

- Appendix D to part 50 of this chapter is re-designated as Appendix D-2.
- A new Appendix D-1 is added to part 50 of this chapter to read as follows:

**Appendix D-1 to 40 CFR —REFERENCE MEASUREMENT PRINCIPLE AND CALIBRATION
PROCEDURE FOR THE MEASUREMENT OF OZONE IN THE ATMOSPHERE – NO
CHEMILUMINESCENCE (NO-CL) METHOD**

1.0 APPLICABILITY

1.1 This NO chemiluminescence (NO-CL) method provides reference measurements of the concentration of ozone (O_3) in ambient air for determining compliance with the national primary and secondary ambient air quality standards for ozone as specified in § 50.9 and § 50.10 of this chapter. The method is applicable to the measurement of ambient O_3 concentrations using continuous (real-time) sampling. Additional quality assurance procedures and guidance are provided in part 58, appendix A, of this chapter and in Reference 10.

2.0 PRINCIPLE

2.1 This reference method is based on continuous automated measurement of the intensity of the characteristic chemiluminescence released by the reaction of the O_3 with nitric oxide (NO) gas. An ambient air sample stream and a specific flowing concentration of NO are mixed in a measurement cell, where the chemiluminescence is measured by a very sensitive photo-detector.

2.2 The measurement system is calibrated by referencing the instrumental chemiluminescence measurements to certified O_3 standard concentrations generated in a dynamic flow system and assayed photometrically to be traceable to a National Institute of Standards and Technology (NIST) primary standard for O_3 (see Calibration Procedure, below).

2.3 An analyzer implementing this measurement principle should include a measurement cell, a suitable photometric detector system with appropriate wave length sensitivity, a pump and flow control system for sampling and drying the ambient air and moving it into and through the measurement cell, a means to supply and mix a constant, flowing NO concentration with the sample air flow in the measurement cell, suitable electronic control and measurement processing capability, and other apparatus as may be necessary. The analyzer must be designed to provide accurate, repeatable, and continuous

measurements of O₃ concentrations in ambient air, with measurement performance as specified in Subpart B of Part 53 of this chapter.

2.4 *Sampling considerations:* The use of a particle filter on the sample inlet line of a NO-CL O₃ analyzer is required to prevent buildup of particulate matter in the measurement cell and inlet components. This filter must be changed frequently, and the sample inlet system used with the analyzer must be kept clean, to avoid significant loss of O₃ in the O₃ sample air prior to the concentration measurement.

3.0 INTERFERENCES

3.1 Aside from potential loss of O₃ in the inlet air sample handling components of the analyzer (and its associated exterior air sampling components) due to buildup of airborne particulate matter, the NO-CL measurement system is relatively free of significant interferences from other pollutant substances that may be present in ambient air.

4.0 CALIBRATION PROCEDURE

1. *Principle.* The calibration procedure is very similar to the calibration procedure described in Appendix D-2 of this part. It is based on the photometric assay of ozone (O₃) concentrations in a dynamic flow system. The concentration of O₃ in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O₃ at 254 nm, (2) the optical path length (l) through the sample, (3) the transmittance of the sample at a wavelength of 254 nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_0 , where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O₃ sample, and I_0 is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_0 . The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha cl} \quad (1)$$

where:

α = absorption coefficient of O₃ at 254 nm = 308 ±4 atm⁻¹ cm⁻¹ at 0 °C and 760 torr,^{1, 2, 3, 4, 5, 6, 7}

c = O₃ concentration in atmospheres, and

l = optical path length in cm.

In practice, a stable O₃ generator is used to produce O₃ concentrations over the required calibration concentration range. Each O₃ concentration is determined from the measurement of the transmittance (I/I_0) of the sample at 254 nm with a photometer of path length l and calculated from the equation,

$$c(\text{atm}) = -\frac{1}{\alpha l} \left(\ln \frac{I}{I_0} \right) \quad (2a)$$

or

$$c(\text{atm}) = -\frac{10^6}{\alpha l} \left(\ln \frac{I}{I_0} \right). \quad (2b)$$

The calculated O₃ concentrations must be corrected for O₃ losses, which may occur in the photometer, and for the temperature and pressure of the sample.

2. *Applicability.* This procedure is applicable to the calibration of ambient air O₃ analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 8.

