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A SURVEY OF CALIBRATION TECHNIQUES FOR ATMOSPHERIC OZONE MONITORS

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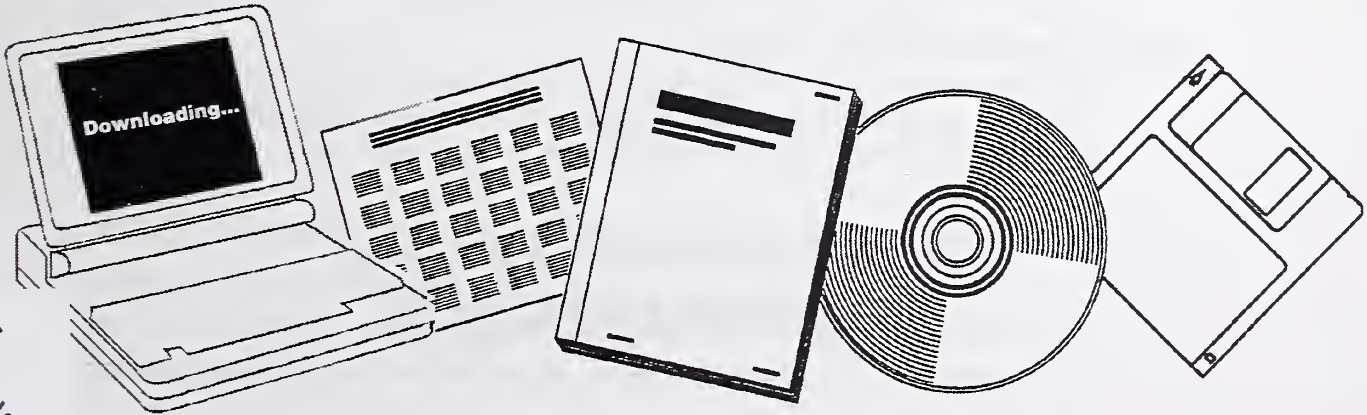

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A SURVEY OF CALIBRATION TECHNIQUES FOR ATMOSPHERIC OZONE MONITORS

Jimmie A. Hogeson

National Bureau of Standards
Department of Commerce
Washington, D. C. 20234

Final Report

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, ***Secretary***
Edward O. Vetter, ***Under Secretary***
Dr. Betsy Ancker-Johnson, ***Assistant Secretary for Science and Technology***
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A Survey of Calibration Techniques for Atmospheric Ozone Monitors

ABSTRACT

A survey is presented of recent studies on calibration techniques for atmospheric ozone (O_3) monitors. These calibration techniques are based on iodometry, ultraviolet photometry (UV) and gas phase titration (GPT). The iodometric procedures include the 1 percent neutral buffered potassium iodide (NBKI) technique used by the Environmental Protection Agency (EPA), a 2 percent NBKI method of the California Air Resources Board and a 1 percent unbuffered KI technique previously used by the Los Angeles Air Pollution Control District (LAAPCD). The UV and GPT approaches are of rather recent application and brief descriptions of the calibration procedures are given. In summary the data show excellent agreement between O_3 determinations by UV or GPT and demonstrate that absolute measurements of trace O_3 concentrations can be made by either technique. On the other hand the NBKI methods yield O_3 measurements 1 to 13 percent higher than absolute values when O_3 in dry air is analyzed. In the presence of humid air the NBKI measurements are high by factors ranging from 15 to 30 percent.

INTRODUCTION

As a result of the Clean Air Act of 1970 and subsequent Federal regulations, ozone (O_3) is one of the six criteria air pollutants for which national primary and secondary air quality standards have been established [1]. Compliance monitoring has been implemented by many state and local air pollution control agencies [2], throughout the country today. Ozone has been recognized as an important air pollutant since its discovery in the Los Angeles basin in the late 1940's. Since that time a considerable volume of literatature has appeared dealing with techniques for and problems associated with atmosphere O_3 monitoring. This literature is adquately summarized in several recent reviews [3-6]. The purpose of this discussion is to update these reviews by a description of some recent, critical and unpublished activities in O_3 monitoring.

