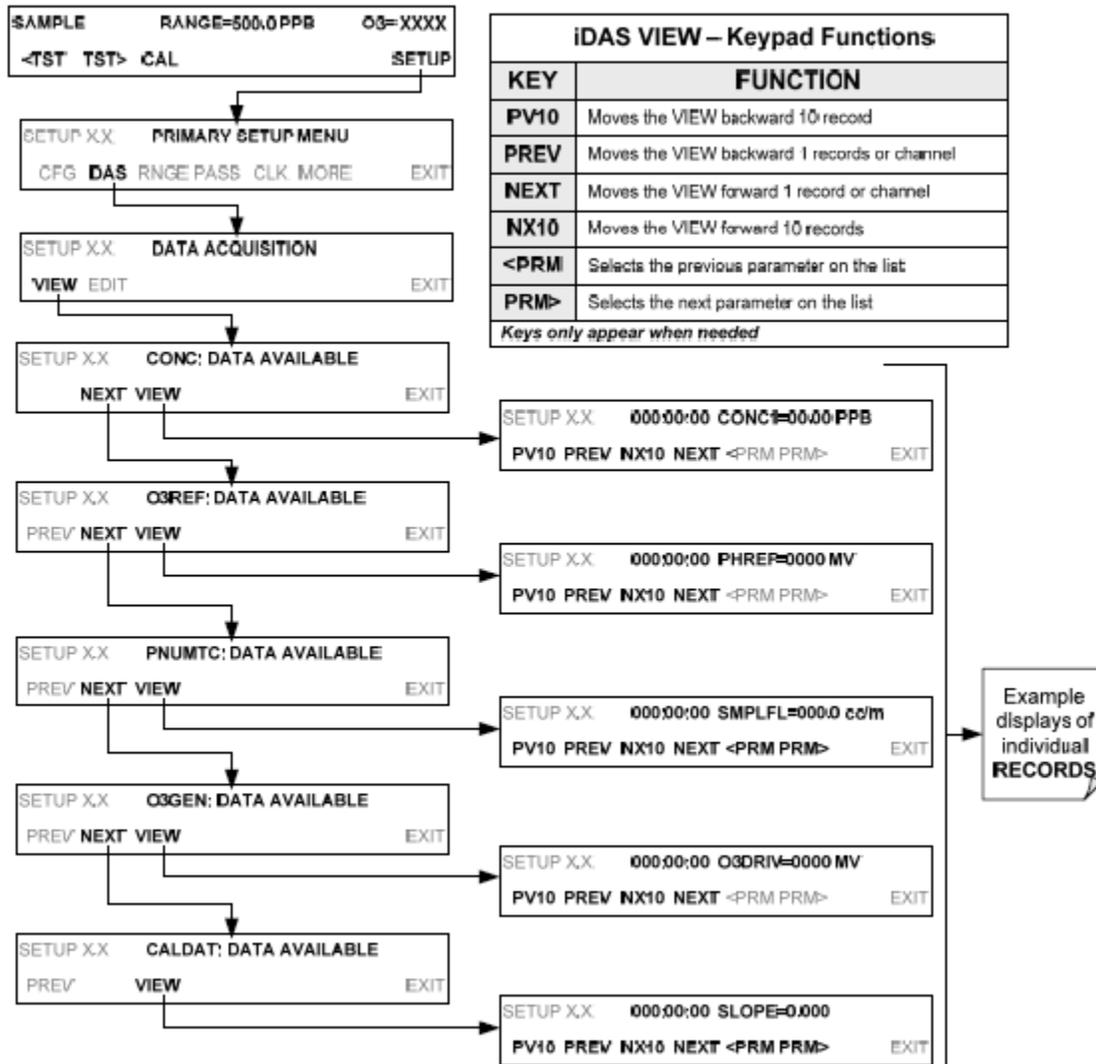
10.6.5 Internal Data Acquisition System Verification

The purpose of this procedure is to ensure that the internal data logging capabilities of the analyzers are functioning properly. The following graphic illustrating the keystroke tree to verify data content in the IDAS is from the 400E manual. Reference the manual on site if a different model is present.

The purpose of the verification is to review the last month of data in the IDAS. Generally, using the PV10 button to move backward ten records is adequate resolution to determine proper IDAS function. If SAMPLE is not present on the top left of the analyzer display, stop and contact senior staff or reference the manual concerning how to return to SAMPLE. Be careful, pressing the wrong button without SAMPLE in the display may recalibrate the instrument.

1. Press SETUP
2. Press IDAS
3. With CONC:... on the top line of the display press VIEW
4. Verify the current concentration and press PV10 occasionally verifying data presence and concurrence until data displays from more than 30 days prior
5. Press EXIT until you return to the main menu.

iDAS data and settings can be viewed on the front panel through the following keystroke sequence.



10.6.6 Leak Check Procedures

The purpose of this procedure is to provide guidance on determining the presence of a leak in the sample stream. The sample stream can consist of the analyzer, a water drop-out, and a sample line. This procedure also outlines how to determine if the sample manifold on a dynamic dilution calibration check system is leaking.

To determine if the sample stream has a leak:

1. Disable analyzer channel on data logger (10.6.1).
2. Select Sample Flow (TST> until shown) and leave displayed on analyzer screen.
3. Cap the sample stream. Either:
 - a. Disconnect the sample line and cap the sample inlet on the back of the analyzer (analyzer leak check).

