IV. CALIBRATION

This chapter describes the procedure for performing the multipoint calibration of the photometric ozone analyzer. It is based upon the current EPA approved procedure using a U.V. photometer as a calibration standard. The information described here is more than adequate to perform the calibration. For greater detail the reader can consult the EPA Technical Assistance Document (TAD) for the Calibration of Ozone Monitors[1] and the Code of Federal Regulations (CFR)[2].

EQUIPMENT REQUIRED

Calibration Photometer

The Thermo Environmental Instruments Inc. Photometric Ozone Analyzer, Models 49 and 49-003, can be modified to operate as a calibration photometer by removing the ozone-removing catalytic converter and plumbing zero air into the common port of the ozone-free solenoid valve (see Figure IV-1).

NOTE

The Calibrator must be dedicated for calibration and not be used for monitoring ozone at any time. As described below, there are certain checks to assure proper operation of the calibration photometer.

CAUTION

A PHOTOMETER BEING USED AS A CALIBRATOR SHOULD NOT BE USED AS A MONITOR (SEE EPA TECHNICAL ASSISTANCE DOCUMENT).

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[1] Technical Assistance Document for the Calibration of Ambient Ozone Monitor, Sept. 1979, EPA 60014-79-057. Available from National Technical Information Service Units (NTIS), Parts of which are excerpted in Appendix A.

[2] 40 CFR Part 50 - National Primary and Secondary Ambient Air Quality Standards - Appendix D (44 FR 8221).

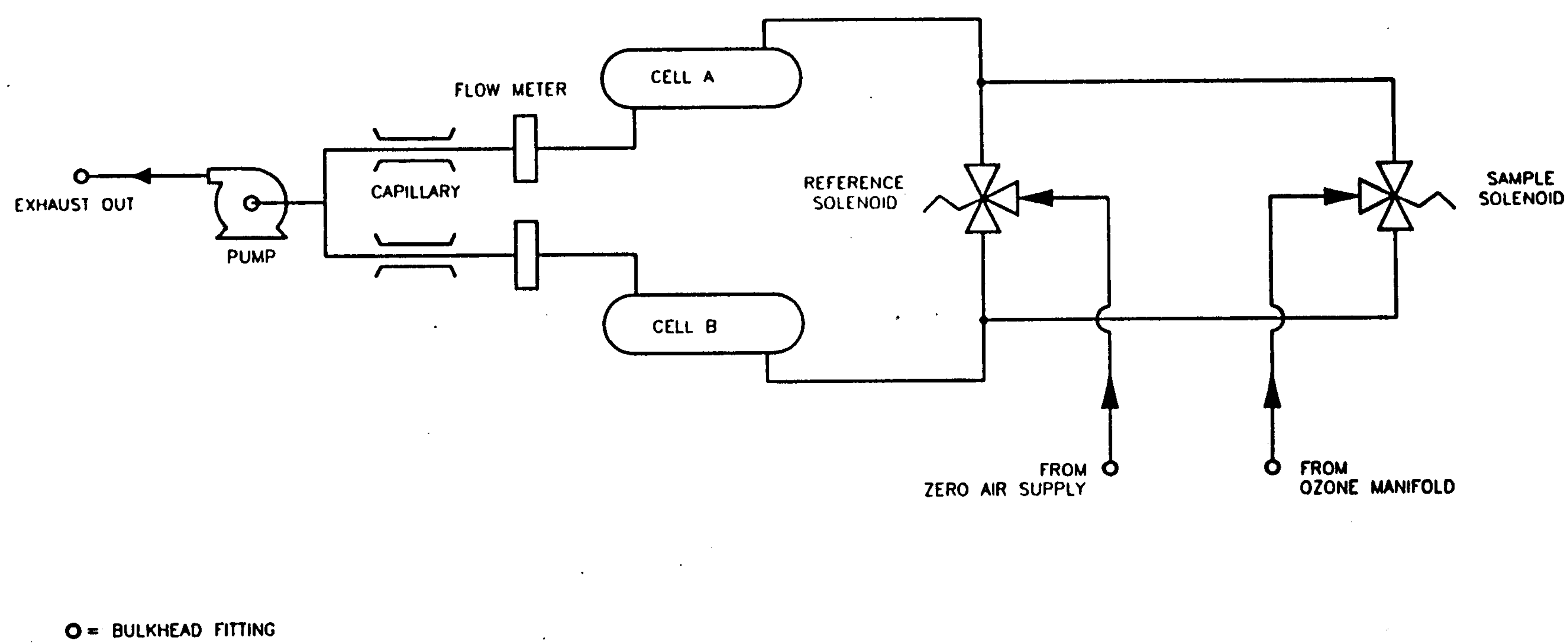

FIGURE IV-1: FLOW SCHEMATIC OF MODEL 49
WHEN CONNECTED AS A CALIBRATOR

Zero Air

Zero air can be obtained either from compressed cylinders or from scrubbed ambient air. If cylinder air is used, it should be actual and not synthetic.

