

LAURA LIANE HODSON. Evaluation of a Passive Sampling Device for Ozone.
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ABSTRACT

A passive sampling device (PSD) for ozone was evaluated under a variety of laboratory and indoor field conditions. The PSD was compared to the U.S. Environmental Protection Agency Equivalent Method for Ozone using a ultraviolet (UV) photometer. The accuracy of the PSD was within 25% of the UV photometer in laboratory experiments conducted over a range of temperatures, humidities, and concentrations. Instability of extract solutions over time was observed. Indoor field studies demonstrated the capability of the PSD to measure ozone under steady state conditions.

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INTRODUCTION

1.0 Objective

Industrial hygienists concern themselves with personnel exposures in the workplace. It is of interest to obtain an easy to use, accurate method for sampling the breathing zone air of a person potentially exposed to ozone. The purpose of this research was to revalidate the laboratory tests reported by the inventors of the Ogawa ozone passive sampling device (PSD), to use the Ogawa PSD on personnel, and to compare the method to the ultraviolet (UV) photometer in two field studies.

1.1 Background

Ozone (O_3) is a bluish gas with a molecular weight of 48 and a density of 1.6. The boiling point is $-112^{\circ}C$ and the melting point is $-193^{\circ}C$ (20). Ozone has a very pungent odor at concentrations of approximately 100-500 ppb (26). Ozone is considered a reactive gas and spontaneously decomposes under ordinary conditions so that it is not encountered except in the immediate vicinity of where it was formed (5).

Ozone is used as an oxidizing agent in the organic chemical industry, as a disinfectant for food in cold storage rooms, as a disinfectant for water, for bleaching textiles and paper pulp, in treating industrial wastes, and in the rapid drying (UV curing) of varnishes and printing inks (26).

Ozone is found indoors in industrial settings since it is formed around electrical sources such as X-ray or ultraviolet generators, electric arcs, mercury vapor lamps, linear accelerators, and electrical discharges. Industrial exposure often occurs near arc welding operations using inert gas shielding (26).

Ozone is found naturally in the atmosphere as the result of the action of solar radiation and electrical storms (26). Ozone concentrations increase in the atmosphere as a result of photochemical reactions of volatile organic compounds and nitrogen oxides (5). Ozone is undesirable in the lower troposphere where detrimental human health effects may occur. This is in contrast to its presence in the stratosphere, where ozone acts as a filter to prevent UV radiation from reaching the earth's surface (2).

1.2 Health Effects

Ozone is irritating to the eyes and all mucous membranes (26). Dryness of upper respiratory passages, choking, coughing, and severe fatigue have been reported in humans exposed to concentrations greater than 100 ppb (15). Lippmann has summarized the health effects data and at concentrations from 80 to 400 ppb, and the following responses have been documented: 5-10% decrease in FEV₁ (forced expiratory volume in one second, i.e. the volume of air expelled from the lungs during the first second of an FEV maneuver), increased cough, reduced athletic performance, increased airway reactivity, increased airway permeability, increased airway inflammation, and accelerated tracheobronchial particle clearance (15). Major factors in the respiratory uptake of ozone, aside from the concentration of the gas in the air, include the structures of the respiratory tract, the influence of the mucus that covers the air passages, and the flow of air (5). NIOSH considers ozone to be immediately dangerous to life and health at 10 ppm, the maximum concentration from which, in the event of a respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing or irreversible health effects (20).

The current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for ozone is 0.1 ppm (0.2 mg/m³) for an eight hour workday, 40 hour work week; with a Short Term Exposure Limit (STEL) of 0.3 ppm for 15 minute intervals (20). The National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) for ozone is a ceiling of 0.1 ppm (20). The American Conference

of Governmental Industrial Hygienist's (ACGIH) Threshold Limit Value (TLV) for ozone is 0.1 ppm for an eight hour workday, 40 hour work week (1). In 1993 the ACGIH recommended lowering the TLV for ozone to 0.05 ppm. The U.S. Environmental Protection Agency (U.S. EPA) has set the National Ambient Air Quality Standard (NAAQS) for ozone at 0.12 ppm for a one hour average (28). In ambient air the NAAQS is often exceeded, and more than half of the U.S. population resides in areas that are out of compliance with the current NAAQS for ozone (15).