3. *Apparatus.* A complete UV calibration system consists of an ozone generator, an output port or manifold, a photometer, an appropriate source of zero air, and other components as necessary. The configuration must provide a stable ozone concentration at the system output and allow the photometer to accurately assay the output concentration to the precision specified for the photometer (3.1). Figure 1 shows a commonly used configuration and serves to illustrate the calibration procedure which follows. Other configurations may require appropriate variations in the procedural steps. All connections between components in the calibration system downstream of the O₃ generator should be of glass, Teflon, or other relatively inert materials. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 9. For certification of transfer standards which provide their own source of O₃, the transfer standard may replace the O₃ generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

3.1 *UV photometer.* The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 1. It must be capable of measuring the transmittance, I/I_0 , at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O₃ is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O₃ from contact with cell walls and gas handling components. See Reference 9 for additional information.

3.2 *Air flow controllers.* Devices capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

3.3 *Ozone generator.* Device capable of generating stable levels of O₃ over the required concentration range.

3.4 *Output manifold.* The output manifold should be constructed of glass, Teflon, or other relatively inert material, and should be of sufficient diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

3.5 *Two-way valve.* Manual or automatic valve or other means to switch the photometer flow between zero air and the O₃ concentration.

3.6 *Temperature indicator.* Accurate to ± 1 °C.

3.7 *Barometer or pressure indicator.* Accurate to ± 2 torr.

4. *Reagents.*

4.1 *Zero air.* The zero air must be free of contaminants which would cause a detectable response from the O₃ analyzer, and it should be free of NO, C₂ H₄, and other species which react with O₃. A procedure for generating suitable zero air is given in Reference 9. As shown in Figure 1, the zero air supplied to the photometer cell for the I₀ reference measurement must be derived from the same source as the zero air used for generation of the ozone concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of ozone, see Reference 8 for guidance on meeting this requirement.

5. *Procedure.*

5.1 *General operation.* The calibration photometer must be dedicated exclusively to use as a calibration standard. It should always be used with clean, filtered calibration gases, and never used for ambient air sampling. Consideration should be given to locating the calibration photometer in a clean laboratory where it can be stationary, protected from physical shock, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

5.2 *Preparation.* Proper operation of the photometer is of critical importance to the accuracy of this procedure. The following steps will help to verify proper operation. The steps are not necessarily required prior to each use of the photometer. Upon initial operation of the photometer, these steps should be carried out frequently, with all quantitative results or indications recorded in a chronological record either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer is established, the frequency of these steps may be reduced consistent with the documented stability of the photometer.

5.2.1 *Instruction manual:* Carry out all set up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

5.2.2 *System check*: Check the photometer system for integrity, leaks, cleanliness, proper flowrates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

5.2.3 *Linearity*: Verify that the photometer manufacturer has adequately established that the linearity error of the photometer is less than 3%, or test the linearity by dilution as follows: Generate and assay an O₃ concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and re-assay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \quad (3)$$

where:

E = linearity error, percent

A₁ = assay of the original concentration

A₂ = assay of the diluted concentration

R = dilution ratio = flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 9.

5.2.4 *Inter-comparison*: When possible, the photometer should be occasionally inter-compared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 *Ozone losses*: Some portion of the O₃ may be lost upon contact with the photometer cell walls and gas handling components. The magnitude of this loss must be determined and used to correct the calculated O₃ concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 Assay of O₃ concentrations.

5.3.1 Allow the photometer system to warm up and stabilize.

5.3.2 Verify that the flowrate through the photometer absorption cell, F, allows the cell to be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

5.3.3 Insure that the flowrate into the output manifold is at least 1 liter/min greater than the total flowrate required by the photometer and any other flow demand connected to the manifold.

5.3.4 Insure that the flowrate of zero air, F_z , is at least 1 liter/min greater than the flowrate required by the photometer.

5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then F_z . The two photometer readings must be equal ($I = I_0$).

NOTE: In some commercially available photometers, the operation of the two-way valve and various other operations in section 5.3 may be carried out automatically by the photometer.

5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of I_0 .

5.3.8 Actuate the two-way valve to allow the photometer to sample the ozone concentration until the absorption cell is thoroughly flushed and record the stable measured value of I .

5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 9 for guidance.)