If ambient air is used, the following compounds must be removed: ozone, nitric oxide, nitrogen dioxide, sulfur dioxide, and hydrocarbons. The following scheme is recommended by the EPA in its technical assistance document:

- Dry air using a Perma-Pure[R] type dryer, followed by a column of indicating silica gel (optional)
- Irradiate the air with ozone generating U.V. lamp to convert nitric oxide to nitrogen dioxide; (alternatively, pass gas through Purafil[3] which oxidizes nitric oxide to nitrogen dioxide)
- Pass through a large column of activated charcoal to remove nitrogen dioxide, ozone, sulfur dioxide, hydrocarbons, etc.
- Pass through molecular sieve
- Pass through final particulate filter to remove particulates which originate in scrubbing columns

An important requirement for the calibration photometer operation is that the zero air used to reference the photometer come from the same source as the zero air used in the ozonator. This is to effectively cancel impurities present in the zero air source.

Ozone Generator

An ozone generator capable of supplying a 0-.5 ppm or 0-1.0 ppm, depending upon the range being calibrated, stable ozone level with a flow of 5 liters per minute in order to satisfy both the photometer and the instrument being calibrated.

Accurate Thermometer and Barometer

A thermometer and barometer is necessary to check calibration of the pressure transducer and temperature transducer of the Model 49.

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[3] TEI P/N 6996 Purafil Scrubber Assembly. Refill with Purafil, TEI P/N 7075.

NOTE

The Thermo Environmental Instruments Inc. Model 49PS Ozone Photometric Primary Standard, satisfies the preceding requirements in a single convenient package. All that is necessary is to connect a zero air supply.

CHECKOUT OF THE MODEL 49 AND 49-003 AMBIENT OZONE ANALYZER

Prior to calibration, the Model 49 or 49-003 should be operating properly. The Model 49's internal diagnostics makes this a quick and simple process:

1. Turn on the instrument and allow it to stabilize for a minimum of one hour. Perform the service checks of Chapter V, "Periodic Maintenance and Service Checks."

2. Connect the Model 49 or 49-003 to the ozone manifold. If a Teflon particulate filter is being used, it must be installed prior to calibration.

CHECK OF THE OZONE U-V CALIBRATION PHOTOMETER

As indicated in the EPA Technical Assistance Document there are several tests that should be performed prior to the use of an ozone U-V photometer as a calibrator to ensure the accuracy of the measurements. These tests include:

- That the instrument is operating correctly
- That the instrument is set up properly, and is clean and leak-free
- That the calculations are complete and accurate
- That the instrument does not destroy ozone in the optical bench or flow components
- That the instrument has a linear response
- If possible, two calibration photometers should be compared (intercompatability)

A step-by-step checkout procedure to verify proper operation of a Model 49PS (or a Model 49 or 49-003 modified as described earlier in this chapter under the "Calibration Photometer" section and Figure IV-1) is as follows:

1. Turn the calibration photometer on; (for the rest of this section, the term "Calibration Photometer" refers to the Model 49PS or the modified Model 49 or 49-003).

2. Turn on the ozonator.

3. Allow the calibration photometer and ozonator to stabilize for one hour.

4. Perform service checks of Chapter V, "Periodic Maintenance and Service Checks."

5. If the Model 49PS passes the balance test of Chapter V "Periodic Maintenance and Service Checks," it is highly unlikely that the system is destroying ozone. If desired, a rigorous test is as follows (this check follows the TAD with the appropriate change for a time-shared, dual cell system). For this test, if the internal ozonator of the Model 49PS is being used, make sure it is in the manual mode.

   A. Calibrate an ozone analyzer using the Model 49PS, assume the photometer is correct.

   B. Generate a stable level of ozone and with the calibrated ozone analyzer measure and note reading as R_m.

   C. Unplug the pump of the calibration photometer from the A.C. power source and plug the exhaust line and zero-air inlet line.