1.3 Measurement Techniques

Ozone can be measured using a variety of techniques including ultraviolet photometry, infrared photometry, chemiluminescence, gas phase titration with nitric oxide, wet chemistry reduction of potassium iodide (using colorimetric or electrometric evaluation) and passive dosimetry (5). The current NIOSH Analytical Method No. 154 recommends collection of ozone in an impinger containing potassium iodide in sodium hydroxide followed by treatment with phosphoric-sulfamic acid reagent and spectrophotometric analysis (20,21). The current EPA Equivalent Method for determining ozone in ambient air uses an ultraviolet photometer, such as the Dasibi UV photometer (28). Historically, portable or personal monitors were not available for ozone, and it was generally assumed that human ozone exposures were representative of those monitored at nearby ambient air quality monitoring sites.

Passive dosimetry has become a frequent technique used in industrial hygiene sampling due to the portability and the opportunity to obtain air concentrations as close as possible to the person's breathing zone (3,4,17,23,24,27). Passive dosimetry is governed by Fick's Law of diffusion given by:

$$JA = (DA/L)(C) \quad (1)$$

where J = mass flux of ozone ($\mu\text{g}/\text{cm}^2\text{s}$), D = diffusion coefficient (cm^2/s), A = cross sectional area of diffusion zone (cm^2), L = length of

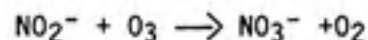
diffusion zone (cm), and ΔC = the gradient between the ambient ozone concentration ($\mu\text{g}/\text{cm}^3$) and the sampler filter surface. If the concentration at the surface of the filter is zero then ΔC = the ambient ozone concentration. For the Ogawa passive sampler, the diffusion zone is defined as the cross sectional area of the holes drilled into both diffusion endcaps. The theoretical collection rate is $24.5 \text{ cm}^3/\text{min}$, while the experimentally determined collection rate reported by the inventors is $18.2 \text{ cm}^3/\text{min}$ for indoor and laboratory settings (12,13,16,17). The experimental collection rate is 74% of the theoretical collection rate for ozone as a result of collection efficiency and starvation effects (13).

Passive sampling devices have been tested for applicability for ozone sampling. Lambert and others at Kansas State University used paper impregnated with 3-methyl-2-benzothiazolinone acetone azine plus 2-phenylphenol (a colorimetric technique)(14). Unfortunately, this PSD did not respond well when used for multi-hour sampling (2). Surgi and Hodgeson employed 10,10'-dimethyl-9,9'biacridylidene suspended in a gas-permeable polymer film. This PSD experienced an erratic response to ozone when further tests were conducted by the Environmental Health Service in California (2). The inventors explained that the originally used polymer film was no longer available (2). Grosjean and Hisham developed a colorimetric passive ozone monitor using indigo carmine as the colorant. However it displays a positive interference from NO_2 (7,8). Kanno and Yanagisawa developed a passive ozone/oxidant monitor which is based on ozone reacting with potassium iodide to liberate iodine, which is determined via constant-current coulometry (11). The shortcoming to this method is that it is a total oxidant monitor, and is not specific for ozone (13).

Febo suggested that nitrite collected by alkaline-coated denuders was oxidized to nitrate when ozone was present in the air sample (6). Further, Sickles and Hodson noted oxidation of nitrite to nitrate on sodium carbonate impregnated filters after exposure to laboratory atmospheres containing ozone as well as to ambient air (25). Koutrakis et.al. at Harvard School of Public Health (HSPH) focused their attention

on the nitrite based oxidation reaction to develop a passive sampling method for ozone (12,13).

The collection medium developed by Koutrakis et.al., includes sodium and potassium salts of nitrite and carbonate, in a solution of glycerol, methanol and water (12,13). In the presence of ozone, the nitrite ions are oxidized to nitrate ions:



The collection solution was used to impregnate glass fiber filters and these filters were placed in an Ogawa passive sampler (see Section 2). The concentration of nitrate in the extracts was determined using ion chromatography by comparing sample peak heights with nitrate calibration standards using a regression equation. Because the number of moles of ozone collected on the filter media is equal to the number of moles of nitrate formed, the average air concentration of ozone can be calculated as follows:

$$\text{From Eqn (1) } JA = (DA/L)(C) = SC \quad (2)$$

$$JAT = SCT \quad \text{where } JAT = \text{mass collected} = MV \quad (3)$$

$$MV = SCT \quad (4)$$

$$C = MV/ST \quad (5)$$

Expressing this equation in units of ppb for ozone concentration the following equation was used;

$$\text{O}_3 \text{ (ppb)} = \frac{M \cdot V \cdot (MW_{\text{O}_3} / MW_{\text{NO}_3})}{S \cdot K \cdot MW(\text{O}_3) \cdot T} \quad (6)$$

where:

M = Net NO_3^- Concentration ($\mu\text{g/ml}$)

V = Extraction Volume (5 ml)

MW = Molecular Weight ($\mu\text{g}/\mu\text{mol}$)

S = Collection Rate (18.2 cm³/min) * (m³/10⁶) at 25°C

K = 0.0409 (μmol/ppb * m³) at 25°C

T = Sampling Time (min)

The mean nitrate concentration of the blank samplers is subtracted from the exposed sample values to obtain the net nitrate concentration.

The collection rate, S, was determined empirically by the inventors from the following equation:

$$S = \frac{M \cdot V \cdot (MW_{O_3} / MW_{NO_3})}{C_{UV} \cdot T} \quad (7)$$

where:

C_{UV} = True mean ozone concentration from the UV photometer

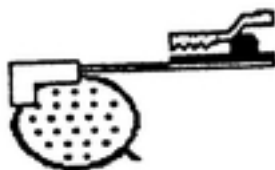
The U.S. EPA (Mulik) and HSPH (Koutrakis, et.al.) were using the Ogawa ozone PSD to quantify weeklong outdoor ozone exposures and the system was presented to researchers active in air pollution (18,19).

EXPERIMENTAL

2.0 Description of the Passive Sampling Device

The passive sampler (Ogawa & Co., USA Inc., Pompano Beach, FL) consists of a cylindrical polymer body (2 cm diameter x 3 cm) and a plastic pin-clip holder (4 x 3 cm), shown in Figure 1. There are two cavities on the ends of the cylinder, each of which hold one coated filter between two stainless steel screens. Because the core of the body is solid, each cavity is isolated from the other. The diffusion barrier endcaps hold the screens and filters in place by friction fit. Prior to exposure, the assembled sampler is sealed in a plastic ziplock bag and placed in a polystyrene bottle. When the PSD is attached to a lapel, the pin clip holder is first attached to a plastic (10 x 10 cm)

**Side View
(Pinclip & Body)**



**Exploded View
(Body)**

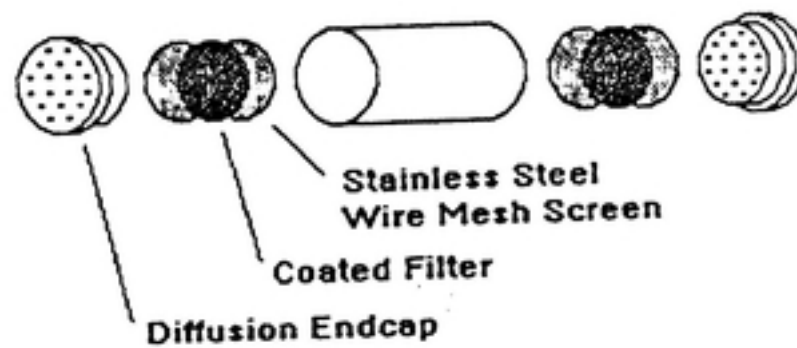


Figure 1 Ogawa Passive Sampling Device

back plate to avoid the influence of ozone deposition to the subject's clothes.

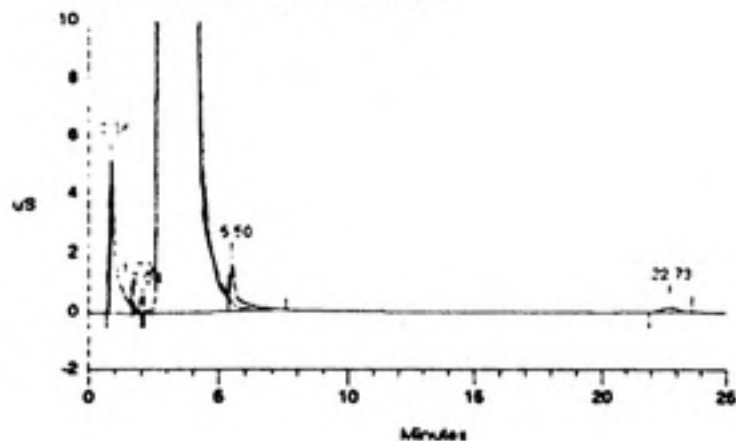
The filters were purchased precoated, and the PSD was assembled and disassembled inside a portable glovebox that was lined with sodium carbonate coated filter paper sheets (Whatman #1) (9). After sampling, the PSD filters were removed and placed in 8 ml Nalgene bottles; 5 ml of deionized water was added; and the filters were sonicated for 15 minutes.