- b. Cap the end of the water drop-out furthest from the analyzer (water drop-out leak check).
- c. Cap the end of the sample line (sample stream leak check).
4. Monitor the sample flow until a reading of less than 10 cubic centimeters per minute is reached.
 - a. If sample flow (SAMP FL) is reached within 2 minutes and pressure (PRES) is < 10 in-Hg the leak check has passed.
 - b. If sample flow (SAMP FL) is not reached within 2 minutes, and/or the sample pressure (PRES) is > 10 in-Hg the leak check has failed, troubleshoot or seek assistance from site operator.
5. Uncap the sample stream by reversing steps taken in step 3.
6. Enable analyzer channel on data logger (10.6.1).
7. Leave a message for central detailing findings, including leak test conducted, passed or failed, actions taken if failed, and initials (10.6.8).

To determine if the dynamic dilution calibration check system manifold bank has a leak:

1. Using the data logger, energize the solenoid that allows gas to escape to the room (usually labeled as the dump solenoid).
 - a. On an 8832, from the main screen select D>O (Display > Outputs) and scroll to the appropriate digital output. Press C for closed (O will open) – in this case the C and O refer to the circuit and C means “energize” while O means “de-energize”.
 - b. On an 8872, in the Site Node Logger Toolbox, switch to the Digital Outputs tab and click the State button in the row with the Dump Solenoid. The State button will change from OPEN to CLOSED indicating the circuit is energized.
2. On the 700, generate zero air at 2-3 Lpm while watching the pressure needle on the solenoid manifold.
 - a. Press Generate
 - b. Press the species button until “zero” appears (it may read CO/SO2/NO, etc)
 - c. Press Enter
 - d. Adjust the total flow to between 2 and 3 Lpm and press enter
3. When the pressure needle reaches >20 (but preferably less than 30) psi, put the 700 into Standby mode.
 - a. It is normal for the pressure needle on the manifold to drop when putting the 700 into Standby. Use the post-drop number for this test.
4. Watch the pressure needle for 2 minutes. A drop of less than 5 psi over 2 minutes indicates there is no sufficient leak.
 - a. If a drop of <5 psi occurs in 2 minutes, the leak check has passed.
 - b. If a drop of >5 psi occurs in 2 minutes, troubleshoot the manifold or the 700 (the leak could be in either in this test) or contact the site operator.

5. Reverse steps taken in step 1 to de-energize the dump solenoid.
6. Leave a message for central detailing findings, including leak test conducted, passed or failed, actions taken if failed, and initials (10.6.8).

10.6.7 Time Change Procedure

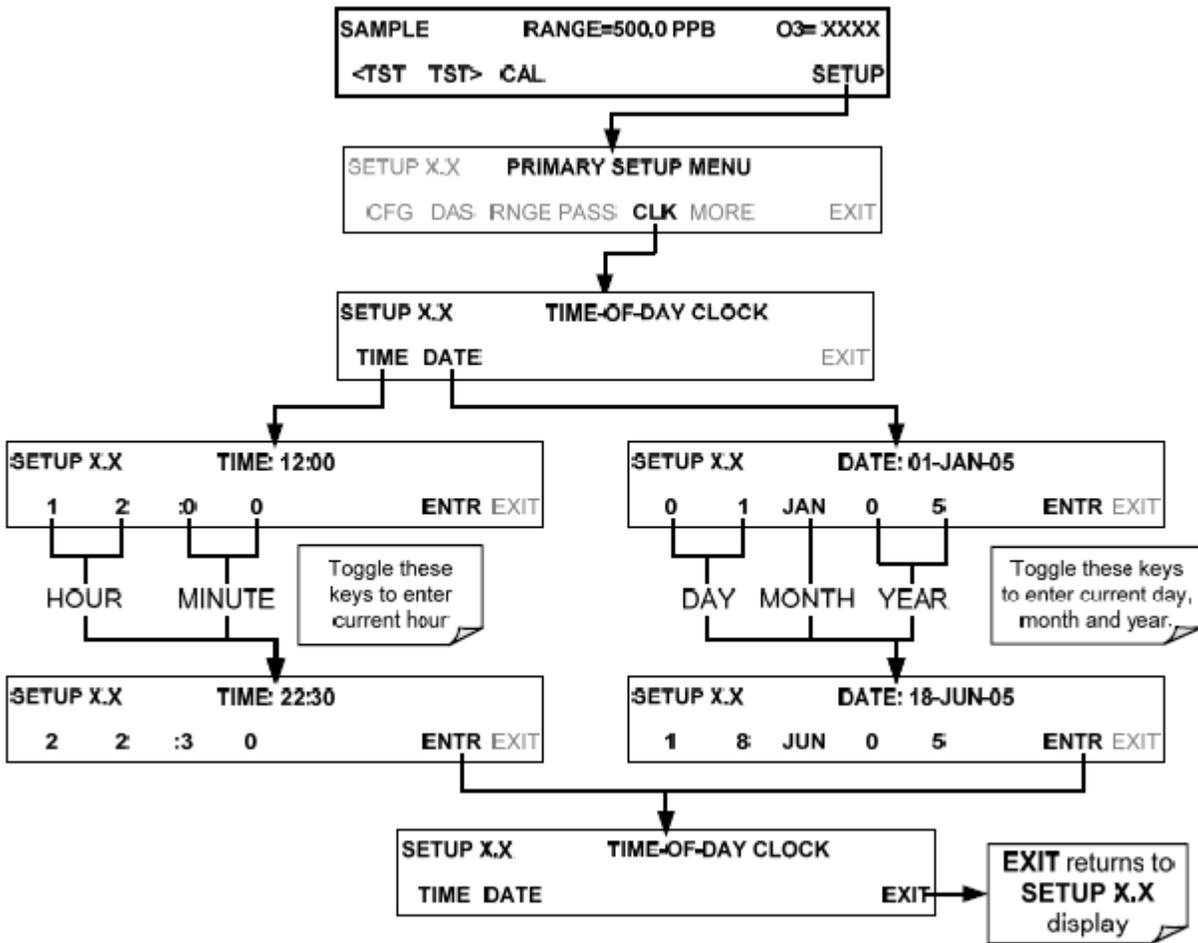
The following describes the standard procedure to change the time on the TAPI ozone analyzer. First compare the analyzer time with the data logger. If it is out of the +/- 2 minute specification then adjust the analyzer time. Check the data logger's time with cell phone time. If it is significantly off, contact the Data Manager.

