Air Pollution Control Division

Technical Services Program

APPENDIX GM3

Standard Operating Procedure for the Determination of
Ozone in Ambient Air – 2BTech Analyzers

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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) special study sites. 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 2bTech M205 analyzers and M306 Ozone calibrator.

1.1 Method Overview

Beginning in the summer of 2014 the APCD/TSP developed and deployed temporary autonomous ozone analyzers to expand the breadth of the ozone monitoring program. These 2bTech M205 analyzers that are operated under this SOP are intended for special study usage and not for regulatory type monitoring. This type of operation is limited in scope and does not meet the same quality control requirements as are required for regulatory monitors.

Ozone is measured continuously using 2B Technologies (2BTech) Model 205 ozone monitors, which are designed to enable accurate and precise measurements of ozone with a precision of 0.0010 ppm (1.0 ppb). The 2BTech Model 205 is light weight and has a low power consumption relative to conventional instruments and is therefore well suited for long-term monitoring at remote locations where power is limited or unavailable. These portable monitors are transported to monitoring locations and operated from a standard 12-V battery charged by a 90-W solar panel. Analyzers are programmed to sample at 1-minute intervals and all data were stored on a data logger (Campbell Scientific) that also recorded air and instrument temperature and battery power. The monitor, battery, and data logger were enclosed in weather-proof instrument shelters mounted along with the solar panels between two T-posts, which were installed about 80 cm apart. Sample inlets, which consisted of Teflon particle filters and Teflon tubing, are located 2 meters above the ground surface. A 2BTech Model 306 ozone source is used to calibrate and perform performance checks on instruments during their installation and during the monthly site visits, respectively.

The Model 205 analyzer operates on the principle of UV absorption. This method has long been used for measurements of atmospheric ozone with high precision and accuracy. The ozone molecule has an absorption maximum at 254 nm, coincident with the principal emission wavelength of a low-pressure mercury lamp. Fortunately, there are few molecules found at significant concentrations in the atmosphere that absorb at this wavelength. However, interferences, such as organic compounds containing aromatic rings, can occur in highly polluted air. Mercury vapor can be a significant interference inside buildings where mercury spills have occurred in the past and in the vicinity of certain mining operations.

1.2 Format and Purpose

This appendix is written for analysis that does not result in data stored in EPA AQS.

The sequence of topics covered in this ozone method follows EPA's 2007 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

General site operation is homogenous in several respects, regardless of analyses being performed. Operations that could be applied to any monitoring shelter are included here. Methods for site operation and maintenance are described below and in appropriate companion SOPs and manuals.

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

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

where:

T = Transmittance of light through the gas to the detector

I = light intensity after absorption by ozone

I_o = 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 (I_o). 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

For a thorough discussion of safety protocols please see the CDPHE Safety Manual available at https://sites.google.com/state.co.us/cdpheintranet/employee-resources/employee-safety. Note that a CDPHE login is required. Information on incident reporting and first aid are provided in the CDPHE Safety Manual. Excerpts below are sections from that manual that pertain directly to site operation.

Walking and Working Surfaces

PPE:

Use footwear appropriate for the surface you are walking or working on.

Slip-on traction control devices may be used as well.

Sidewalks, walkways:

Snow and ice should be cleared as much as practical before the majority of employees arrive on site to allow safe access.

Ice/Snow melt and/or sand may be used to provide additional traction.

Trails, roads and other passageways:

Do not attempt to walk or drive across flooded roadways or trails where the depth is unknown.

Bridges:

Do not attempt to cross bridges that appear to be unsafe, especially in vehicles.

Housekeeping

Good housekeeping is a means of prevention of personal injury. Good housekeeping leads to efficiency of work within the space. The following housekeeping and storage rules must be followed:

Aisle ways and exit routes shall be kept clear and unobstructed.

All indoor walking surfaces shall be reasonably free from oil, water, trash, tripping hazards, etc.

Materials that have exceeded their shelf life or no longer meet original specifications should be properly disposed of.

Cabinets or files drawers above head-height and window sills shall not be used for storage.

No material should be stored on the top surface of any storage cabinet, locker, or other structure that is not specifically designed for this purpose and provided with a protruding ledge to prevent falling of stock.

In no case should storage exceed six feet in height; for buildings equipped with sprinkler systems for fire suppression, no material should be stored within 18 inches of a sprinkler head.

Heavy objects should never be stored above waist height or on elevated decks, unless mechanical lifting equipment is used.

Dollies or wheeled carts should be available to move materials.

Adequate lighting should be provided for reading labels and identifying materials.

Every way of exit should be continuously maintained free of obstructions or other impediments to immediate use. Exits shall be clearly marked and adequately lit.

Free, unobstructed access should be maintained to electrical panels, safety disconnect switches, and fire extinguishing equipment or alarms. A minimum 18 inch clearance should be maintained.

All places of employment, passageways, storerooms, and service rooms shall be kept clean and orderly and in a sanitary condition.

The floor of every work area shall be maintained in a clean and, so far as possible, a dry condition. Wet floors shall either be dried or reported to building maintenance. Cords, hoses and tools shall not be left on floors when not in use and shall not be run across ANY walkways.

Portable Ladders

Step stools should be used as needed to access stored items. If items cannot be accessed safely by the employee, or if a step stool is not available, employees should contact their supervisor or building operations for assistance.

APCD uses telescoping ladders at sites where a ladder is not available. This ladder should be extended a minimum of three rungs above the level being climbed to.

Fire Prevention

Smoking is not allowed in any state building or vehicle. Smoking is only allowed in designated outdoor smoking areas. Do not throw matches, cigars, cigarettes, etc., into wastebaskets – use only ashtrays made of non-combustible material.

Follow all fire ban rules as defined by local authorities.

Fire prevention procedures**:**

- Store all flammable liquids in approved safety containers with flame arrestors and spring actuated caps.
- Keep acids and bases or oxidizers in separate cabinets.
- Store poisons separately.
- Keep fire equipment, such as fire extinguishers, accessible at all times.
- Never use oil or grease on oxygen equipment.

Fire extinguishers

Fire extinguishers must be immediately accessible by the responding fire department. They should not be used by employees on the CDPHE campus.

Fire extinguishers will be mounted so that employees can easily locate and identify them. Typically signage is used indicating the location of extinguishers. Fire extinguishers may be installed in vehicles for field use in lieu of a fire extinguisher at each monitoring shelter. They shall be maintained in a fully charged, operable condition.

Discovering a Fire

Call 911

Alert other persons in the immediate hazard area. Notify the supervisor and/or emergency services.

Working Alone / Isolated Workers

Isolated workers must ensure their safety by letting someone else know where they are. Traveling workers should leave word with their supervisor or a co-worker of their intended destination and expected time of arrival and return, with contact information for the destination if available. At a minimum, contact another person periodically to confirm your location, if you remain isolated. If your destination changes, advise your designated contact your new location as soon as possible. When traveling by vehicle, practice defensive, courteous driving habits. Try not to drive at night, especially at the end of a long field trip when being tired might be a factor. Carry a change of clothing, a coat, food and water, and a first aid kit. Be prepared mentally and physically to survive in a bad situation.

Additional precautions are necessary for many employees, who routinely work alone in remote locations.

First, assess the hazards including ease or difficulty of motorized access, likelihood of radio or cell phone coverage, and equipment or tools to be used. Consider the likelihood of fatigue, and the legality to perform the task alone. For example, it is illegal to enter a permit-required confined space alone. Consider the ability and tools necessary if the vehicle breaks down or gets stuck, and adverse weather conditions.

Have a backup method to let someone know your location before you are out of reach.

In addition to items listed above, employees are encouraged to carry maps, a compass, and/or a GPS unit (with spare battery) and know how to use them. If going to the backcountry during hunting season, wear blaze orange.

If the designated contact does not hear from the isolated worker on schedule, that person should attempt to contact the person, either visually or by radio or phone. If unable to contact the person, notify at least one other person and begin a search.

Lifting and Material Handling

Store heavy hand carried items at heights where little or no lifting or reaching is required to move them. Do not lift more than 50 pounds or, if more, you must have assistance. Do not unnecessarily place objects on the ground if they must be picked up again soon after. Minimize your risk of injury by getting proper exercise and building up leg and abdominal muscles. When lifting, use the strong leg muscles to do most of the work. Do not try to hold a heavy object away to avoid getting dirty. Lift and carry items close to your body with a towel or similar object to protect your clothing. Use hand carts or dollies to move heavy objects. Get help to lift or move heavy objects. Plan your movements. Be sure shelves will support the weight of objects placed on them.