5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(\frac{-1}{\alpha l} \ln \frac{I}{I_0} \right) \left(\frac{T}{273} \right) \left(\frac{760}{P} \right) \times \frac{10^6}{L} \quad (4)$$

where:

$[O_3]_{OUT}$ = O_3 concentration, ppm

α = absorption coefficient of O_3 at 254 nm = 308 atm⁻¹ cm⁻¹ at 0° C and 760 torr

l = optical path length, cm

T = sample temperature, K

P = sample pressure, torr

L = correction factor for O_3 losses from 5.2.5 = (1–fraction of O_3 lost).

NOTE: Some commercial photometers may automatically evaluate all or part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For “automatic” photometers which evaluate the first term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O₃ levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O₃ concentration standards as necessary by repeating steps 5.3.6 to 5.3.10 or by Option 1.

5.4 *Certification of transfer standards.* A transfer standard is certified by relating the output of the transfer standard to one or more ozone standards as determined according to section 5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 8 for guidance.

5.5 *Calibration of ozone analyzers.* Ozone analyzers are calibrated as follows, using ozone standards obtained directly according to section 5.3 or by means of a certified transfer standard.

5.5.1 Allow sufficient time for the O₃ analyzer and the photometer or transfer standard to warm-up and stabilize.

5.5.2 Allow the O₃ analyzer to sample zero air until a stable response is obtained and adjust the O₃ analyzer's zero control. Offsetting the analyzer's zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as “Z”.

5.5.3 Generate an O₃ concentration standard of approximately 80% of the desired upper range limit (URL) of the O₃ analyzer. Allow the O₃ analyzer to sample this O₃ concentration standard until a stable response is obtained.

5.5.4 Adjust the O₃ analyzer's span control to obtain the desired response equivalent to the calculated standard concentration. Record the O₃ concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.5.2 to 5.5.4.

5.5.5 Generate several other O₃ concentration standards (at least 5 others are recommended) over the scale range of the O₃ analyzer by adjusting the O₃ source or by Option 1. For each O₃ concentration standard, record the O₃ and the corresponding analyzer response.

5.5.6 Plot the O₃ analyzer responses (vertical or Y-axis) versus the corresponding O₃ concentrations (horizontal or X-axis). Compute the linear regression slope and intercept and plot the regression line to verify that no point deviates from this line by more than 2 percent of the maximum concentration tested.

5.5.7 *Option 1*: The various O₃ concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O₃ concentration generated in steps 5.3.6 and 5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system may be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O₃ generator. A mixing chamber between the O₃ generator and the output manifold is also required. The flowrate through the O₃ generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NIST. Each O₃ concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O + F_D} \right) \quad (5)$$

where:

[O₃]'_{OUT} = diluted O₃ concentration, ppm

F_O = flowrate through the O₃ generator, liter/min

F_D = diluent air flowrate, liter/min

NOTE: Additional information on calibration and pollutant standards is provided in Section 12 of Reference 10.

5.0 FREQUENCY OF CALIBRATION

The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking will vary by analyzer; however, the minimum frequency, acceptance criteria, and subsequent actions are specified in Reference 10, Appendix D: Measurement Quality Objectives and Validation Template for O₃ (pages 3 and 4 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

6.0 REFERENCES FOR THIS NO-CL O₃ CALIBRATION PROCEDURE

[References 1 – 7 below are from the original Appendix D and are cited in this procedure (Equation 1). They seem quite old to use, but there may not be any appropriate, newer ones available.]

1. E.C.Y. Inn and Y. Tanaka, "Absorption coefficient of Ozone in the Ultraviolet and Visible Regions", *J. Opt. Soc. Am.*, 43, 870 (1953).

2. A. G. Hearn, "Absorption of Ozone in the Ultraviolet and Visible Regions of the Spectrum", *Proc. Phys. Soc. (London)*, 78, 932 (1961).

3. W. B. DeMore and O. Raper, "Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon", *J. Phys. Chem.*, 68, 412 (1964).

4. M. Griggs, "Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions", *J. Chem. Phys.*, 49, 857 (1968).

5. K. H. Becker, U. Schurath, and H. Seitz, "Ozone Olefin Reactions in the Gas Phase. 1. Rate Constants and Activation Energies", *Int'l Jour. of Chem. Kinetics*, VI, 725 (1974).

6. M. A. A. Clyne and J. A. Coxom, "Kinetic Studies of Oxy-halogen Radical Systems", *Proc. Roy. Soc.*, A303, 207 (1968).