   D. Connect the calibrated ozone analyzer up to the access port on the inlet of Cell A (Figure 8). (For user convenience, the Model 49PS has provided caps at all access points so the Teflon lines do not have to be disconnected).

   E. Actuate Test B pushbutton to put solenoids in Sample A mode and note the steady reading as $R(a)_{in}$.

   F. Repeat (d) above on Cell B. Actuate Test A pushbutton to put solenoids in Sample B mode and note steady reading as $R(b)_{in}$.

   G. Replace access fittings used in steps (d) and (f) above and make sure they are leak tight.

   H. Connect the calibrated ozone analyzer to the access port on the outlet of absorption cell of Cell A (Figure I-8).

   I. Actuate Test B pushbutton to put solenoids in Sample A mode and note steady reading as $R(a)_{out}$.

   J. Repeat step (h) for Cell B.

   K. Actuate Test A pushbutton to put solenoids in Sample B mode and note steady reading as $R(b)_{out}$.

   L. Replace access fittings used in steps (h) and (j), and make sure they are leak tight.

M. Compute percent of ozone loss from the following equation:
Percent of Ozone Loss =

$$\frac{R_m - 1/4\ [R(a)_{input} + R(a)_{output} + R(b)_{input} + R(b)_{output}]}{R_m} \times 100\% \quad (3)$$

6. If the ozone loss is greater than 2%, check that the absorption cells and Teflon tubing have not become contaminated by dirt (see Chapter V "Period Maintenance and Service Checks," for more information about cleaning of the optical bench). If the cells and Teflon tubing are clean, recondition the optical bench by setting the ozone generator for maximum ozone (i.e., gain set to "0"; ozone level to 1200) and adjust the pressure regulator for minimum dump flow (about 1/2 liter per minute). Let Model 49PS run overnight sampling the high level of ozone. Then repeat ozone loss test.

7. Since the Model 49 instruments are inherently linear over the range of interest (0-1 ppm), a linearity test is an effective overall test that the instrument is operating properly. The checks of 1-5 above should identify whether any causes of non-linearity are present. The possible causes (as identified in the TAD) are:

- Dirty or contaminated cell, lines, or manifold
- Inadequate "conditioning" of system
- Leaky solenoid or other leaks in system
- Contamination in zero air
- Non-linear detectors in photometer
- Faulty electronics

In order to demonstrate linearity, generate a concentration of ozone near the upper range limit of the calibration photometer and accurately dilute the ozonated air with zero air. In order to do this test accurately, two calibrated flow meters and a mixing chamber are needed: one flow meter to measure the flow into the ozonator, and the other to measure the flow of the dilutant zero air. The percent of non-linearity is calculated as follows:

$$R = \frac{F_o}{F_o + F_d} \quad (4)$$

$$E = \frac{A_1 - \frac{A_2}{R}}{A_1} X\ 100\%\ (5) \qquad (5)$$

where

F_o = Ozonator flow

F_d = Dilutant zero air flow

E = Linearity error, in percent

A_1 = Assay of original concentration

A_2 = Assay of diluted concentration

R = Dilution ratio

Note that the inherent linearity accuracy of the Model 49PS (or modified Model 49) is greater than the accuracy of mass flow meters that may be used to perform a multipoint linearity check.

8. To check the calculations are complete and accurate:

- With the ozone generator in the manual mode, i.e., gain set to zero, adjust ozone level to generate a level in excess of 0.5 ppm. Wait until ozone concentration is stable
- Actuate Test A pushbutton (solenoid LED should indicate sample B), wait for stable frequency reading and note as $I_o(A)$
- Actuate Test A pushbutton again (solenoid LED should indicate sample A) and wait for stable frequency reading, note as I(A)
- Actuate Test B pushbutton (solenoid LED should indicate sample A), wait for stable frequency reading, note as $I_o(B)$
- Actuate Test P/T, note pressure (P) in mm Hg and temperature (T) in degrees Celsius
- Compute C(A) and C(B) from Equation 6

$$C = \frac{10^6}{(308)37.84} \frac{760\ (273 + T)}{273\ \ P} \ln(\frac{I_o}{I}) \qquad (6)$$

This value should agree with the value noted in the Run mode. Note that the concentration determined in this manner does not correct for lamp fluctuation and thus will be noisier than the concentration determined in the Run mode.