The filters were analyzed for nitrate ion by ion chromatography. A Dionex Model DX 300 was used with a #AS4A Separator column, a #AG4A Guard column, and an Anion MicroMembrane Suppressor Model #AMMS-1. A dilute anion eluant was used consisting of 1.08 mM Na_2CO_3 , 1.02 mM NaHCO_3 (10). The data were integrated using Dionex AI450 software with advanced computer interface. An example chromatogram is displayed in Figure 2. The nitrate was integrated as a small peak / shoulder coming on the much larger nitrite peak. Filters were analyzed in batches that included blanks, spikes, Quality Assurance samples and replicates.

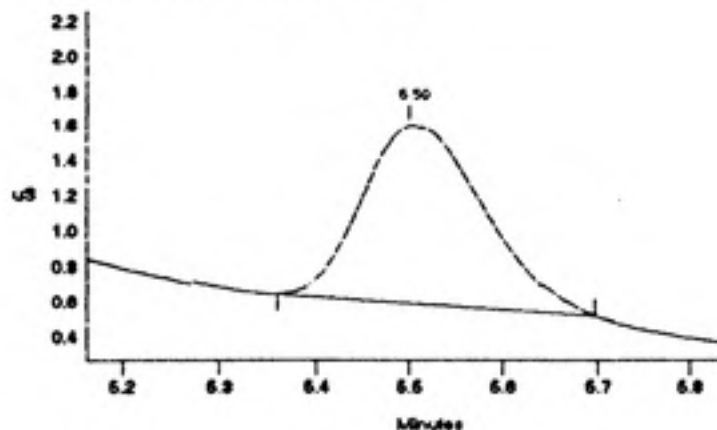
2.1 Chamber Design

The exposure chamber consisted of a large (68.8 L volume) glass bell jar (Figure 3). The airflow into and out of the chamber was set at a nominal 2 liters per minute. A 3 inch fan (Radioshack No. 273-242) was used to insure good mixing in the chamber. The fan was connected to a variac to control the fan speed. The air velocity was measured with a Kurz Air Velocity Meter model 4415, and was maintained at 70 fpm (35 cm/sec) across the face of the PSD's for most of the experiments. The air mixing characteristics of the chamber were observed by placing a smoke tube in the inlet airstream and visually observing the air flow. Good mixing was observed as the chamber became instantaneously smokey with no voids.

File: NITRATE1.D08 Sample:



File: NITRATE1.D08 Sample:



Data Reprocessed On 07/02/1993 10:05:30

```

=====
: Sample Name: LOW SPIKE                               Date: 07/01/1993 19:49:33
: Data File   : C:\DX\DATA\070193\NITRATE1.D08
: Method      : C:\DX\METHOD\ANION1.met
: ACI Address : 1 System: 1 Inject#: 8                 Detector: CEM-2
: Analyst     :                                         Column:
=====

```

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Calibration Volume Dilution Points Rate Start Stop Area Reject
-----
External           1           1 7500 5Hz 5.16 5.84 50000
-----

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=====
***** Peak Report: All Peaks *****
=====

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Pk. Num	Ret Time	Component Name	Concentration PPM	Height	Area	Bl. Code	Delta
1	0.86		0.000	5156555	83309145	3	
2	1.70		0.000	276793	2382730	4	
3	5.50	NITRATE	0.482	598502	9054580	1	1.85
Totals			0.482	6431849	94746455		