Vehicle Safety

All field personnel operating a state of Colorado fleet vehicle must read and sign the Vehicle Safety portion of the CDPHE Safety Manual. Transportation of large gas cylinders (described below) requires the use of an appropriate vehicle with bottle straps and/or stands, and the bottles must be in a separate compartment from the passenger. An exception to the separate compartment requirement may be made for small calibration gas cylinders.

Chemical Hazards:

Purafil is used in the zero air generators to remove nitrogen oxide from air. Sodium permanganate is a component within Purafil and should be handled with care. Sodium permanganate is a known irritant and care should be taken to avoid exposure to open wounds, burns, or mucous membranes. Prolonged exposure (usually over many years) to heavy concentrations of manganese oxides in the form of dust and fumes, may lead to chronic manganese poisoning, chiefly involving the central nervous system.

Condenser coil cleaner is used during HVAC maintenance and cleaning. Read, understand, and respect all indicated safety precautions and directions on the cleaner label.

Gas Hazards

Carbon monoxide (CO) is a colorless, odorless and tasteless gas. It is a hazardous compound as it combines with hemoglobin and reduces the oxygen carrying ability of the blood. Carbon monoxide is produced by the incomplete combustion of fossil fuels. In major urban areas of developed nations, its major source is the exhaust from light-duty motor vehicles.

As CO is a poisonous gas, calibration source tanks and delivery systems, or any other calibration span gas, should be vented to the atmosphere rather than into the shelter or other sampling area. The majority of APCD's sites vent inside the shelter. The concentrations vented by the delivery systems are low and below the OSHA action levels of 50 ppm. However if the operator experiences lightheadedness, headache or dizziness, the operator must leave the area immediately and limit exposure to CO by getting fresh air every 5 to 10 minutes. Shelters that monitor for CO, SO2, and NO and their oxides use compressed gas cylinders as the quality control standard. Compressed gasses require placards and pose the primary threat of oxygen displacement (particularly SO2 and NO which are balance nitrogen). Regulators and calibration gas supply lines should be regularly inspected for leaks and repaired, if needed, immediately.

Transportation of compressed gas cylinders must follow DOT guidelines. Use of an oxygen sensor while transporting cylinders is highly recommended.

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. In the event that it is necessary to clean the optical bench, be careful to avoid damaging the interior of the sample chamber. In addition, some instruments have a series of mirrors that deflect the light in order to increase the path length. The mirrors are aligned at the factory. If the mirrors become misaligned, the IR light beam will not be directed to the detector. Use extreme caution when cleaning or servicing the sample chamber(s). In addition, the mirrors are very fragile. Avoid dropping the instrument. This may damage, misalign or crack the mirrors and cause expensive repairs. Clean the optical bench carefully to avoid damaging the interior of the bench, cleaning should be performed only if needed. Use cleaning procedures outlined in the manufacturer's instruction manual. Avoid touching the mirrors unless cleaning is absolutely necessary. Refer to the appropriate analytical SOP for cautions about analyzers and meteorological equipment.

2. Keep the interior of the analyzer shelter 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. For example, the permeation dryer (48i models) may rest upon parts that vibrate, such as the air pump.

6. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts.

7. Use and transport of cylinders are a major concern. Gas cylinders may contain pressures as high as 2000 pounds per square inch. Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and the valve breaks off, the cylinder can become explosive or a projectile. It is

strongly recommended that all agencies have material safety data sheets (MSDS) at all locations where CO cylinders are stored or used. MSDS can be obtained from the DOT or from your vendor.

8. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders.
9. Sample gas should be delivered to the instrument at atmospheric pressure.
10. It is possible (and practical) to blend other compounds with CO. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders.

6 INTERFERENCES

In order to measure in the ppb range, it is important for the detector to be operated at a very stable temperature. To obtain a stable baseline, the temperature of the detector and optical bench must be maintained within ±1.0 degree Celsius (°C) of the set value. Interferences are physical or chemical entities that cause measurements to be higher (positive) or lower (negative) than they would be without the entity. Many analyzers have interference from water vapor. Water absorbs very strongly across several bands of IR spectra.

6.1 O_3 Interferences

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 new 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 interferents 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 and as messages to Central.

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. 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.

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^{o}C (79-81^{o}F), if possible, in areas where dew point temperatures are high. Outdoor ambient air dew point temperatures can exceed 27^{o}C (80^{o}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. Monitor the internal shelter temperature 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^{o} C (5-7^{o} F) above ambient temperature. Use a thermostat 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.

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.

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

8.1 Monitoring Equipment

8.1.1 Instrument Shelter

A weather-proof Hammond gray fiberglass enclosure (or similar) contains the analyzer, power system, data logger, modem, and zero-air charcoal container. A CPU style fan near the top and a protected opening below the battery allow for air flow. The fan is actuated if the internal temperature gets warm enough to merit the power consumption. Figure 1 shows the layout of the enclosure. Note that the modem is moved to the inside of the enclosure lid, an inch or so above the bottom of the inside of the enclosure. This is to keep any potential water from getting into the modem. The data logger and battery (though the battery is sealed) are also above the bottom of the enclosure. Water has been observed to enter the enclosure during severe storms.

The solar panel is wired into the voltage regulator following labeling on the voltage regulator. The battery should be wired to the voltage regulator again following the labeling. Power for all internal components should be pre-wired. The circuitry is protected by two 2-amp tube fuses.

Teflon tubing should be used for all connections from the sample port on top of the enclosure to the sample inlet. The sample inlet should have a filter holder with a filter at the end of the line. The sample inlet should be set so that it points downward preventing water from entering the sample stream.

The enclosure is based on a 12 volt system including a solar panel, a voltage regulator, and a lead acid storage battery. Under normal summer conditions the system shown is sufficient to run all equipment therein including modems that have limited connectivity, thereby increasing their common draw. Initially the shelters have been configured as seen in Figure 2 where the solar panel is above and opposite the shelter. However, when possible, the solar panel should be used as a canopy for the enclosure by placing them both on the same side of the posts. This will reduce the amount of dirt collected on top of the enclosure and may reduce the amount of space for birds and other nuisance animals to congregate.

Two t-posts are to be pounded into the ground at least one foot, at a width that matches the mounting hardware on the back of the enclosure. Then the enclosure is slid onto the posts and tightened into place, leaving at least two feet between the bottom of the enclosure and the ground. The solar panel should then be placed above the enclosure such that the door of the enclosure is unobstructed. Finally, a PVC pipe is attached to a post to get the sample inlet as high above the ground as reasonable, keeping in mind the sample filter therein should be changed at least monthly.

8.1.2 Monitoring Equipment

The 2B Technologies 205 Dual Beam Ozone Monitor™ is designed to enable accurate measurements of atmospheric ozone over a wide dynamic range extending from a limit of detection of 1 part-per-billion by volume (ppbv) to an upper limit of 100 parts-per-million (ppmv) based on the well established technique of absorption of ultraviolet light at 254 nm. The 205 Dual Beam Ozone Monitor™ is light weight (4.7 lb., 2.1 kg.) and has low power consumption (~5 watt) relative to conventional lab-type instruments.

Ozone is measured based on the attenuation of light passing through two separate 15-cm long absorption cells fitted with quartz windows. A single low-pressure mercury lamp is located on one side of the absorption cells, and photodiodes are located on the opposite side of the absorption cells. The photodiodes have built-in interference filters centered on 254 nm, the principal wavelength of light emitted by the mercury lamp. An air pump draws sample air into the instrument. A pair of solenoid valves switches in unison so as to alternately send ozone-scrubbed air and unscrubbed air through the two absorption cells. Thus, the intensity of light passing through ozone-scrubbed air (*Io*) is measured in Cell 1 while the intensity of light pass through unscrubbed air (*I*) id measured in Cell 2. Every 2 seconds, the solenoid valves switch, changing which cell receives ozone-scrubbed air and which cell receives unscrubbed air.