Atmospheric O_3 measurements can conveniently be divided into the areas of sampling, calibration and analysis or monitoring. Sampling procedures and manual and instrumental analysis methods are adequately covered by prior reviews. The attached appendix [3] provides a description of both manual and continuous techniques for monitoring. The most recent activities and the source of considerable controversy lies in the area of O_3 calibration, and these activities are discussed below.

The nature of the O_3 calibration problem is worth reviewing. Air pollution monitors, including those for O_3, do not, in general, provide a measurement of the absolute concentration of the pollutant in the atmosphere. Instead they provide an output signal which is linearly proportional to pollutant concentration. The instrument must then be calibrated by sampling from a flowing air stream into which the pollutant has been introduced at a known concentration. Where feasible primary standards, such as National Bureau of Standards certified gas cylinders or permeation tubes, are used to generate known concentrations. In the case of the unstable O_3 molecule, no primary standard is available. Instead a photolytic generator [7] is used to produce trace concentrations of O_3 in air and the air stream sampled and analyzed by a manual, wet-chemical procedure. Various manual procedures have been used in the past but the technique used most predominantly now employs oxidation of a neutral buffered potassium iodide solution [1]. The iodine produced is determined spectrophotometrically.

The recent controversy involves the accuracy and reproducibility of iodometric calibration procedures. Questions have arisen because of discrepancies observed in comparisons of different variations of iodometric procedures and because of the application of two alternative gas phase techniques for absolute O_3 measurement. These techniques employ ultraviolet (UV) absorption by O_3 of 254 nm radiation and gas phase titration (GPT) of O_3 with known concentrations of nitric oxide (NO). The discussion below gives a brief description of the UV and GPT calibration procedures. In addition, results of recent comparisons of the various calibration techniques are summarized.

DISCUSSION

Calibration Procedures - UV and GPT

Ultraviolet Absorption Technique. Details of the absolute measurement of O_3 in the subpart per million (ppm) range have been given by Demore and Patapoff [8] and by Hodgeson, et al. [9]. The basic absorption equation for determining ozone concentrations by photometric measurements is:

$$[O_3], \text{ ppm} = \frac{10^6}{\alpha_o \ell} \frac{P_o}{P} \frac{T}{T_o} \log_e (I_o/I),$$

where $\alpha_o = 308.6 \text{ atm}^{-1}\text{cm}^{-1}$ (base e) is the O_3 absorption coefficient at 253.7 nm, a value which has been determined to within an accuracy of 1 percent by several investigators [8]. In this equation ℓ is the pathlength in cm, $P_o = 1$ atm and $T_o = 273K$.

The absorption coefficient and the optical pathlength are known to within 1 per cent. Thus the absolute O_3 determination requires only the measurement of the ratio of the transmitted light intensities in the absence of and in the presence of O_3. It is instructive to examine the degree of light attenuation expected for O_3 concentrations in the sub-ppm range. At low ozone concentrations the light attenuation is very small and the log term reduces to the linear form,

$$\log_e I_o/I \cong \Delta I/I_o \quad \text{where } \Delta I = I_o - I.$$

For an O_3 concentration of 0.1 ppm, an optical path of 100 cm and at P = 760 mm, T = 298K, the fractional attenuation is

$$\frac{\Delta I}{I_o} = 2.8 \times 10^{-3}$$

Thus, the determination of O_3 at the 0.1 ppm level requires the measurement of a light attenuation of only 3 parts per thousand (0.3%). This is a difficult task and indeed 0.1 ppm is the approximate lower limit of detection for a 100 cm photometer.