Intercomparability

In order to perform an intercomparability test of a Model 49PS, it may be necessary to have the Model 49PS sample ozone from a source other than the one contained in the instrument. This can be done by:

- Set ozone level thumbwheel to zero
- At the Teflon distribution manifold, disconnect the line from the ozonator to the manifold and cap fitting
- Cap bulkhead labeled VENT
- Connect Teflon line from bulkhead labeled ozone to manifold of ozone source being utilized for intercomparability study
- Make sure the same zero air is feeding the Model 49PS as the ozone source and second photometer being used in study
- If it is desired to hold usage of zero air to a minimum, adjust the pressure regulator feeding the ozonator to zero pressure
- Perform intercomparability test
- After completion of test, reconnect ozonator and leak check following the directions of Model 49PS External Leaks in Chapter V "Periodic Maintenance and Service Checks"
- If in addition to the two ozone photometers being checked for intercomparibility, an ozone analyzer is available, an easier intercomparibility check is to calibrate the ozone analyzer against each photometer individually and then compare the two ozone calibration curves

Span Adjust

1. Generate an ozone concentration standard of approximately 80% of the desired upper range limit (URL) of the ozone analyzer (i.e., 0.4 or 0.8 ppm for the 0.5 and 1.0 ppm ranges respectively). Allow the Model 49 Ozone Analyzer to sample this ozone concentration standard until a stable response is obtained.

2. If the recorder reading does not agree with the calibration photometer reading, adjust the span thumbwheel switches (Figure I-1) to obtain a recorder response as indicated in the following equation:

$$\text{Recorder Response (\% Scale)} = \frac{[O_3]_{out}}{URL} X\, 100 + Z \qquad (7)$$

where

URL	=	Upper range limit of the Model 49, ppm
Z	=	Recorder response with zero air, % scale
$[O_3]_{out}$	=	Ozone concentration as determined by the calibration photometer, ppm.

Changes of the span thumbwheel no greater than ±6% from the nominal 500 are expected. Changes greater than ±6% are unusual and might indicate an error in determining the generated ozone concentration or an analyzer malfunction.

3. Record the ozone concentration as determined by the calibration photometer and the corresponding analyzer response.

Additional Concentration Standards

1. Generate several other ozone concentration standards (at least 5 others are recommended) over the scale range of the Model 49 Ozone Analyzer, by adjusting the ozone source, by adjusting the "ozone level" thumbwheel on the Model 49PS to the desired value, or by dilution of the span concentration (see Appendix B).

2. For each ozone concentration standard, record the ozone concentration as determined by the calibration photometer and record the corresponding Model 49 analyzer response. If a Model 49PS is being used as the calibration photometer, use the ozone concentration as determined by the photometer and not the value of the "ozone level" thumbwheel.

Calibration Curve

Plot the Model 49 Analyzer responses versus the corresponding ozone concentrations. Connect the experimental points by using a straight line, preferably determined by linear regression techniques. Points that lie more than ±4% from this line are an indication of an error in determining the calibration curve. The error may be due to a malfunction of the calibration photometer, or a malfunction of the analyzer being calibrated. The most likely malfunctions in both the analyzer and calibration photometer which would give non-linear results are leaks, a malfunctioning ozone removing catalytic converter, a dirty solenoid, or dirt in the optical system. The calibration curve is used to reduce subsequent ambient data.

Frequency Of Calibration

In order to generate data of the highest confidence, it is recommended that a multipoint calibration be performed every three (3) months, any time major disassembly of components is performed, or any time the zero or span checks give results outside the limits described in Periodic Zero and Span Checks below.

Periodic Zero and Span Checks

In order to achieve data of the highest confidence, it is suggested that periodic zero and span checks be performed. These checks can be performed by:

1. Periodically challenging the Model 49 with zero air. (The output flow of the zero air supply should be greater than the flow demand of the Model 49. In addition, an atmospheric dump bypass should be utilized to ensure that the zero air gas flow is being delivered at atmospheric pressure). Record the analyzer response in percent of scale as A_o. Compute the zero drift from the following equation:

$$Zero\ Drift\ \% = A_o - Z \qquad (8)$$

   where Z is the recorder response obtained at the last calibration for zero air, % scale.

2. Periodically challenging the Model 49 with an ozone level of approximately 80% URL from a previously calibrated stable ozone generator. (The output flow from this generator should be greater than the flow demand of the Model 49. In addition, an atmospheric dump bypass should be utilized to ensure the span gas flow is being delivered at atmospheric pressure). Record the analyzer response in % of scale as A_{80}. Compute the span error from the following equation:

$$\frac{[(A_{80} - Z)\,\frac{URL}{100}] - [O_3]}{[O_3]} \times 100 \qquad (9)$$