Ozone concentration is calculated for each cell from the measurements of *Io* and *I* according to the Beer-Lambert Law. The 2B Technologies instrument uses the same absorption cross section (extinction coefficient) as used in other commercial instruments. A new ozone measurement is made every 2 seconds for both cells, based on updated values of *I* and *Io*. These two values are averaged and then output as both serial data and an analog voltage between 0 and 2.5 V. (2B Technologies, Inc., 2011)

8.1.3 Test Gas System

2B Technologies manufactures an ozone source intended for field use on a 12 volt system, the model 306 Ozone Calibrator. Additionally, quality assurance personnel within the APCD use Teledyne 703 ozone sources. The APCD has certified both systems against a NIST traceable standard.

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. 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.

The ozone monitor is equipped with a solenoid in the sample stream that can be switched to a zero-path with a charcoal scrubber. At a prescribed frequency, or as triggered by the operator, the sample stream is switched to the charcoal scrubber so that both cells sample air that has been scrubbed. This constitutes measurement for zero drift of the analyzer.

8.1.4 Data Acquisition System

A Campbell Scientific CR1000 data logger is used to gather, aggregate, and store data. Details about the CR1000 can be found in the owner's manual.

For troubleshooting purposes, Figure 6 provides an illustration of how the CR1000 should be wired. Note this diagram is limited to the data logger and the subsequent relays. It is implied that the wiring continues from the relays to the appropriate systems.

The CR1000 has two serial ports. One is proprietary and cannot be used, labeled CS IO. The other can be connected to the modem or a laptop, labeled RS-232.

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), Fluoroethylpropylene (FEP) Teflon™, perfluoroalkoxy (PFA) tubing be used. PTFE or FEP Teflon is the best choice for the connection between an intake manifold and the bulkhead fitting. PFA is a newer formulated Teflon than FEP. Like FEP, it is translucent which is also not machined, but unlike FEP, it can be molded into fittings. It has been accepted as equivalent to FEP Teflon but there is no real advantage to using PFA. Examine the tubing and discard if particulate matter has collected on the tube's interior. 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

The 2bTech does not require any reagents since the instrument uses photometry to analyze for Ozone. All gas calibration and quality control concentrations for the Ozone method are obtained by direct generation.

8.1.7 Spare Parts and Incidental Supplies

In addition to the wiring, tubing, and fittings in Section 8.1.3, 1-micron Teflon sample filters, activated charcoal, and Purafil will be required for site maintenance.

Sample filters should be changed once per month at a minimum depending on the dusty nature of the location. Tube fuses may blow, it is best to have spare 2-amp tube fuses on hand. The Teflon inline sample filter and the charcoal zero filter should last longer than the field campaign but it is possible they will need replacement in exceptionally polluted environments.

In shady areas or in cases where the best sun angle cannot be achieved for the solar panel, a spare lead acid battery should be maintained on a battery cycling tender and used to swap when voltages drop below 11.5 volts.

8.2 Calibration Equipment

The 205 Ozone Analyzer can be calibrated by any NIST traceable source. Refer to the parent Appendix GM2 – Gaseous Analyzer Calibration SOP for required calibration equipment. In addition to the traditional TAPI 401 and 703 calibration sources, the 2B Technologies model 306 ozone generator (M306) may also be used as a calibration source.

9 CALIBRATION

9.1 Introduction and Summary

In principle, the measurement of ozone by UV absorbance requires no external calibration; it is an absolute method. However, non-linearity of the photodiode response and electronics can result in a small measurement error. Therefore, each instrument is compared with a NIST-traceable standard ozone spectrophotometer in the laboratory and/or field over a wide range of ozone mixing ratios (typically 0-300 ppbv for atmospheric applications). These results are used to calibrate the ozone monitor with respect to an offset and slope (gain or sensitivity). The user may change the calibration parameters from the front panel if desired. It is recommended that the ozone monitor be recalibrated at least once every six months and preferably more frequently. The offset may drift due to temperature change or chemical contamination of the absorption cell. As discussed below, an accurate offset correction can be measured from time to time using the ozone scrubber supplied with the instrument. The user may change the slope and offset calibration parameters by entering the Menu option on the analyzer display.

9.2 Calibration Procedure

This procedure was developed from 2B Technologies Technical Note No. 015, Recommended Calibration Procedure for 2B Tech Ozone Monitors. The following procedure applies both for in-lab or in-field calibration of 2B-Tech Ozone monitors. While in the lab, the O_3 level two transfer standard response will be used to calibrate the ozone monitor, rather than the ozone generator (level 3 transfer standard) reading.

9.2.1 Calibration Train Setup

See Figure 3

9.2.1.1 Calibration Adjustment

- Set up the calibration train. If using the M306 an external vent is required, also. All calibrations must be done through the sample probe with a Teflon filter in place.
- Record the 2B-tech analyzer's offset (Z) and slope (S).
- Set the calibration parameters to, Z = 0.0 and S = 1.00
- Generate zero air with the ozone calibrator and allow the ozone monitor to stabilize for several minutes.
- Collect 1 minute average data from the ozone monitor's front display or through the data logger's serial communication port.
- The new offset (Z) is the negative of the average instrument offset.
- Generate 5 different ozone levels that are equally spaced through the analyzer's range. Allow sufficient time for each point to stabilize and record the 1 minute averages.
- Perform a linear regression with the analyzers response and the Ozone generator's output data.
- The new slope (S) will be given by 1/(LR-slope), where LR-slope is the slope of the linear regression line.
- Z must be within the range of -9 to 9 ppb and S within the range 0.99 to 1.09 ppb, if not then the instrument needs to be repaired or cleaned and all calibration activities must stop until rectified.
- Enter the new Z and S parameters into the ozone monitor using the front panel menu.
- Perform a post-calibration check by generating zero, precision, and span to ensure calibration is accurate. If it is not, then adjust the Z and S parameters and repeat the multipoint linear regression.

9.3 Reporting and Filing of Calibration Results

Capture the data in the Calibration Database, see Figure 4.

10 OPERATION AND MAINTENANCE

10.1 Introduction and Description of Monitoring

Ozone is measured continuously using 2B Technologies (2BTech) Model 205 ozone monitors, which are designed to enable accurate and precise measurements of ozone with a precision of 0.0010 ppm (1.0 ppb). The 2BTech Model 205 is light weight and has a low power consumption relative to conventional instruments and is therefore well suited for long-term monitoring at remote locations where power is limited or unavailable. These portable monitors are transported to monitoring locations and operated from a standard 12-V battery charged by a 90-W solar panel. Analyzers are programmed to sample at 1-minute intervals and all data were stored on a data logger (Campbell Scientific) that also recorded air and instrument temperature and battery power. The monitor, battery, and data logger were enclosed in weather-proof instrument shelters mounted along with the solar panels between two T-posts, which were installed about 80 cm apart. Sample inlets, which consisted of Teflon particle filters and Teflon tubing, are located 2 meters above the ground surface. A 2BTech Model 306 ozone source is used to calibrate and perform performance checks on instruments during their installation and during the monthly site visits, respectively.

10.2 Equipment and Supplies

For a complete listing of supplies and equipment please see Section 8.1 of this standard operating procedure.

10.3 Logs and Forms

All actions at the site, scheduled and non-scheduled, are logged on forms. 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 SOP.

The forms in routine use are:

- Figure 5 2bTech site log form**.**

10.4 General Operations

This section provides an overview of 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 TSP, using the inspection criteria documented in this chapter. Below is a general summary of the types of maintenance check performed.

Data from each site is evaluated daily. There is a daily morning review of overnight quality control checks, data validity flags, data completeness, data representativeness, 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 monthly inspection is performed once each calendar month or as needed.

The Precision tests and Zero/Span cycles are required to be performed once every monthly visit.

Upon completion of an inspection, log entries onto the 2bTech site log form. Enter all tasks performed, any malfunctions, or other actions needed, 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.

10.4.1 Connecting to the CR1000

Diagnostic, meteorological, and analytical parameters can be viewed by connecting a laptop to the CR1000. The laptop must have Campbell Scientific PC200W software installed and correctly configured. The laptop must also have an RS-232 cable (straight, with a male end for the CR1000) connected to it.

Once physically connected, open PC200W and click on Monitor Data. The program will attempt to connect and, if successful, display all available parameters in a grid, updating in real-time. Any audits or calibrations done to the ozone monitor should use this display.

In the event information needs to be obtained from the ozone monitor itself, Figure 7 may be referenced, in addition to the manual, to display average data.