The laboratory photometer employed by the author in a previous study [9] is illustrated in figure 1. The optical components were mounted on a shock mounted 2 meter optical rail. The detector was a ultraviolet phototube with a high rejection to room light. An interference filter was coupled to the phototube to isolate the 253.7 nm component of the low pressure mercury lamp. The absorption cell was a 1 meter Pyrex tube, 1 inch in diameter, with air inlet and outlet connections at each end. The light pource was collimated and apertured in a manner such that a parallel beam of light, 1 to 2 mm in diameter, passed through the center of the absorption tube to the phototube. This arrangement was chasen to avoid optical reflections off the walls of the absorption tube and in order to define a well known optical path length.

The relative light intensity is determined by measuring the anode output current of the photodiode by either analog or digital current measuring devices. In the single beam system it is advantageous to integrate the output over selected time intervals during both the sample and reference cycles in order to obtain maximum precision. A digital photometer output arrangement employing a charge-to-frequency conversion and a multi-channel analyzer is described in reference 9.

The basic procedure for making O_3 measurements with a single beam photometer system was as follows. The reference beam intensity, I_o, measurement was made by purging the photometer cell with clean air from an auxiliary air source. When a stable reference intensity signal was obtained, the ozonized air stream was pased through the cell and the sample beam intensity, I, measured. Once a stable measurement of I was obtained the cell was again purged with clean air to remeasure I_o. The total time required for the single beam photometric measurement via this cycle was approximately 5 minutes.

Gas Phase Titration Technique. Gas phase titration (GPT) as a technique applied to the calibration of atmospheric monitors of O_3 and nitrogen dioxide (NO_2) has been described in detail elsewhere [10, 9]. The GPT technique has been employed extensively in recent years by the Environmental Protection Agency (EPA) and other groups. Portable GPT apparatus are commercially available for calibrations in the laboratory or in the field.

A laboratory calibration manifold used for GPT O_3 measurements [9] is illustrated in figure 2. Typical clean air flow rates were of the order of 5 liters per minute. In the mode illustrated in figure 2 the clean air flow was split such that only 10% of the air passed through capillary 1 and through the variable O_3 source. The remainder of the air flow passed through capillary 2 and mixed with the ozonized air stream downstream of the reaction flask. The reaction flask and the mixing flask were approximately 250 cm^3 in volume. The split stream design was employed in order to generate locally higher O_3 and NO concentrations in the reaction flask and promote complete reaction over a wide concentration range.

The GPT approach is based upon the rapid reaction between NO and O_3.

$$NO\ (excess) + O_3 = NO_2 + O_2 \qquad (6)$$

A constant NO concentration, $(NO)_o$, in the ppm range is produced by dilution of the flow from a cylinder containing a known concentration of NO in nitrogen (50-100 ppm)

$$(NO)_o = F_{NO}/F_T \times (NO)_{cylinder}$$

where F_{NO} = flow from NO cylinder
$F^*_{O_3}$ = air flow through O_3 source
$F_T = F_{NO} + F_{O_3}$

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*In the case in which the air flow is split upstream of the O_3 source, F_{O_3} represents the sum of the flow through the source and bypass arms.

Once the initial NO concentration is established, a series of O_3 samples at lower concentrations are added and the decrease in NO observed with the chemiluminescence detector. Over the range of O_3 concentrations for which the reaction is complete, the following relation holds,

$$(NO)_o - (NO)_i = (O_3)_i \times F_{O_3}/F_T = (NO_2)_i \qquad (8)$$

where $(O_3)_i \times F_{O_3}/F_T$** is the O_3 concentration added and $(NO_2)_i$ is the concentration of NO_2 produced. For the GPT system described in this work, essentially complete reaction was obtained at an initial NO concentration of 1 ppm for O_3 concentrations up to 0.7 ppm.

The GPT approach is a method for relating the concentration of the three components, NO, O_3, and NO_2. For an actual measurement to be made the concentration of one of the species must be known and the change in concentration observed upon reaction. In the usual application the initial NO concentration is known based on a standard NO cylinder, which is referenced to an NBS certified NO cylinder, and the measurement of a flow dilution ratio, F_{NO}/F_T. The GPT measurement

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**The flow ratio term, F_{O_3}/F_T, is included because the O_3 concentration in the absence of added NO is desired. At typical flow rates, e.g., F_{O_3} = 5000 cm^3/min and F_{NO} = 100 cm^3/min, this ratio is close to unity.

then yields a calibration of the O_3 source and the generation of a known concentration of NO_2.