Important Note! – All times on data loggers and analyzers are to be set to Mountain Standard Time and do not adjust for daylight savings. Data logger and analyzers clocks should appear to be running 1 hour late from March to November (daylight savings time period, clocks move one hour forward). Reference a calendar or other source to determine the exact and end dates of daylight savings.

Analyzer

The following graphic was taken from the TAPI 400E manual. Reference the manual on site if a different model is present. Make sure SAMPLE appears in the top left of the analyzer display. If it does not, stop, and contact senior staff or reference the manual for methodology to return to SAMPLE. Be careful. If the wrong button is pressed while not in SAMPLE mode the instrument could be recalibrated.

1. Press SETUP
2. Press CLK
3. Press TIME or DATE
4. Enter the appropriate time or date
5. Press ENTER
6. Press EXIT until you return to the main menu.



Data logger

If the clock on a data logger is incorrect, there may be more serious issues to consider including data validity and proper operation of the data logger. Contact the Data Manager.

10.6.8 Message to Central Procedure

ESC 8816 or 8832

1. Log in to the data logger.
2. From the top level menu Type **SMC** (**S** Status Menu > **M** Message Menu > **C** Leave a Message for Central) followed by hitting the **Enter** or **Return** key.
3. When the text entry display appears, type in up to 80 characters of text explaining the site visit, followed by your initials, example, “Weekly completed. No problems noted. – JJ” then hit the **Enter** or **Return** key on the keyboard to accept the log entry.

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1. Log in to the data logger using the AirVision™ application.

2. Select the **Home** tab > then **Data Editors** drop down menu.
3. From the drop-down menu select, **LogBook Entry Editor**, and click the round green icon with white “plus” symbol, entitled, **New Log Entry**.
4. Next, click on the **Category:** drop-drop down menu and choose **Logger Message**.
5. Select the drop-down menu item, **Site** and choose the appropriate site, for example, **Welby**.
6. Enter text explaining the purpose of the site visit, followed by your initials. Example, “Weekly completed. No problems noted. – JJ” hit the **Save** button at the top left to save your comments. The application will allow more characters than 80, but they are truncated for the Central computer.

10.6.9 Line change Procedure

1. All sample lines are to be changed annually or as needed if defects are suspected. Through the probe calibration lines are to be changed once every three years or when defects or degradation are suspected. Sample lines should be trimmed by approximately 1’ six months after installation and replaced annually.
2. Disable analyzer channel on data logger (10.6.1).
3. Perform a leak check on the existing sample line to confirm data validity prior to changing the line (10.6.6).
4. Remove the existing line and measure out and cut a length of new sample line of approximately the same length as the old line. Use a designated tubing cutter to cut the Teflon tubing to ensure the cut is straight, at a 90 degree angle to the tubing’s outer wall, and not beveled.
5. Cover or cap the end of the new line prior to installation. This ensures dirt does not enter the line during the installation process. Remove the line cover or cap once the line is installed.
6. Note the final length of sample line.
7. Ensure fitting used in the sample train are made of Teflon. Stainless steel fittings can be used, however, their usage is less desirable and Teflon fittings should be used if available. The usage of dissimilar fitting materials is discouraged because of the potential for thread damage and improper sealing.
8. Clean water dropout manifold (if equipped).
9. Perform a leak check on the new sample line (10.6.6).
10. If the line replaced is a sample line, note sample line length and determine residence time. All residence times must be < 20 seconds. The calculation of residence time requires knowledge of the sample flow rate, length of sample line, additional static volumes such as water dropouts, and the internal cross-sectional area of the tubing. When determining an additional a static volume, such as a water dropout, use only the volume that sees active gas flow. For example, the water catch flask on the bottom of the water dropout should not be included in volume calculations, only the upper portion of the manifold. Below is a table of internal cross-sectional areas for common types ¼ Teflon tubes that can be use in residence time calculations. Sample flow should be measured with a Flow Transfer Standard, as the sensors within the analyzer do not always accurately reflect the correct flow rates.