10.5 Routine Preventative Maintenance and Scheduled Activities

Preventive maintenance inspections and services should follow the recommended intervals set by this SOP, 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. Analyzer log sheets 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 1. Routine Preventative Maintenance and Schedule Activities

Procedure or Resource	Description
Every Onsite Visit	
	Check station for general condition and proper operation of box fan, zero air solenoid, met instrument, and sample pumps.
	Check all equipment for faults and operability. Verify that the data logger is working correctly and reported values match the analyzer display.
	Remove trash from the area.
	Document the site visit with a summary of all maintenance performed.
Every 2 Weeks or Monthly	
	Perform Manual Quality Control Zero and Precision Test – Performed by APCD staff Record in the Site log the results, if calibration is needed perform a 7 point calibration as per Section: **9**

Procedure or Resource	Description
	Change the Filter, Section: 10.6.2 and perform a leak check, Section: 10.6.3

10.6 Maintenance Procedures

10.6.1 Check Analyzer Calibrations Factors and Diagnostic Test Parameters Procedure

Refer to the appropriate manual for navigation trees to find diagnostic parameters (Figure 7). Copy parameter values from the display to the appropriate form.

10.6.2 Filter Change Procedure

1. Remove the old filter from the filter housing at the end of the sample line.
    a. The 2bTech use an external filter holder that may require holder wrenches.
2. Place new 5um filter into the filter housing using tweezers to handle the filter.
3. Tighten the filter holder closed with the filter wrenches.
4. Inspect lines and fittings for seal.
5. Perform a leak check from the back of the analyzer (10.6.3).

10.6.3 Pump and Leak Check Procedure

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, and a sample line. “As a first check, hold your finger over the air inlet to determine whether air is being drawn in. If there is flow, measure the flow rate by removing the bottom cover and attaching a high conductance flow meter to the exit port of the pump. Air flow should be greater than 0.7 L/min. If flow is lower, check for leaks. If there are no leaks, replace air pump.” (Model 205 Operators Manual)

11 HANDLING AND PRESERVATION

Atmospheric Ozone criteria pollutant 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 Atmospheric criteria pollutant analysis 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 vibration from other equipment causing an effect?
2. Is the box fan operational?
3. Are the sample pumps running?
4. Is the solar panel functioning and charging the battery?

13.2 General Factors

Other factors linked to the shelter and manifold design can contribute to data loss. The sample probe, water dropouts, and sample lines should be checked on a regular basis to ensure integrity. Dirty sample lines can artificially suppress readings of reactive analytes. The sample probe weather cap inlet should be cleaned every six months and the sample lines replaced every year. Inlet and sample line maintenance should be done in accordance with section 10 above. Ozone sample lines are to be trimmed mid-year, where 2 feet of sample line is trimmed from the end of the inlet of the sample line to remove dirt that normally collects along the inside of the sample line near the inlet. The particulate filters used to protect the analyzers should be changed on a regular basis, as outlined in the specific instrument manuals and SOPs. Filters should be changed during the monthly site visit at a minimum.

Power to the site is another factor that can contribute to data loss. Incoming power needs to be stable and have a good waveform.

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. Equipment used in troubleshooting includes flow meters, calibration standard, pressure gauges, and digital voltmeters.

Troubleshooting techniques for the data logger and the 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

14.1 Data Acquisition

Data is acquired from the CR1000 data loggers by use of the proprietary Campbell Scientific PC200W software. Installation instructions for the software can be found in section 4.2.3 of the Campbell Scientific CR1000 Measurement and Control System Operator's Manual (Campbell Scientific, 2/2018).

Any laptop used to manually collect data from the data loggers should be configured on campus. All data is stored (even if delivered by way of a laptop) in a folder structure existing on the share \\APCPOLLING1\Technical Services 1\2BTech folder. File naming convention should be as follows:

Minute Average Data	SiteName_Sample01
Hour Average Data	Site Name_Sample1
Zero sequence results (nightly zero checks)	SampleName_Zero

A folder should be created for each new site. After the folder is created, the PC200W software can be instructed to download data to that folder.

The PC200W software is also used to view data in both tabular and graphical forms in order to review for data quality and to check diagnostic parameters. Once the software is open (a connection to a data logger is not required), click the Tools menu and select View. This opens a new window wherein you may open data files. With a data file open, select a column of data by clicking on the header, then click the graph icon in the ribbon near the top of the window. Figure 5 is an example of a fully open data file.

14.1.1 Primary Onsite Data Acquisition Systems

Data are collected and stored on Campbell Scientific CR1000 data loggers, where all averaging occurs.

14.2 Calculations and Data Reduction

Data are polled automatically via modems (analog phone, wireless cellular, or DSL) by the Central polling computer and save to text files.

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.

15 DATA MANAGEMENT AND RECORDS MANAGEMENT

15.1 Data Management

Data is captured from the 2bTech analyzer and instrumentation and stored in minute and hourly averages. The data are polled from the data loggers via the Campbell Scientific LoggerNet software at routine intervals and stored as text files on the J: Drive. The hourly text files can be manually ingested into Airvision.

15.2 Records Management

Continuous ambient air monitoring data are archived in electronic formats. Electronic data and calibration files from the primary DAS are archived..

16 QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance and quality control 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 precision, bias, representativeness, completeness, comparability, and sensitivity. The principal MQO's are parameter specific and are listed in CDPHE's QAPP. Guidance for developing DQI's and MQO's is given in EPA's Quality Assurance Handbook. Quality control covers specific procedures established for obtaining and maintaining data collection within those limits.

16.1 Quality Assurance

The goal of the quality assurance program is to control measurement uncertainty to an acceptable level through the use of various quality control 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 Quality Assurance and Quality Control 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.

16.1.1 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.

- 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. Detailed information about how specific audits are performed can be found in the Quality Assurance SOPs section.

16.1.2 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.

16.2 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 Quality Control 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 Quality Control 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 Quality Control function. Three of the most significant Quality Control procedures are described below.

16.2.1 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 the above mentioned precision level test gas concentrations. These two tests are called Performance checks and QC Precision checks. The former is an automated performance test that is performed nightly and is used to evaluate the health of the sample system. The latter is a manual evaluation performed by qualified personnel who can attest to their validity and are reported to the EPA. With regards to this SOP the only checks performed are performance checks. These checks are used to determine the health of the analytical system and for determinations of data validity. These checks are not uploaded to EPA's AQS system.

16.2.2 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 my require calibrations be performed at the longer frequency of every 6-months. A 6-month calibration frequency still meets EPA recommended calibration frequency criteria.

16.2.3 Documentation

Documentation is an important component of the quality control system. Extensive certification paperwork and log sheet must be rigorously maintained for procedures, standards and analyzers. APCD takes special care to prepare and preserve backup copies of all data, especially calibration data.

17 BIBLIOGRAPHY

2B Technologies, Inc. (2011). *Ozone Monitor Dual Beam Operation Manual.* Boulder.

Campbell Scientific. (2/2018). CR1000 Datalogger Operators Manual. Logan, UT.

US EPA. (2007). *Guidance for Preparing Standard Operating Procedures.* Research Triangle Park, NC: US EPA OAQPS AQAD.