Evaluations of Calibration Techniques

Early Studies. In the original version [11] of the Federal Reference Method (FRM) now employed by EPA, a stoichiometry factor (moles I_2 released/moles O_3 absorbed) of 1.0 was employed. This factor was later refuted by Boyd et al. [12] who observed a factor of 1.5 upon static abosrption of relatively high O_3 concentrations (10-100 ppm). This work was immediately followed be several investigations in the early 1970's all of which obtained stoichiometry factors near unity for ppm concentrations of O_3 in flowing systems [13-15]. These studies seemed to satisfactorily answer questions over calibration uncertainties for a time. However, since 1973 extensive applications of the EPA-FRM and interagency comparative and collaborative studies have yielded results which have actively revived the issue of the accuracy and the precision of iodometric methods.

For example in a recent interlaboratory collaborative test conducted by EPA, different laboratories employing the same reference method obtained a significant spread in results upon the analysis of precalibrated O_3 generators supplied by NBS [16]. Ozone generators were calibrated by

NBS at 5 concentration from 0.05 to 0.5 ppm and supplied to ten different laboratories for analysis. The calibration of the generators was then checked by NBS after the tests were completed. The statistical analysis of results from this study revealed that the mean percentage difference between the average observed value and the NBS reference value at these five concentration levels ranged from 16 to 37 percent.

Several factors might contribute to these observed interlaboratory biases, including instability of O_3 generators or failure of collaborators to adhere to test procedures. However, the nature of these studies indicated that the calibration procedure was a primary suspect cause for the observed lack of reproducibility. This suspicion was reinforced by data presented at a joint NBS-EPA workshop on ozone calibration. The summary of this workshop [17] discusses uncontrolled variables in written procedures which may contribute to uncertainties in iodometric O_3 analyses. These include such factors as impinger design, reaction time after sampling and reagent impurities.

State of California Studies. Comparative studies began in the State of California in 1973 to check the accuracy obtainable with iodometric calibration procedures. Two separate procedures were used in that state, each different from the EPA-FRM. Throughout California outside the county of Los Angeles, the

California Air Resources Board (CARB) employed a method similar to EPA, differing in that 2% NBKI (vs 1% for EPA) was used and humidified air was passed through the O_3 generator. The Los Angeles Air Pollution Control District (LAAPCD) calibrated their analyzers by a method in which 2% unbuffered KI was used and in which the liberated iodine was determined by titration with thiosulfate.

Significant measurement discrepancies between the LAAPCD and CARB were first observed in 1973, during studies in which a CARB mobile van obtained oxidant data within 2 miles of the LA Pomona station (Spring 1973) and then adjacent to the LA Azusa station (Summer 1973). In Pomona averaged LAAPCD oxidant data were 38 percent lower than simultaneous CARB data and in Azusa 30 percent lower than CARB measurements [18, 19]. The measurement discrepancy was traced to the different calibration procedures employed in laboratory studies conducted by calibration teams from CARB and the California Air and Industrial Hygiene Laboratory [19, 20]. These studies demonstrated that the county calibration method gave results 27 to 30 percent lower than the CARB method when analyzing the same ozone sample.

In order to further investigate the measurement disparity and provide a recommended course of action, CARB in the summer of 1974 appointed an "ad hoc" committee to evaluate various calibration procedures. In October 1974, this committee conducted a study at the CARB El Monte Laboratory, in which the following calibration procedures were simultaneously compared by sampling from a common manifold - 1% NBKI (EPA), 2% NBKI (CARB), 2% UBKI (LAAPCD), UV and GPT. Six O_3 concentrations over the nominal concentration range, 0.1-0.8 ppm, were analyzed on 3 consecutive days. The iodometric measurements were performed by representatives from each of the agencies involved. The data were analyzed by linear regression with the UV measurement as the reference and the following relations were obtained [21].