7. J. W. Simons, R. J. Paur, H. A. Webster, and E. J. Bair, "Ozone Ultraviolet Photolysis. VI. The Ultraviolet Spectrum", *J. Chem. Phys.*, 59, 1203 (1973).

8. Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone, EPA publication number EPA-454/B-10-001, November, 2010. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711. [Available at www.epa.gov/ttnamti1/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf.]

9. Technical Assistance Document for the Calibration of Ambient Ozone Monitors, EPA publication number EPA-600/4-79-057, EPA, National Exposure Research Laboratory, Research Triangle Park, NC 27711. [Still available at www.epa.gov/ttnamti1/files/ambient/criteria/4-79-057.pdf.]

10. QA Handbook for Air Pollution Measurement Systems—Volume II. Ambient Air Quality Monitoring Program. EPA-454/B-08-003, December 2008.

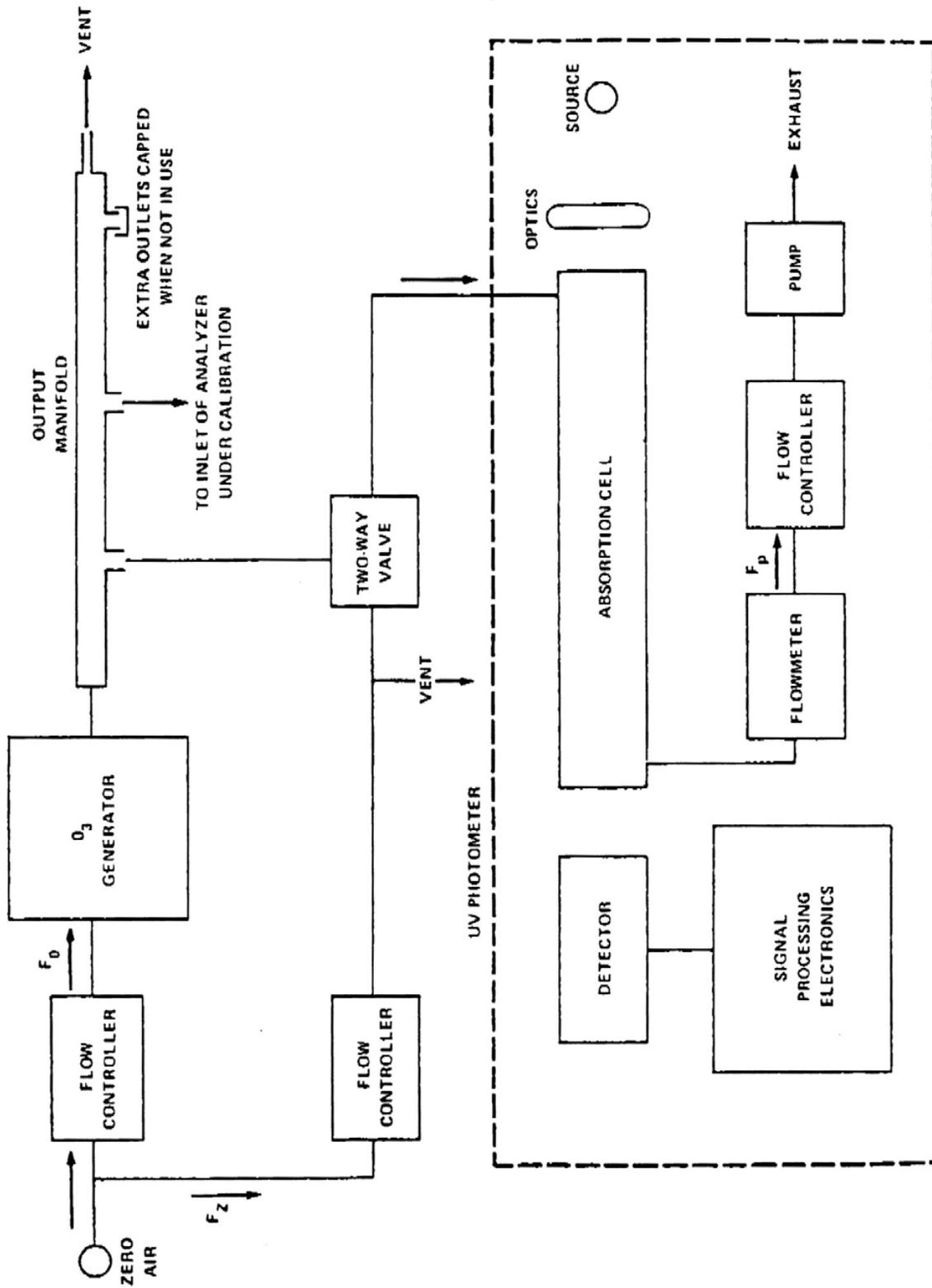


Figure 1. Schematic diagram of a typical UV photometric calibration system.