Appendix A

A.1 Ozone Analyzer Programming

For reference, the program, which can be edited in a text editor, and exported to the data logger, is listed here:

```
'Declare Variables and Units
'T_Int is CR1000 thermistor temperature
Public SerNo,V_Batt,T_Int,T_Air
Public Analyzer_Serial_Raw as string * 80
Public Analyzer_Serial(9)
Alias Analyzer_Serial(1)=O3
Alias Analyzer_Serial(2)=T_inst
Alias Analyzer_Serial(3)=Cell_Pres
Alias Analyzer_Serial(4)=Flow
'Flag1=2B on/off
'Flag2=Cooling fan on/off
'Flag3=Zero solenoid on/off
Public Flag(3) as boolean
Alias Flag(1)=O3_Status
Alias Flag(2)=Fan_Status
Alias Flag(3)=Zero_Status
Const On=True
Const Off=False

Units V_Batt=Volts
Units O3=ppb
Units T_Int=Deg C
Units T_Air=Deg C
Units Cell_Pres=mbar
Units Flow=cc/min

'Define Data Tables
'Sample15 is the output table for 15-minute average ozone
DataTable(Sample15,1,-1)
        DataInterval(0,15,Min,0)
        Sample(1,SerNo,FP2)
        Average(1,O3,FP2,False)
        Maximum(1,O3,FP2,False,False)
        Minimum(1,O3,FP2,False,False)
        StdDev(1,O3,FP2,False)
        Sample(1,T_Int,FP2)
        Average(1,Flow,FP2,False)
        Average(1,Cell_Pres,FP2,False)
        Sample(1,T_Air,FP2)
        Sample(1,O3_Status,FP2)
        Sample(1,Fan_Status,FP2)
        Sample(1,Zero_Status,FP2)
        Sample(1,V_Batt,FP2)
EndTable
'Zero is the output table for zero data, taken every seventh day
DataTable(Zero,Zero_Status,-1)
        DataInterval(0,5,Min,0)
```

```
        Sample(1,SerNo,FP2)
        Average(1,O3,FP2,False)
        Maximum(1,O3,FP2,False,False)
        Minimum(1,O3,FP2,False,False)
        StdDev(1,O3,FP2,False)
        Sample(1,Zero_Status,FP2)
        Sample(1,V_Batt,FP2)
EndTable

'Main Program
BeginProg
PortsConfig(&B11,&B11)
SerialOpen(COM2,4800,0,500,240)
Scan(1,Min,1,0)
'CR1000 internal battery voltage measurement
Battery(V_Batt)
'Receives serial string from analyzer
If O3_Status=On then
        SerialIn(Analyzer_Serial_Raw,COM2,6000,CHR(13),80)
        'Splits analyzer serial data into separate variables
        SplitStr(Analyzer_Serial(),Analyzer_Serial_Raw,",",9,5)
        'Flushes serial input buffer
        SerialFlush(COM2)
EndIf
'Assigns null values to analyzer variables if analyzer is off
If O3_Status=Off then
        O3=NAN
        T_inst=NAN
        Cell_Pres=NAN
        Flow=NAN
EndIf
'Datalogger temperature measurement
'Measures interior temperature
PanelTemp(T_Int,_60Hz)
'Measures external temperature on Diff channel 2:
TCDiff(T_air,1,mV25C,2,TypeT,T_Int,True,0,_60Hz,1,0)
'Conditions for powering-up ozone analyzer
'Turns on analyzer if battery voltage is sufficient and T_Int>+3C
If O3_Status=Off then
        If V_Batt>12 then
                If T_Int>3 then
                        PortSet(1,1)
                        O3_Status=On
                        Delay(1,2,2)
                        PortSet(1,0)
                EndIf
        EndIf
EndIf
'Conditions for turning off ozone analyzer and fan
'Turns off analyzer and fan if battery voltage is too low OR if T_Int<0C
If O3_Status=On then
        If V_Batt<11 or T_Int<0 then
                PortSet(2,1)
```

```
        O3_Status=Off
        Delay(1,2,2)
        PortSet(2,0)
        PortSet(9,0)
        Fan_Status=Off
    EndIf
    'Turns on cooling fan if battery voltage is sufficient and datalogger T>30
    If T_Int>30 and V_Batt>11 then
        PortSet(9,1)
        Fan_Status=On
    EndIf
EndIf
If Fan_Status=On and T_Int<25 then
    PortSet(9,0)
    Fan_Status=Off
EndIf
'Writes ouput to internal storage
CallTable(Sample15)
CallTable(Zero)
'Executes zero check every 168 hours at 0015
'Zero equilibration 0015-0020
'Sample 0020-0025
'Ambient equilibration 0025-0030
If (IfTime(15,10080,min)) and O3_Status=On then
    PortSet(1,1)
    Zero_Status=On
EndIf
If (Iftime(25,10080,min)) then
    PortSet(1,0)
EndIf
If (Iftime(31,10080,min)) then Zero_Status=Off
NextScan
EndProg
```

A2 2BTECH OZONE SOURCE M306 CERTIFICATION

The certification of the 2bTech M306 O_3 follows the same general procedure for O_3 source certification outlined in APCD's Standards SOP. However the 2bTech M306 certification requires a different approach than the TAPI O_3 sources. Due to the low flow and different zero air sources the M306 cannot be directly output to the Level II O_3 transfer standard. Rather an O_3 analyzer, either a TAPI 400 or 2bTech M205, must be calibrated against the Level II O_3 transfer standard and a calibration curve developed. Refer to APCD's Gas Analyzers Calibrations SOP on procedures for calibrating O_3 analyzers. Figure 10 is an example of the certification workflow. Calibration data are entered into the Calibration database, using CDPHE lab as the site. Once complete, the 2bTech M306 can be directly hooked up (has an internal vent) to the calibrated O_3 analyzer and O_3 produced for seven points (two zero points, and five O_3 concentrations). The O_3 analyzer response is recorded and corrected with the calibration curve coefficients. These data are then entered into the Ozone database. Figure 11 shows the certification setup.

A2.1 2Btech O_3 Source Certification Procedure.

A2.1.1 Calibrate O_3 Analyzer

To calibrate an O_3 analyzer to the Level II O_3 transfer standard, an ozone source and an ozone analyzer (either TAPI or 2bTech) is needed. The O_3 source will output ozone to both the Level II O_3 transfer standard and the O_3 analyzer to be calibrated. The following procedure outlines the steps to accomplish the calibration.

1. Turn on O_3 analyzer, O_3 source, and the Level II O_3 transfer standard and let warm up sufficiently.
2. Hook up the O_3 source and Level II O_3 standard to the same Zero air source.
3. Take the output of the O_3 source and connect it to the sampling manifold.
4. Connect the O_3 analyzer to the same sampling manifold.
5. Generate zero and span O_3 concentrations and adjust the O_3 analyzer's response to the Level II O_3 transfer standard readings.
6. Generate at total of five O_3 concentrations and record the O_3 analyzer and the Level II O_3 transfer standard responses to generate the calibration curve coefficients.
7. Enter the responses into the Calibration database form to generate the calibration coefficients.
8. Once complete, the O_3 analyzer is calibrated.

A2.2 Certify the 2bTech O_3 source with the Calibrated O_3 analyzer

1. Turn on the 2bTech M306 O_3 source and let warm up.
2. Connect the M306 output directly to the calibrated O_3 analyzer. The M306 is internally vented, so no vent is required.
3. Follow the O_3 source certification outlined in APCD's Standards SOP. Generate two zeros and five O_3 concentration points.
4. Record the O_3 analyzer readings and correct to the Level II O_3 transfer standard using the calibration curve coefficients.
5. Enter the corrected O_3 analyzer readings in to the Ozone Cert database 7 point Certification Form. The O_3 analyzer corrected readings are placed in the "Primary Lab" row (Figure 8).
6. Enter the M306 target O_3 points into the "Transfer" row.
7. Capture the data.
8. Open the 7 Point 6x Certification Form and generate the certification sheet and label to determine if it passed.
9. If the M306 fails see the APCD's Standards SOP for next actions and troubleshooting. Otherwise, the M306 certification is complete.