$$(O_3)_{GPT} = 1.09\ (O_3)_{UV} - 0.003$$

$$(O_3)_{CARB} = 1.29\ (O_3)_{UV} - 0.005$$

$$(O_3)_{EPA} = 1.24\ (O_3)_{UV} - 0.035$$

$$(O_3)_{LAAPCD} = 0.96\ (O_3)_{UV} - 0.032$$

The following comments should be made regarding these data. Both the CARB and the EPA results are significantly higher than the absolute UV measurements while the LAAPCD measurements are slightly lower. The discrepancy observed between the CARB and LAAPCD measurements was approximately the same as observed previously. The EPA* and LAAPCD iodometric results show significant negative intercepts. The effect of the negative intercept is that the EPA and UV measurements tend to converge at lower concentrations. The GPT procedure was not the same as that normally applied by EPA, but a late modification especially designed to be compatible with the sampling manifold employed. Finally, according to CARB practice the air stream was humidified to a 50 percent RH upstream of the O_3 source.

<u>EPA Study</u>. Shortly after the El Monte study, a similar investigation was undertaken at EPA's research facility at Research Triangle Park, NC. In this study the CARB, EPA and LAAPCD methods were compared to GPT as the reference. Three ozone concentrations (0.1, 0.3 and 0.5) were analyzed over a 9 day study in a random fashion such that 12 determinations/concentration/method resulted. In this study dry air was used for the O_3 source as specified in the EPA-FRM. The GPT measurement was performed at the start and conclusion of each experiment. The GPT measurement was traceable both to an NBS standard reference NO cylinder and to the NO_2 generated from an NBS certified NO_2 permeation device. The results of

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*In a separate study [9] employing the same reagents and impingers used here, a negative intercept was also observed and by indirect evidence attributed to an O_3 demand of the reagents or distilled water used. In the absence of this demand the slope would not be affected.

this study are summarized below in terms of the average ratio of the iodometric results to GPT [22].

Nominal Concentration	EPA/GPT	CARB/GPT	LAAPCD/GPT
0.1	1.05	1.07	0.592
0.3	0.964	1.01	0.604
0.5	1.01	1.04	0.650
Average Ratio	1.01	1.04	0.615

The results of this study differ from the El Monte data in that the EPA and CARB measurements were only slightly higher than the reference O_3 values obtained in this case by GPT. The large discrepancy between the NBKI and the unbuffered KI measurements was again confirmed.

Effect of Water Vapor. The most disturbing disparity between the El Monte and EPA-RTP studies was the different relations observed between the iodometric techniques and the reference techniques employed, since both UV and GPT presumably provide an absolute measure of the O_3 concentration. A substantial portion of the descrepancy was subsequently accounted for in three separate studies by EPA at their research laboratories in Las Vegas, NV [23] and Research Triangle Park, NC [24] and by CARB in California [25]. These studies demonstrated that humidified air has a significant effect upon some of the techniques employed.

In these studies the responses of the various techniques and instruments to O_3 in dry air were compared to responses obtained when air containing the same O_3 concentration and relative humidities of 20 to 80 per were analyzed. A portion of these data are summarized in Table I. The Dasibi and GPT measurements are unaffected by the presence of water vapor. The chemiluminescence O_3 detector shows a net positive response of 5-8 per cent. The unbuffered KI procedure has a slight negative response to water vapor whereas the NBKI procedures have positive responses of 6-13%. Thus in presence of water vapor the NBKI results will be ca. 10 per cent higher with respect to reference UV or GPT measurements. A correction of the El Monte NBKI data for water vapor would give closer agreement to the EPA-RTP measurements. Some discrepancy would remain which may be attributed to different procedures followed in the GPT measurements or unknown variables in the KI procedures.