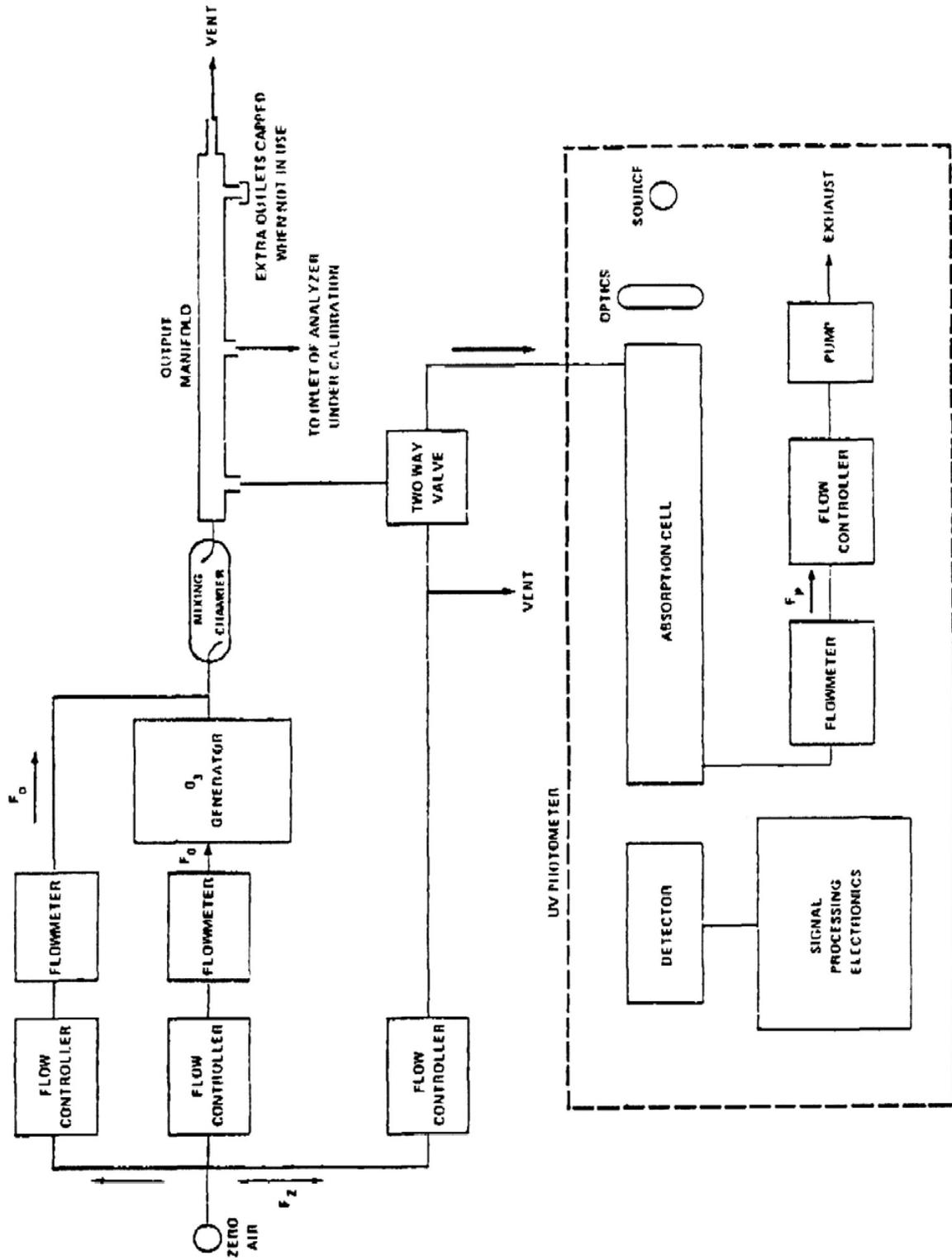


Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).