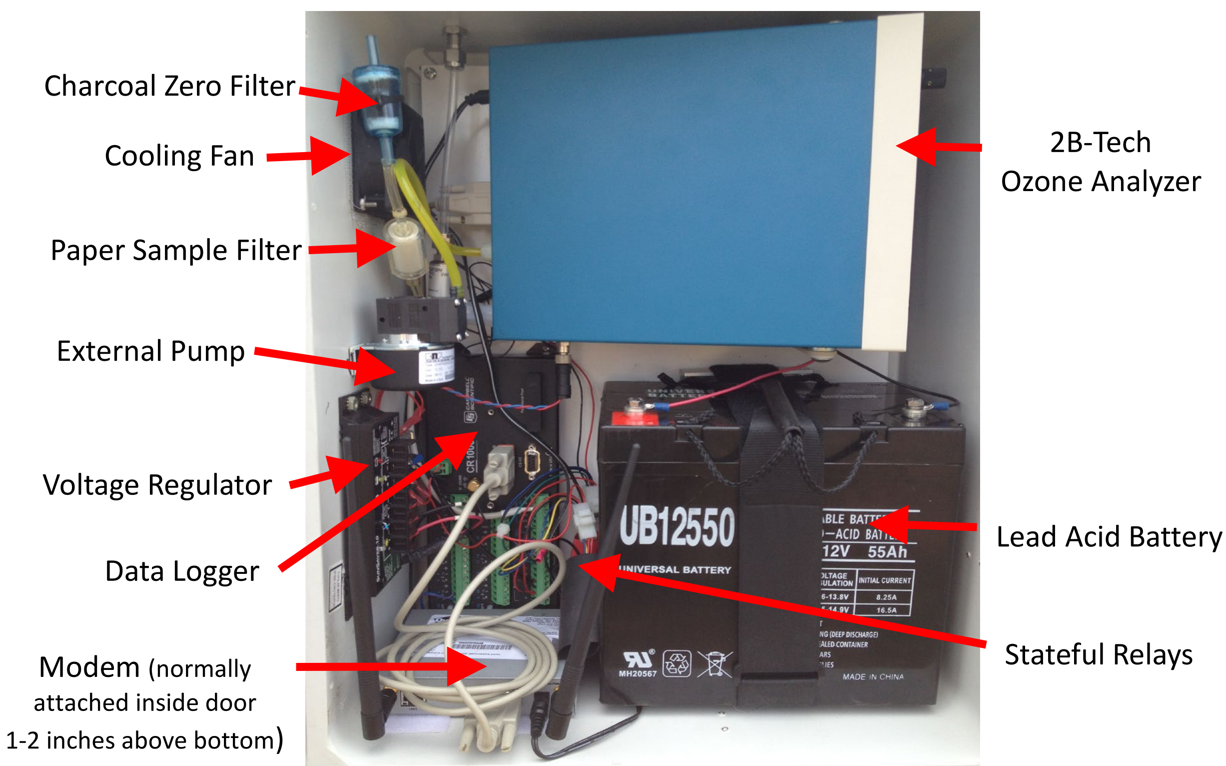


Figure 1. Internal Station Setup

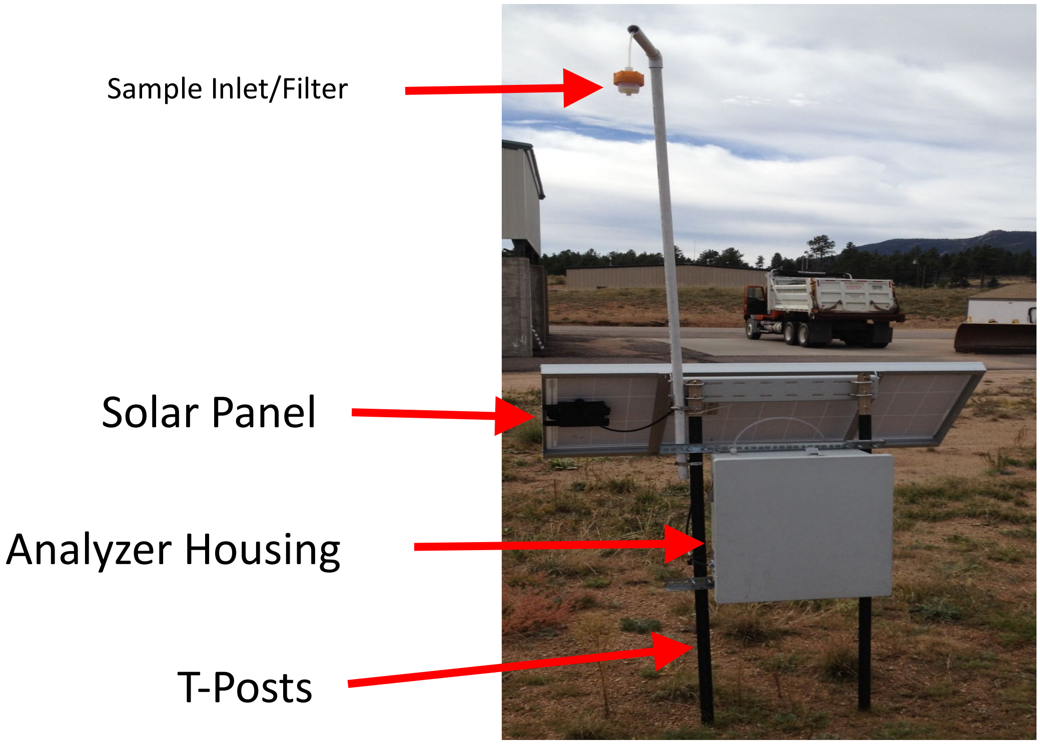


Figure 2. Exterior Enclosure Setup

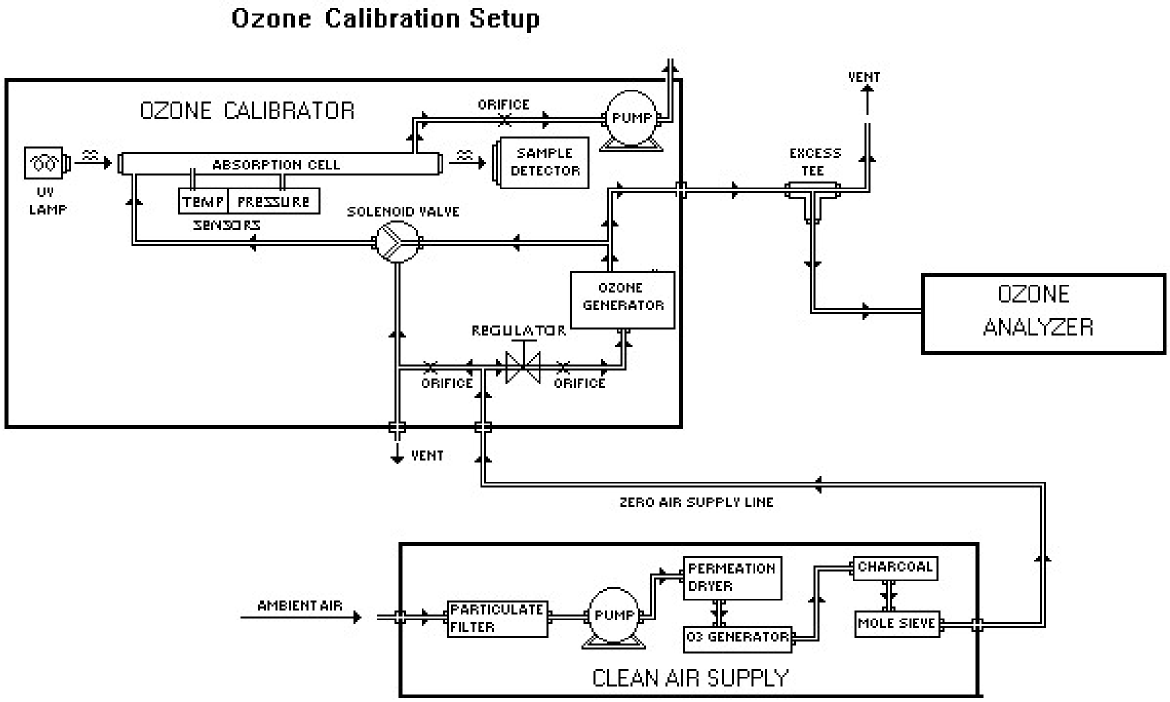


Figure 3. O_3 Calibration Setup

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.	
AQS ID:	
Parameter:	
Analyzer Type:	
Analyzer SN:	
Site Precision Source Info.	
Source Type:	
Source SN:	
Conc.:	
Exp. Date:	

Date Time	
Date (mm/dd/yy)	
Time (hh:mm)	
Prev Cal. Date (mm/dd/yy)	
Calibrator's Initials:	

Calibration Equipment Info	
Calibrator Type:	
Calibrator SN:	
Calibrator Cert Date:	
Cert. Slope (m):	1.00000
Cert. Intercept (b):	0.00000
Calibration Gas Info.	
Bottle SN:	
Conc.:	
Exp. Date:	

Pre-Calibration System ZSP Evaluation

Pre-Calibration Analyzer Slope:

Pre-Calibration Analyzer Intercept:

Set Point	Source Conc.	Display Conc.	DAS Conc.	Display % Diff	DAS % Diff
Zero					
Span					
Precision					

Post-Calibration System ZSP Evaluation

Post-Calibration Analyzer Slope:

Post-Calibration Analyzer Intercept:

Set Point	Source Conc.	Display Conc.	DAS Conc.	Display % Diff	DAS % Diff
Zero					
Span					
Precision					

Pre-Calibration Points

Set Point	Conc. Out Conc.	DAS Conc.	Conc. Adj Conc.	DAS % Diff	Best Fit DAS Conc.	Best Fit (% RE)
Zero						
Level 1						
Level 2						
Level 3						
Level 4						
Level 5						
Level 6						
Level 7						