Recent Individual Investigations. Most of the previous investigations discussed involved interagency or interlaboratory investigations of several procedures. While such studies have been useful for the rapid generation of qualitative information, they suffered several shortcomings which have limited the definitive determination of the quantitative relations among the various calibration procedures. The involvement of several investigators and laboratories requires that rigid procedural protocols be written and followed. Such protocols leave little room for changes in direction of the experiment detailed by the nature of the data obtained. In addition such studies were conducted within such a relatively short time frame that it is almost impossible to repeat suspect experiments or to perform problem solving. Finally, the involvement of many different people and apparatus makes the problem of quality control over the whole experiment quite complex.

The most definitive information about relations among calibration procedures can be obtained in one laboratory over an unlimited time frame by a single investigator who is able to control all aspects of the study. Fortunately several studies of this sort have recently been completed for O_3. In an August 1975 meeting of the ASTM in Boulder Colorado, three separate papers discussed observed relations among UV, GPT and NBKI. These reports were based on carefully controlled experiments in which multiple, simultaneous analyses of O_3 were performed by the various procedures. DeMore and Patapoff [8] used a 5 meter laboratory photometer and observed agreement within 1 per cent between UV and GPT measurements over the concentration range of 0.05 to 1 ppm. Similar agreement was obtained by Paur [26], who used 2 separate modified Dasibi analyzers to make absolute UV measurements. Hodgeson et al. [9] used a 1-meter laboratory photometer for comparison of UV to GPT and the 1 per cent NBKI method employed by EPA. Again a 1:1 agreement was obtained between UV and GPT over the concentration range from 0.1 to 0.8 ppm. However, the NBKI method gave measurements that were ca. 10 per cent higher than either of the gas phase techniques. Finally, results obtained at the Statewide Air Pollution Research Center in California, showed good agreement between absolute O_3 measurements by UV photometry and long-path infrared spectrophotometry [27].

While excellent agreement has been obtained between the photometric and GPT measurements, the situation is still somewhat vague regarding the relation between iodometric and absolute O_3 measurements. Paur [28] has summarized recent published and unpublished data in which iodometric measurements were compared to UV or GPT determinations. This summary is repeated here as table II. The EPA 1% NBKI yields O_3 measurements higher than obtained by UV or GPT by factors ranging from 1 to 11% for studies conducted in the absence of water vapor. It is interesting to note that if the ratios from references 24 and 21 are corrected by 10% for the water vapor effect, then ratios of 1.02 and 1.13 are obtained for the 1% NBKI method. With attention focused on the EPA method, it is apparent that a factor of 1.07 ± 0.06 would encompass all the data given here. It should be emphasized that these are best possible results obtained by trained personnel in dedicated experiments and therefore may not represent the accuracy obtainable in routine field calibrations.

SUMMARY AND CONCLUSIONS

The studies discussed above demonstrate that excellent agreement can be obtained between UV and GPT calibration procedures and that either technique may be used for the absolute measurement of sub-ppm concentrations of O_3. On the other hand results obtained in separate studies by the EPA 1 percent NBKI procedure (using dry air) have been higher than absolute O_3 measurements by factors ranging from 1.01 to 1.13. A factor of 1.07 ± .06 encompassed all the studies discussed here. This small deviation from unity and the relatively large uncertainty which must be assigned to the factor dictates against the application of correction factors to NBKI calibration results at the present time. In the presence of moist air, O_3 measurements by NBKI procedures are higher than absolute values by 15 to 30 percent. The reasons for the observed water vapor effect are unknown at the present time.

The main conclusion is that greater accuracy can be achieved by a replacement of iodometric calibration procedures by UV photometry or GPT. At the present time the choice of

UV or GPT is a matter of convenience. In principal calibrations by the UV procedure are simpler because this technique is inherently flow independent. A lack of absolute laboratory photometers is the primary limitation, since at the present time there are only three operational systems - at the Jet Propulsion Laboratory, EPA-Las Vegas and NBS. Absolute determination of O_3 by the GPT procedure requires the accurate measurement of a flow dilution ratio. However, the technique may be readily applied now by many calibration groups through the availability of NBS certified NO cylinders and commercially available GPT apparatus.