Table 4. Internal Cross-Sectional Area for Teflon Tubing

Tubing Diameter	ID	OD	ID Area
Thin Wall (3/16 x 1/4)	4.8 mm	6.35 mm	18.10 mm ²
Medium Wall (5/32 x 1/4)	4.0 mm	6.35 mm	12.57 mm ²
Thick Wall (1/8 x 1/4)	3.2 mm	6.35 mm	8.04 mm ²

(Note* 1 cm³ = 1 ml)

Equation 5. Residence Time

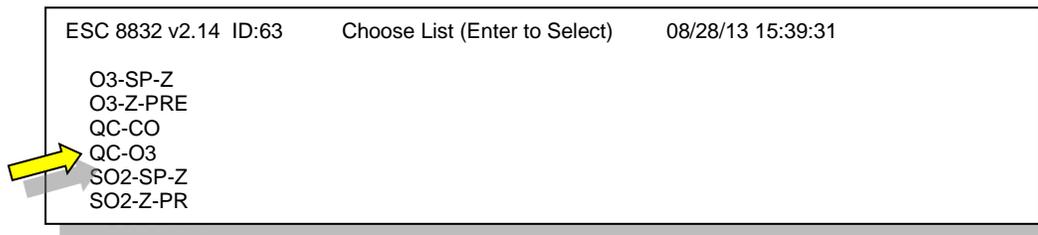
$$Residence\ Time\ (sec) = \left(\frac{\left(\left(\frac{ID\ area\ of\ tube\ (mm^2) \times Tube\ Length\ (in) \times 2.54 \left(\frac{cm}{in} \right)}{100 \left(\frac{mm^2}{cm^2} \right)} \right) + Static\ Vol.\ (cm^3)}{Sample\ Flow\ \left(\frac{cm^3}{min} \right)} \right) \times 60 \left(\frac{sec}{min} \right)$$

11. Enable analyzer channel on data logger (10.6.1).
12. Note line change activities on log sheet.
13. Enter message to central, including the new residence times and/or sufficient information to determine residence time based upon the analyzers flow rate (10.6.8).

10.6.10 Perform Manual Precisions

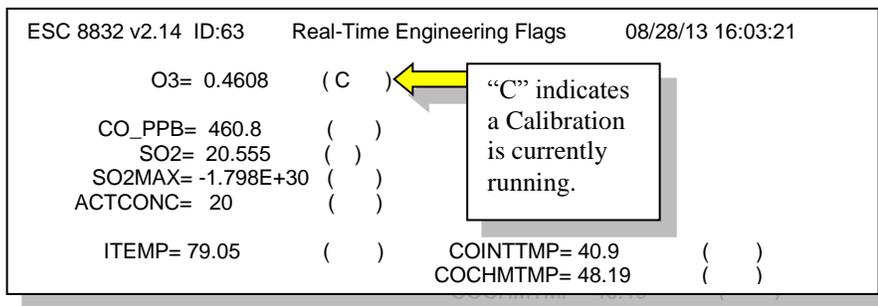
ESC 8816 or 8832

1. Login to the data logger.
2. From the top level menu type **CCS (C Configuration Menu > C Configure Calibrations > S Start a Calibration Program.)**
3. A list of calibration options appears. To run a QC Precision test, select **QC-O3** by scrolling down to that option and hitting the **Enter** or **Return** key.



CCS Menu Option Results

4. Hit the Esc (escape) key twice to get back to the top level menu, then type, DF to verify the QC Precision test was initiated. You should see the letter, “C” next to the O3 reading indicating it is in the calibration mode. After a Manual Precision has run to completion, the new precision value will appear in the RL list.



5. Hit the **Esc** key twice to get to the top level menu then type **RL** to view.

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1. Login to the 8872 data logger.
2. From the **Home** tab select **Utilities > Site Node Logger Toolbox**.
3. When the **Site Node Logger Toolbox** tab appears, select the **Calibration** tab and click on the proper calibration sequence. Each QC manual Precision choice will have QC" in the Sequence Name. If a sequence has "PRE" or "PR" in the name, it is primarily for nightly Performance tests.
4. Select **Start** at the right side of the window, in the "QC-O₃" row to run the QC-O₃ manual Precision. Next, look in the "Phase Name" column to see the current phase (progress) of the calibration. For SO₂ and NO₂ it can take up to an hour or longer to get results. For CO and O₃ it takes approximately 25 minutes.
5. Once the Precision has completed, on the **Home** tab click **Reports**. From the drop-down menu, select **Calibration Results**.
6. When the "Report Criteria" window appears, notice the "Parameter Selection" section. On the keyboard, hold the **Ctrl** button down and click on each parameter for which you wish to see calibration results. Options are, **ACTCONC**, **CO**, **NO**, **NO₂**, **NOX**, and **O3CAL**, and **SO₂**. Select all or a subset depending on the site, available equipment, and result needed.
7. Now look at the "Date Range" section of the window. Modify the "Start Date" and time and "End Date" and time to coincide with the Precisions just run.
8. Finally in the "Calibrations Results" section click on **Generate Report** to see the Precision results, presented in a report format.
 - a. The "Value" column will show the average value collected by the analyzer. The "Expected Value" column contains the value that should have been generated by the calibration equipment. With O₃, the O₃ Cal "Expected Value" column shows the value the O₃ calibration equipment was attempting to generate and the "Value" column shows what it actually did generate. With NO₂, the ACTCONC section "Expected Value" column shows the value the NO₂ calibration equipment was attempting to generate and the "Value" column shows what it actually did generate.
9. Import the Manual QC Precision results into the ZSP Tracking Database. This procedure can be found in the Gaseous and Meteorological Data Validation SOP, Appendix D3.

10.7 Calibration Standards

Refer to the Standards Verification/Calibration SOP in the CDPHE/APCD/TSP QAPP for more detailed information on standards and traceability ozone transfer standards.

11 HANDLING AND PRESERVATION

Atmospheric ozone concentrations are monitored continuously; no discrete samples are collected, handled, or preserved. Therefore a section for sample handling and preservation in this SOP is not required.