Post-Calibration Points

Set Point	Conc. Out Conc.	DAS Conc.	Conc. Adj Conc.	DAS % Diff	Best Fit DAS Conc.	Best Fit (% RE)
Zero						
Level 1						
Level 2						
Level 3						
Level 4						
Level 5						
Level 6						
Level 7						

Pre - Regression Results	
Slope:	
Intercept:	
R2:	

Post - Regression Results	
Slope:	
Intercept:	
R2:	

Comments:

Figure 4. Calibration Report

Colorado Department of Public Health and Environment
Air Pollution Control Division - Technical Services Program

STATION: ______
/

2bTech STATION/MET

Lat: Lon:

SN:		Date					
Box Temp		<90F					
Cell Temp		<50F					
Cell Press		< Ambient					
Slope		0.97-1.2					
Offset		-10 -- 10					
DAT AVG		10s					
O3 Flow		.500 - 4.0					
Filter Change		Per Visit					
Check: Zero, record response		O3 Source: 0ppb					
1 point Calibration Check		O3 Source: 60ppb	Analyzer Response				
Wind Direction		0-360 deg					
Wind Speed		0-100 mph					
		Operator					

Box Fan operational:
Zero Solenoid operational:

Day	Time	Action	Initials	Time

Use ✓ for yes and in-range and ✗ for no and out-of-range, Δ for changed

Figure 5 2bTech site log form

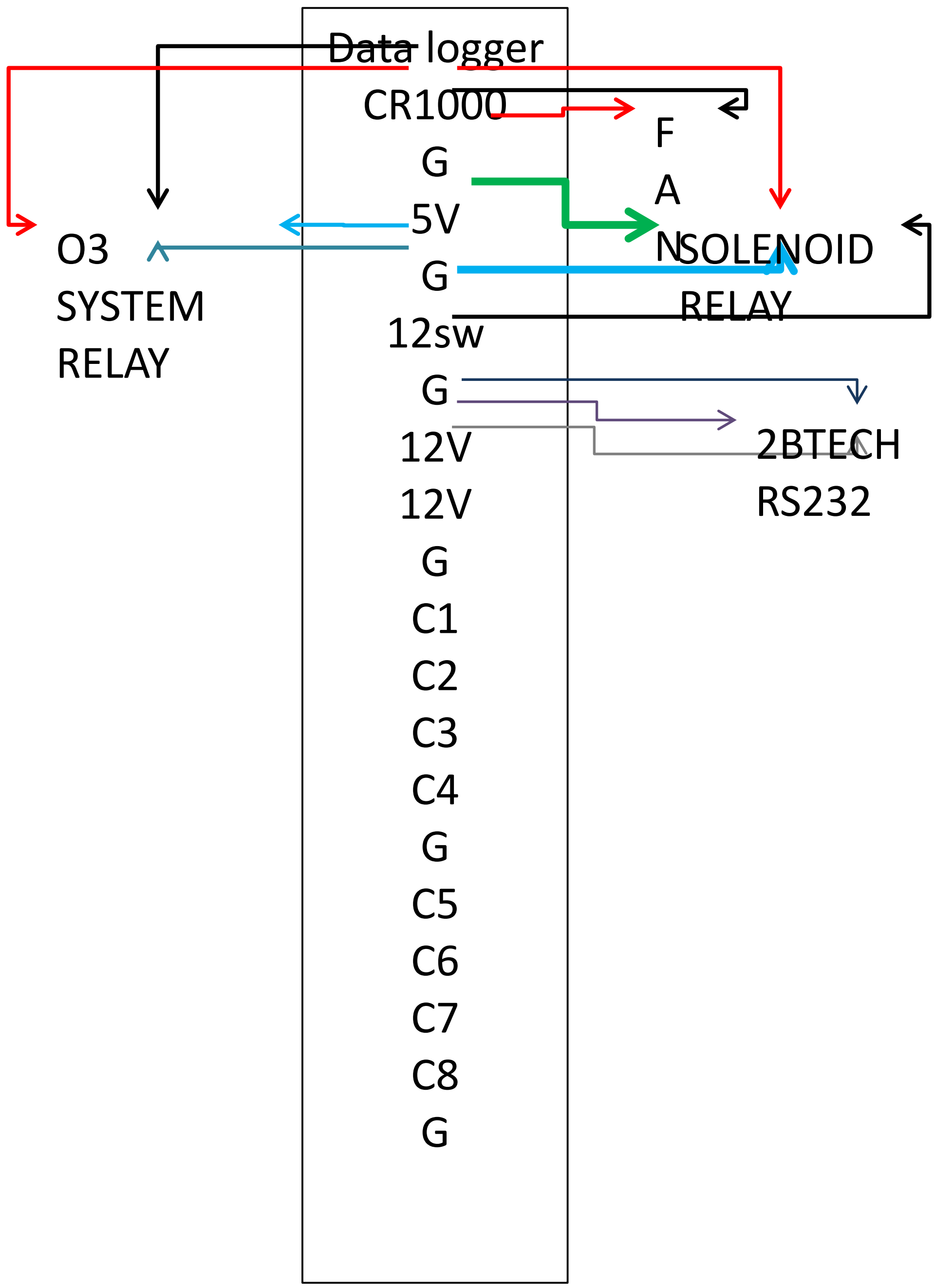


Figure 6. CR1000 Wiring Diagram

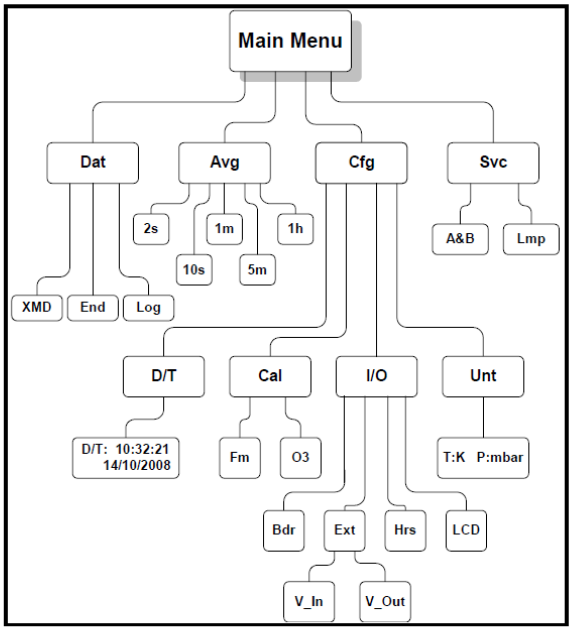


Figure 7. Ozone Monitor Menu Tree

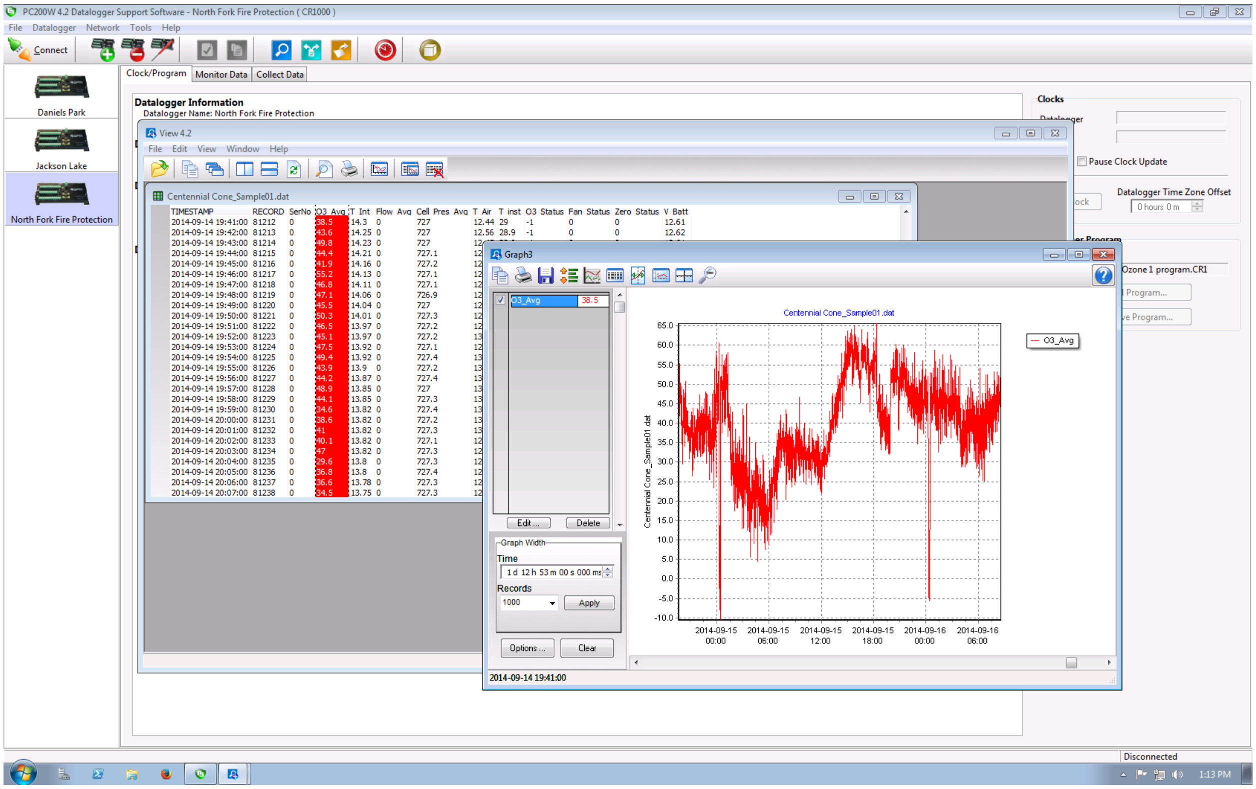


Figure 8. Example PC200W Window

COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

Air Pollution Control Division - Technical Services Program

7 Point Ozone Standard Verification Data Form

Date:		Time:		Initials:		New Data Form

Primary Lab Standard		Backup Lab Standard		Transfer Standard	