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TABLE I

EFFECT OF HUMIDIFIED OZONE SAMPLES

	Relative Response, Wet/Dry		
Technique	Ref. 23 (40%RH)	Ref. 24 (50%RH)	Ref. 25 (60%RH)
1% KI	1.05	1.08	1.10
2% KI	-	1.06	1.13
2% UBKI	-	-	0.96
GPT	-	0.990	-
Dasibi	1.00	0.995	1.00
Chemilum.	1.05	1.08	1.07

TABLE II[a]

SUMMARY OF RECENT DATA ON OZONE CALIBRATION

Study	KI Method	Reference Method	Ratio $\frac{KI}{Reference}$	O_3 Conc. Range, ppm	Relative Humidity
Reference 22	1% NBKI	GPT	1.01 ± 0.04	0.1 - 0.5	~0
	2% NBKI	GPT	1.04 ± 0.03	0.1 - 0.5	~0
	2% UBKI	GPT	0.61 ± 0.04	0.1 - 0.5	~0
Reference 24	1% NBKI	GPT	1.05 ± 0.05	0.4	~0
	1% NBKI	GPT	1.12 ± 0.07	0.4	40 - 60%
	2% NBKI	GPT	1.13 ± 0.03	0.4	~0
	2% NBKI	GPT	1.18 ± 0.05	0.4	40 - 60%
Reference 21	1% NBKI	UV	1.25	0.1 - 0.8	~50%
	2% NBKI	UV	1.29	0.1 - 0.8	~50%
	2% NBKI	UV	0.96	0.1 - 0.8	~50%
Reference 9	1% NBKI	UV	1.11 ± .02	0.05 - 10.0	~0
Beard, EPA-RTP	1% NBKI	GPT	1.08 ± .035	0.08 - 0.8	~0
Smith, EPA-RTP	1% NBKI	GPT	1.11 ± .02	0.2 - 0.4	~0
Reference 27	2% NBKI	IR			