12 SAMPLE PRESERVATION AND ANALYSIS

Ozone samples receive no special preparation prior to analysis. Therefore a section for sample preservation and analysis in this SOP is not required.

13 TROUBLESHOOTING

13.1 Environmental Factors

Environmental conditions can play a role in the operational characteristics of analyzers. Some external factors may be constant while others are sporadic in nature. External factors to check include:

1. Is the shelter temperature stable throughout the day?
2. Is vibration from other equipment causing an affect?
3. Is the air conditioner or heater blowing directly on the instrument?

13.2 General Factors

Other factors linked to the shelter and manifold design can contribute to data loss. The sample probe, water dropouts, sample lines and external pump lines should be checked on a regular basis to ensure integrity. Dirty sample lines can artificially suppress readings of reactive analytes. Low sample flow rates causes increased residence times within the sample train and may lead to the premature degradation of reactive species. Sample pumps should be maintained to ensure proper flow rates. Sample line bulkhead fittings to the exterior of the shelter are to be sealed to prevent inside air from exiting the shelter near the sample inlet resulting in a biased measurement. Power to the site is another factor that can contribute to data loss. Incoming power needs to be stable and have a good waveform. All power strips are to be in good working order and power loads are to be balanced across all station outlets.

13.3 Instrument Troubleshooting

Troubleshooting of problems with analyzers is specific to each analyzer and its design. Common problems with instruments include:

1. Low or erratic flow
2. Erratic or noisy readings
3. No readings or off-scale readings
4. No display
5. No output
6. Analyzer completely inoperative

Troubleshooting sections in specific analyzer operation and service manuals, located at each site or in the APCD office, should be consulted to assist in resolving instrument problems.

Chapter 12 outlines troubleshooting techniques in the TAPI 400E manual. Troubleshooting techniques for the data logger and remaining sample system, including any external solenoid manifolds and calibration systems, are the purview of their respective manuals and the experience of qualified operators.

14 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION

Originally, ink-pen strip chart recorders were used by the APCD as a primary record of data from air monitoring instruments. Hourly averages were then hand-interpreted from these charts. Today, due to advances in data storage and retrieval systems, these ink-pen strip chart recorders are no longer in use. Instead, all data are now collected, stored, and retrieved digitally from data loggers. The terms data logger and onsite data acquisition system are used interchangeably throughout this SOP.

14.1 Data Acquisition

All data is collected, stored, and retrieved digitally from data loggers. The terms data logger and onsite data acquisition system (DAS) are used interchangeably throughout this SOP.

14.1.1 Primary Onsite Data Acquisition Systems

The APCD employs three different models of onsite DAS in the operations of its air monitoring network. These are the ESC 8816 data logger, the ESC 8832 data logger, and the Agilaire 8872 data logger. The 8816 data logger is the oldest type of data logger in the network and is a predecessor to the 8832 and 8872 data loggers. See Section 8.1.4 for a more detailed description of these data loggers.

14.1.2 Secondary Onsite Data Acquisition Systems

The APCD uses a backup data acquisition system to provide backup data in case of failure of the primary systems. The backup data acquisition system is the analyzer based on-board data acquisition systems that are unique to each manufacturer. In the event an on-board data acquisition system is not available, a digital strip chart recorder can be used. Internal data logging is available on the newer Thermo and TAPI analyzers. A description of these secondary data acquisition system is as follows.

Teledyne iDAS System

The TAPI internal data acquisition system (iDAS) is available on all TAPI analyzers. The non-volatile memory retains the data even when the instrument is powered off or the firmware is updated (back up before update advised). Access to the iDAS is available either through the front panel or the APICOM remote interface. The remote interface allows for data to be automatically downloaded to a remote PC. The iDAS is flexible in the parameters stored and triggering events to initiate data storage. The maximum iDAS data storage is limited to the analyzers available memory and the number of data parameters and channels.(Teledyne-Monitor Labs, 2009).

14.1.3 Central Polling System

The APCD uses the AirVision software package for its central data management system. “AirVision is a centralized data management and polling software system that is used to acquire, edit, validate, analyze, and report air quality data. AirVision supports open data acquisition and data imports thru modular drivers that can be added to provide connectivity to a data source. The system has combined data editing and quality control tools that can be utilized in evaluating and validating data in the post-processing environment. The post-processing environment allows user control of the data from the management of raw data within the server environment through the exporting of validated data through built in reports or for external statistical evaluations and reporting. A more detailed

description of this application can be found in APCD's Data Logger and Central Polling Standard Operating Procedure." (Agilaire, 2009)

Central Polling Daily Tasks

1. Task managers within Air Vision polls data from remote air quality monitoring sites at the top of each hour, at a minimum. Some sites may be polled at a greater frequency depending upon data needs. Data from each site is stored in a SQL database and made available for review and analysis after polling has been completed.
2. Ambient data on the AirVision Central polling computer is reviewed every business day in the morning, the previous 24 hours (or 3 days on Mondays) worth of data is reviewed for completeness and accuracy. This data review is used to determine if a physical site visit is required.
3. Low level (precision) and high level (span) test gas sequences are run on alternate days. The precision and span level tests are followed by a zero test and a two-minute recovery period. The results are reviewed each morning and plotted on control charts. It is the responsibility of one individual within TSP to review the daily Zero/Span results, plot them on the control charts, and notify the technician responsible of any out of control condition. "Out of control" is defined as:
 - a. trending toward warning limit as defined on the control chart
 - b. points plotted exceeding the warning limit
 - c. points plotted exceeding the action limit as defined on the control chart

14.2 Calculations and Data Reduction

As mentioned above, data collected on a DAS are available as soon as the averaging period is complete. Data are polled automatically via modems (analog phone, wireless cellular, or DSL) by the Central polling computer hourly. If needed, sub-hourly polls or remote checks can also be performed.