Model:		Model:		Model:	
SN:		SN:		SN:	
SRP Cert Date:		SRP Cert Date:		DCPS (MV):	
O3 bkgrd:		O3 bkgrd:		Box Temp (C):	
O3 coef.:		O3 coef.:		O3 Offset (PPB):	
5 Volt:		5 Volt:		O3 Slope:	
+15 Volt:		+15 Volt:		Reg Press (IN-HG):	
-15Volt:		-15Volt:		O3 Gen Temp (C):	
Battery:		Battery:		O3 Gen Flow (LPM)	
Bech Temp:		Bech Temp:		Ana Lamp Temp (C):	
Bench Lamp:		Bench Lamp:		Sample Temp (C):	
O3 Lamp:		O3 Lamp:		Sample Flow (CC/MIN):	
Pressure:		Pressure:		Sample Press (IN-HG):	
Flow Cell A:		Flow Cell A:		O3 Drive (MV):	
Flow Cell B:		Flow Cell B:		O3 Gen Ref (MV):	
Int Cell A:		Int Cell A:		O3 Ref (MV):	
Int Cell B:		Int Cell B:		O3 Set:	

Measurement Compairsons

Standard	zero (ppb)	100 (ppb)	200 (ppb)	300 (ppb)	400 (ppb)	500 (ppb)	zero (ppb)	Slope	Intercept	Corr. Coeff.
Primary Lab										
Primary Zero Corr.										
Backup Lab										
Backup Zero Corr.										
Transfer								Primary Regression:		
Transfer Zero Corr.								Backup Regression:		

Analyzer Checks

DFU Condition		Sample Flow Check	☐
DFU Charcoal		O3 Gen Flow Check	☐
Charcoal Renewed		Visual Cell Check	☐

Field Setup Checkout

1 Volt D/A Check:	☐	Pump Swith = ON:	☐
Event = AZ2S:	☐	O3 Gen = 360:	☐
Wait = 01 15 min:	☐	Cover Secure:	☐
Inlet Cap To Scrubber:	☐	Feet OK:	☐

Comments

Figure 9 APCD's 7 Point Ozone Standard Verification Data Form

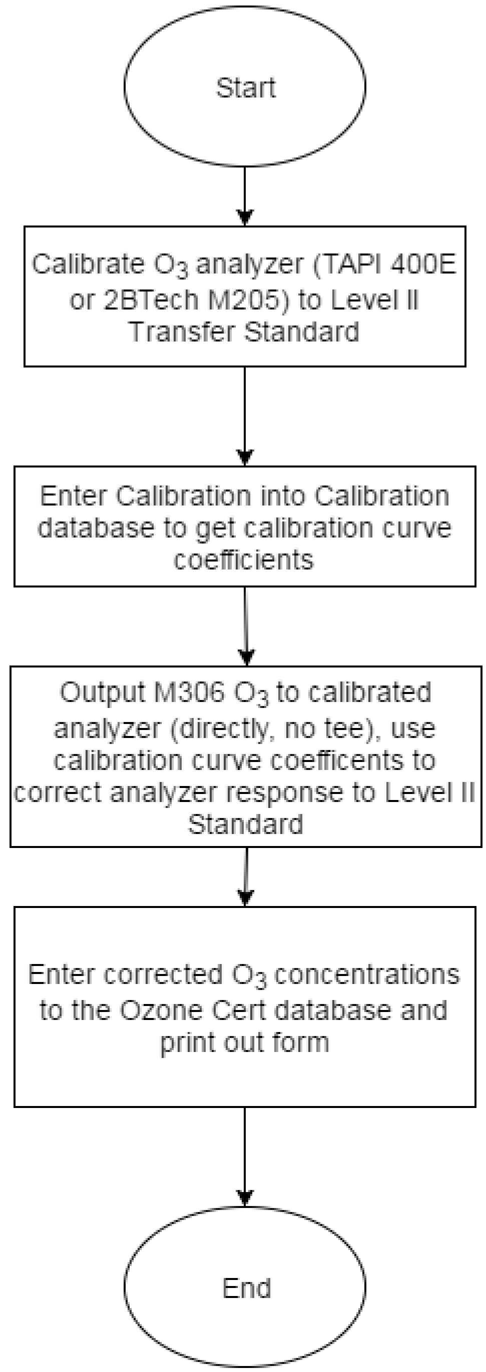
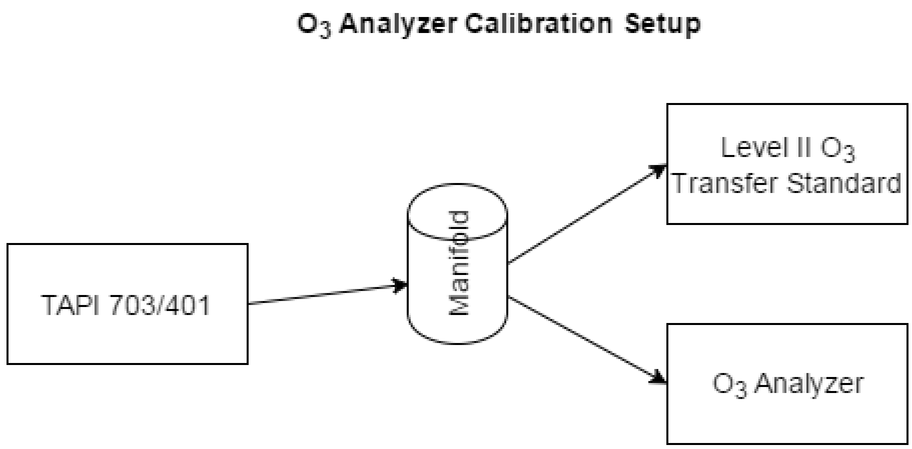


Figure 10 2bTech M306 O_3 source certification workflow



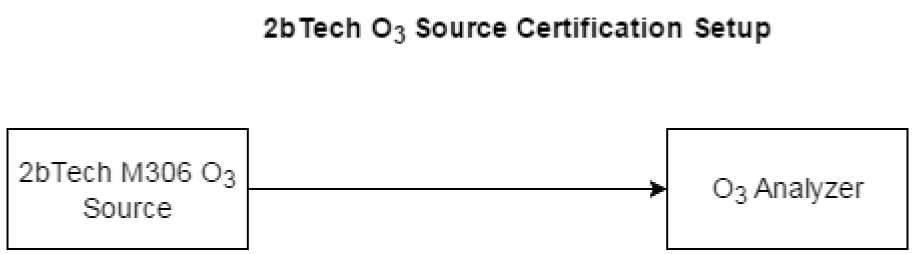


Figure 11 2bTech M306 O_3 source certification setup