[a] From Reference 28

FIGURE 1

ONE-METER LABORATORY
PHOTOMETER

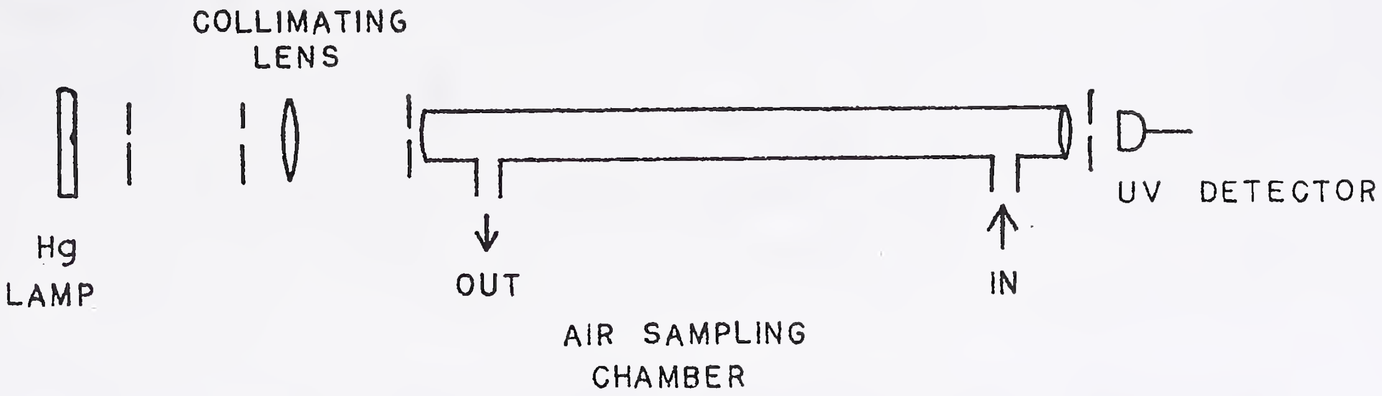
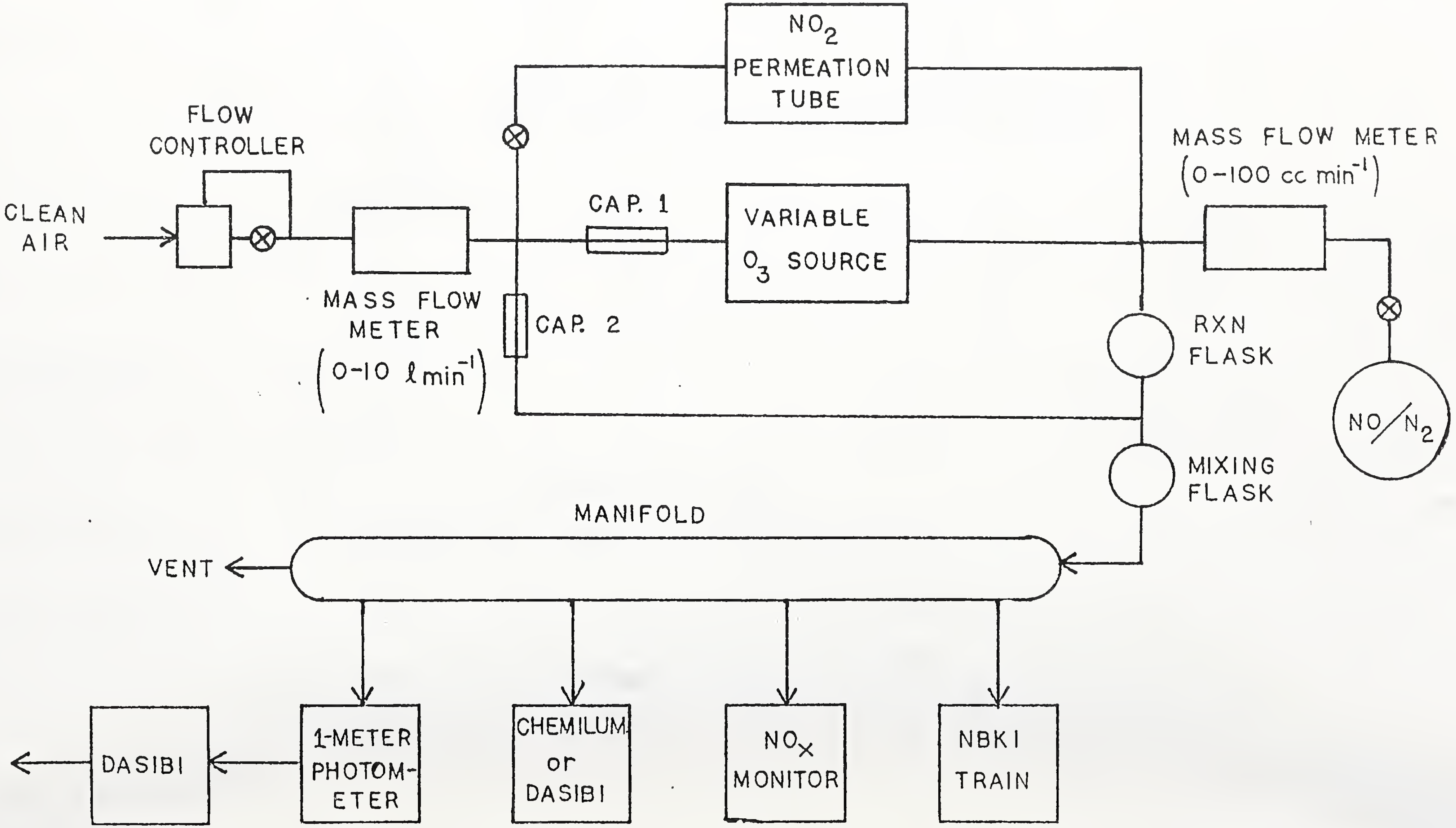


FIGURE 2

LABORATORY $O_3/NO/NO_2$ CALIBRATION SYSTEM



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