Data from the continuous air monitoring equipment are generally stored at hourly and minute resolution averages. The software on the Central polling computer stores the downloaded minute and hourly averages and is capable of aggregating these averaging intervals into larger averaging intervals such as 8-hour or 24-hour averages.

A more detailed description of the DAS is given in the CDPHE/APCD/TSP QAPP and in the manufacturers' manual.

14.2.1 Zero Adjustment Methods

Ozone analyzers base line response, as measured by the nightly performance checks, can change over time at a significant magnitude relative to the analytical system's method detection limit. Base line shifts can occur for numerous reasons, these reasons can include changes in lamp intensity due to normal aging, accumulation of dirt and contaminants in the sampling systems, and detector drift. A drifting baseline does not necessarily necessitate the invalidation of data. If the drift is small and reproducible over the course of several days, then post processing of data to remove the baseline bias can be performed. A more detailed description of APCD's zero adjust methods can be attained in APCD's Gaseous and Meteorological Data Validation SOP, Appendix D3.

15 COMPUTER HARDWARE AND SOFTWARE

The data acquisition system (DAS) used by the APCD/TSP for collecting data from continuous air monitors is generally described in Section 14 and in the CDPHE/APCD/TSP QAPP.

The primary DAS Central polling computer is a Windows based server. The Airvision data system on this server provides for polling the sites using dial-up modems and broadband access for data. A printer is attached to the system for printing out reports. The primary repository for data, and the engine for information assembly, is the Microsoft SQL Server operated and maintained by the Governor's Office of Information Technology. The CDPHE/APCD/TSP maintains a database owner position responsible for logical maintenance of the data system.

The 8872 is a Windows based PC with attached monitor, keyboard, and mouse. The 8832 and 8816 are proprietary hard-circuit systems that may or may not have attached screens and keyboards. Sites usually include other computer hardware and software such as switches, RS232 cables, Ethernet cables, and analog cables.

16 DATA MANAGEMENT AND RECORDS MANAGEMENT

16.1 Data Management

Data are generated from the analyzer at intervals internally set, ranging from an averaging time of 20 seconds to 5 minutes. The data is collected by the on-site data logger as near-real-time data (often every 3 to 10 seconds) and is aggregated into 1-minute averages, which are in turn aggregated into 1-hour averages. Some data streams may be stored at a user defined third averaging interval. Note the capacity of the on-site data logger is limited to three time-base averaging intervals. The Central polling computer collects these averages routinely.

For reporting purposes, other averaging intervals are derived, such as an 8-hour moving average for ozone. In these cases, the data is aggregated by the Central polling computer for the purpose of the report and are often not stored independently. The Central polling computer connects to a SQL server, which is maintained, and backed up, by the Office of Information Technology.

Data are sent to the EPA centralized Air Quality System (AQS) database for long-term storage. The APCD submits both hourly average data to AQS. Additionally, the data are stored and archived by the APCD/TSP in both electronic and hard copy formats. Monthly electronic data files and related printed material packets (maintenance forms, etc.) are produced.

A more detailed description of the data management is given in the Gaseous and Meteorological Data Verification SOP, Appendix D3 in the CDPHE/APCD/TSP QAPP.

16.2 Records Management

Continuous ambient air monitoring data are archived both in electronic and hard-copy formats. Electronic data and calibration files from the primary data acquisition system are archived. Data from the backup electronic strip chart recorders, where used, are downloaded annually and archived on a computer hard drive. Hard copy printouts of the data are kept at the APCD office for a minimum of three calendar years before being sent to an off-site archive/storage facility.

17 QUALITY ASSURANCE AND QUALITY CONTROL

The APCD has in place robust Quality assurance (QA) and quality control (QC) programs to ensure all methods and procedures are done accurately and systematically to ensure data quality. QA and QC are two terms commonly discussed, but often confused. Quality assurance refers to the overall process of ensuring that the data collected meet previously stated Data Quality Indicators (DQI) and associated measurement quality objectives (MQOs). The principal DQIs are accuracy, precision, bias, representativeness, completeness, comparability, and sensitivity. The principal MQO's are parameter specific and are listed in CDPHE's QAPP. Quality control covers specific procedures established for obtaining and maintaining data collection within those limits. Field staff are predominantly responsible for the implementation of QC procedures, however, data attained from these procedures is utilized in QA evaluations.

17.1 Quality Assurance

The goal of the quality assurance program is to control measurement uncertainty to an acceptable level through the use of various QC and evaluation techniques. The entire Quality Assurance effort put forward by the APCD is too large to include here. The scope of this SOP will describe efforts taken by site operators and data validation personnel to ensure the quality of the data collected meets standards set forth in various sections of the *Code of Federal Regulations*. For a complete description of the QA and QC process undertaken by the APCD, see the appropriate quality assurance appendices in the QAPP. Two of the most significant Quality Assurance procedures are described below.

17.1.1 Audits

Audits are evaluation processes used to measure the performance of effectiveness of a system and its elements. APCD quality assurance staff performs two types of audits. These audits are performed at a frequency as described in APCD QAPP.

Systems Audits - A systems audit is an on-site review and inspection of an ambient air monitoring program or air monitoring site to assess its compliance with established regulations governing the collection, analysis, validation, and reporting of ambient air quality data.

Performance Audits - A performance audit is a type of audit in which the quantitative data generated in a measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst, laboratory, or measurement system. Two types of performance audits discussed below.

- **Monitoring Organization Performance Audits** - These performance audits are used to provide an independent assessment of the measurement operations of each instrument being audited. This is accomplished by comparing performance samples or devices of “known” concentrations or values to the values measured by the instruments being audited.
- **National Performance Evaluation Program (NPEP)** – These performance audits are implemented at the federal level although some programs may be implemented by the monitoring organizations if certain requirements are met.

17.1.2 Data Quality Assessment

Data Quality Assessment is used to assess the type, quantity, and quality of data in order to verify that the planning objectives, Quality Assurance Project Plan components, and sample collection procedures were satisfied and that the data are suitable for its intended purpose. Data Quality Assessment is a five-step procedure for determining statistically whether or not a data set is suitable for its intended purpose. This assessment is a scientific and statistical evaluation of data to determine if it is of the type, quantity, and quality needed and is performed annually by quality assurance staff to check if objectives were met.

17.2 Quality Control

Quality Control is the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the EPA. Quality control includes establishing specifications or acceptance criteria for each quality characteristic 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.

Quality control refers to procedures established for collecting data within pre-specified tolerance limits. These pre-specified tolerances are defined in the Measurement Quality Objectives as defined in APCD’s QAPP. While all QC procedures are important, the most significant procedure employed by the APCD is the routine measurement of a known test gas by gaseous analyzers. All procedure documented in this SOP are QC procedures because they allow the analytical systems to continue running in exceptional condition and serves to minimize out-of-control conditions as defined by APCD MQO’s. By definition, the creation and use of this SOP is a QC function. All QC procedures

are described in Sections **Error! Reference source not found.** and 9.1 of this SOP. Three of the most significant QC procedures are described below.

17.2.1 Performance and Precision Tests

A primary quality assurance task carried out by site operators is the performance of routine QC checks. The APCD performs two types of QC checks at designate precision level test gas concentrations. These two tests are called Performance checks and QC Precision checks. The Performance check is an automated performance test that is performed nightly and is used to evaluate the health of the sample system. The QC Precision check is a manual evaluation performed by qualified personnel who can attest to their validity and are reported to the EPA. The former are not reported to the EPA to prevent an artificial bias introduced by sample pools of different size. Sites operated by subcontractors are not required to manually perform QC Precision checks. Instead, one performance check is selected at random from each two-week period to satisfy the QC Precision check requirement. The performance check is selected by APCD personnel and is included with the APCD-operated QC Precision check submission to the EPA's AQS.

For instructions on performing a manual QC precision test, see Section 10.6.10.

17.2.2 Calibrations

Calibration of an analyzer or instrument establishes the quantitative relationship between the actual value of a standard, be it a pollutant concentration, a temperature, or a mass value, and the analyzer's response (chart recorder reading, output volts, digital output, etc.). This relationship is used to convert subsequent analyzer response values to corresponding concentrations. Once an instrument's calibration relationship is established, it is checked at reasonable frequencies to verify that it remains in calibration. It is the goal of APCD to perform calibrations on all analyzers quarterly, however, circumstances may require calibrations be performed at the longer frequency of every 6-months. A 6-month calibration frequency still meets EPA recommended calibration frequency criteria.

For instructions on performing a calibration, see Section **Error! Reference source not found.**

17.2.3 Documentation

Documentation is an important component of the QC system. Extensive certification paperwork and log sheet must be rigorously maintained for procedures, standards and analyzers. APCD takes special care to prepare and preserve electronic and paper backup copies of all site log sheets, ambient sample data, QC data, and calibration data. All data and supporting documentation should be held on-site for a minimum of three calendar years then sent for offsite archive. See Section 16 for additional information.

18 REFERENCES

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Ozone Calibration Setup

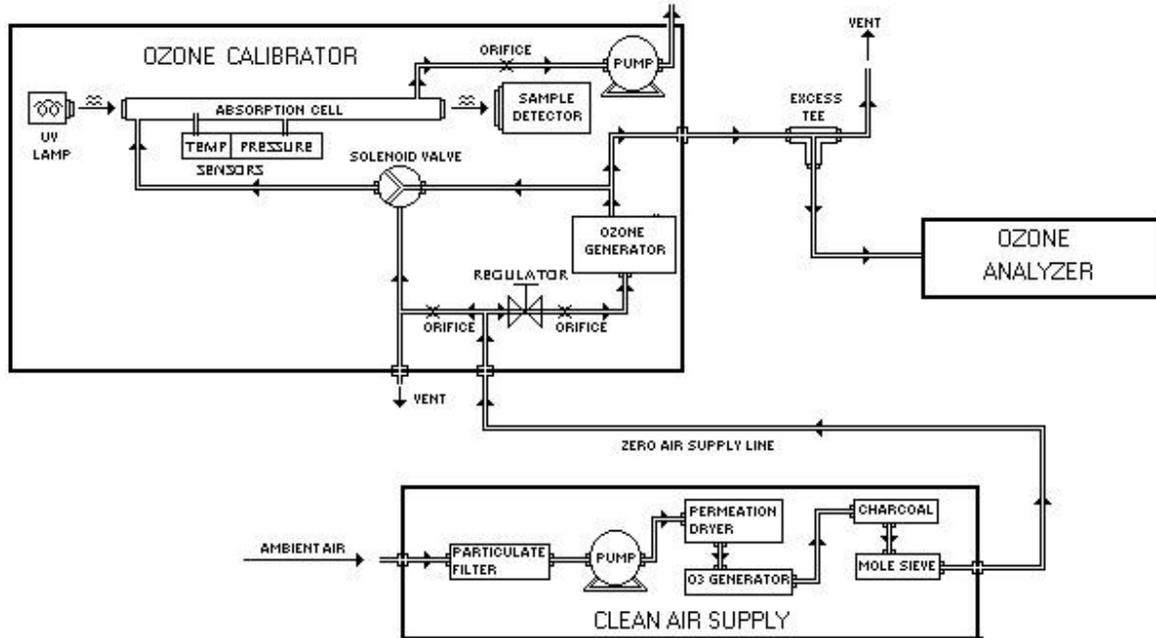


Figure 1. O₃ Calibration Setup

OZONE

API 400/400A/400E

_____ OF _____

Calibration \ Audit: AA ET SC

STATION _____ TIME OFF LINE _____ / _____ DATE _____
 O3 MEAS _____ mV O3 REF _____ mV S/N _____ Last AA/Cal _____
 IZS REF _____ mV PRES _____ "Hg Performed by _____ Lk chk _____
 SMPL T _____ C ANA LAMP T _____ C Sample flow, prior _____
 IZS LAMP T _____ C BOX T _____ C Current flow _____ / _____
 DCPS _____ mV TEST _____ mV D.A.S. _____
 SLOPE _____ / _____ OFFSET _____ / _____ (before/after adj.)

CALIBRATOR Setting	PPM OUT	DATA AQ. SYS.			DVM	CHART			DISP	COMMENTS
		read	corr	%re		read	corr	%re		
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____

SLOPE = _____ CORR. COEF. = _____ Linear regression
 (0.500 ppm) X Y %RE
 INTCP = _____ %REL.ERROR F.S. = _____ % .500 _____
 .400 _____
 COMMENTS _____ .300 _____
 _____ .200 _____
 _____ .100 _____
 _____ .050 _____

Figure 2. Ozone Calibration/Audit Worksheet API 400/400A/400E

OZONE

STATION _____ DATE _____

BAROMETRIC Press. "Hg _____ / 29.92 = _____ atm.

CALIBRATOR S/N _____

CSI Photocal

API 401

TEMP _____ C PRESS _____ atm.
 Idk _____ Io _____
 AIRFLOW Total _____ Excess _____
 Rotometer _____
 ZERO AIR _____
 _____ "Vac _____ Psig

Pres _____ "Hg Reg _____ "Hg
 Samp Fl _____ ccm Box T _____ C
 Samp T _____ C DCPS _____ mv
 Alamp T _____ C
 O3 Fl _____ Lm
 Olamp T _____ C

CALIBRATOR DISPLAY

ANALYZER DISPLAY

'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____
'	'	'	'	'	'	'	X=_____	'	'	'	'	'	'	'	'	X=_____

Figure 2 (continued)



COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

Air Pollution Control Division - Technical Services Program
 Ozone, Carbon Monoxide, Sulfur Dioxide Calibration Form



Site Name: _____													
Site Info.				Date Time				Calibration Equipment Info					
AQS ID: _____				Date (mm/dd/yy) _____				Calibrator Type: _____					
Parameter: _____				Time (hh:mm) _____				Calibrator SN: _____					
Analyzer Type: _____				Prev Cal. Date (mm/dd/yy) _____				Calibrator Cert Date: _____					
Analyzer SN: _____				Calibrator's Initials: _____				Cert. Slope (m): 1.00000					
Site Precision Source Info.								Cert. Intercept (b): 0.00000					
Source Type: _____								Calibration Gas Info.					
Source SN: _____								Bottle SN: _____					
Conc.: _____								Conc.: _____					
Exp. Date: _____								Exp. Date: _____					
Pre-Calibration System ZSP Evaluation						Post-Calibration System ZSP Evaluation							
Pre-Calibration Analyzer Slope: _____						Post-Calibration Analyzer Slope: _____							
Pre-Calibration Analyzer Intercept: _____						Post-Calibration Analyzer Intercept: _____							
Set Point	Source Conc.	Display Conc.	DAS Conc.	Display % Diff	DAS % Diff	Set Point	Source Conc.	Display Conc.	DAS Conc.	Display % Diff	DAS % Diff		
Zero						Zero							
Span						Span							
Precision						Precision							
Pre-Calibration Points						Post-Calibration Points							
Set Point	Conc. Out Conc.	DAS Conc.	Conc. Adj Conc.	DAS % Diff	Best Fit DAS Conc.	Best Fit (% RE)	Set Point	Conc. Out Conc.	DAS Conc.	Conc. Adj Conc.	DAS % Diff	Best Fit DAS Conc.	Best Fit (% RE)
Zero							Zero						
Level 1							Level 1						
Level 2							Level 2						
Level 3							Level 3						
Level 4							Level 4						
Level 5							Level 5						
Level 6							Level 6						
Level 7							Level 7						
Pre - Regression Results						Post - Regression Results							
Slope: _____						Slope: _____							
Intercept: _____						Intercept: _____							
R2: _____						R2: _____							
Comments: <div style="background-color: #e0ffe0; height: 100px; border: 1px solid black;"></div>													

Figure 3. Calibration Report