Figure 2 Ion Chromatogram

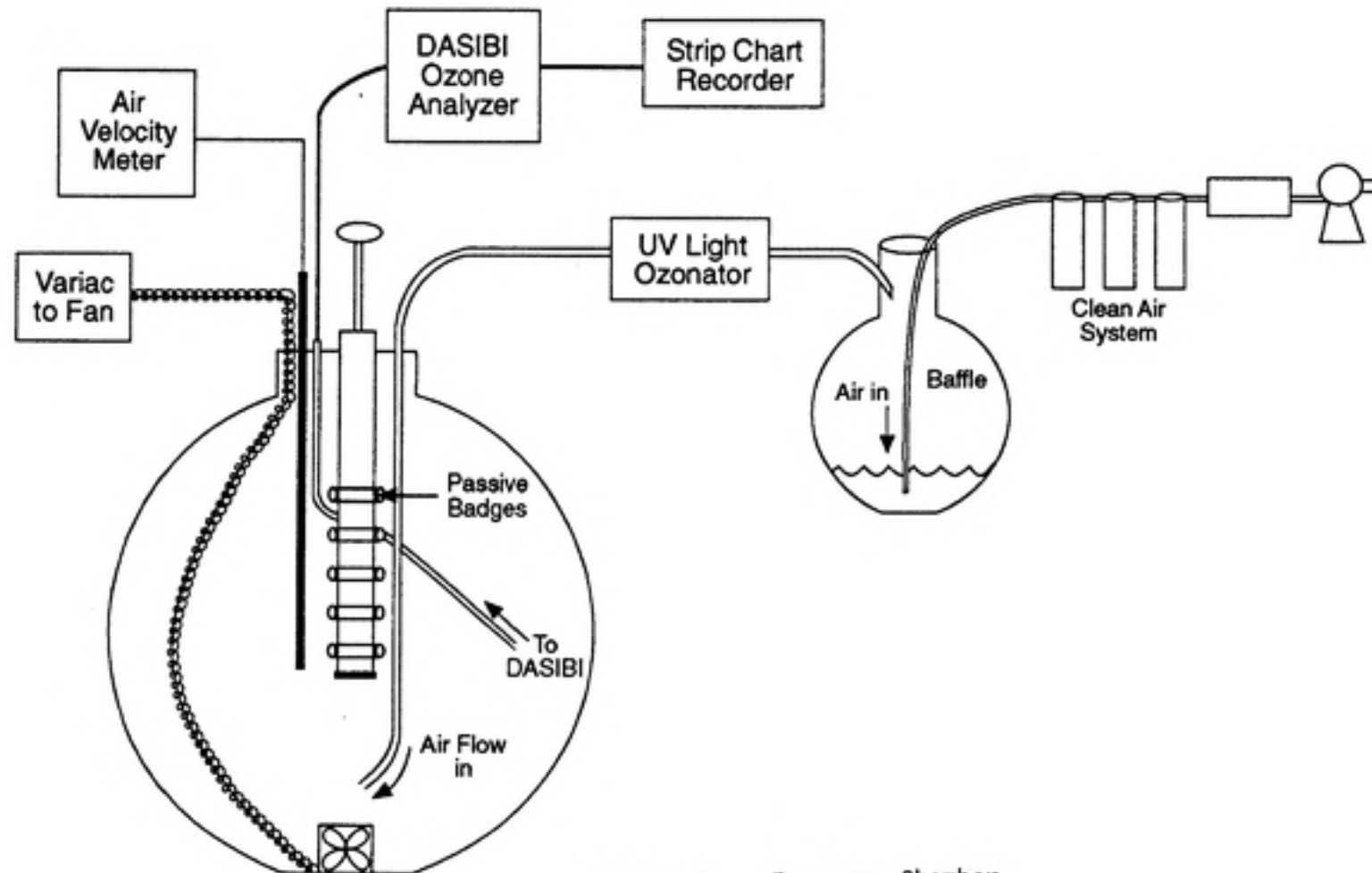


Figure 3 Exposure Chamber

The exposure chamber was located inside of a constant temperature room. The humidity was controlled by passing the clean air stream through a water jar/ large impinger. The humidity was measured with an EG&G Model 880 thermoelectric Dew Point Hygrometer.

2.2 Ozone Generation

Ambient air was delivered to an air cleaning system consisting of a coarse filter, Permapure® drier, a catalyst column (0.5% palladium on alumina spheres at approximately 175° C), silica gel, Purafil®, and charcoal. The clean air stream flow was regulated using a mass flow controller to a nominal 2 liters per minute. The air flow to the chamber and to the UV photometer were measured using a bubble flowmeter. The clean air was passed through a ozone generator consisting of a mercury vapor lamp which irradiates the airstream flowing through a quartz tube to produce nominal ozone concentrations of 50 to 200 ppb.

A Dasibi UV photometer (S/N 003026) calibrated by the procedures outlined in Appendix 2 was used as the primary standard. This was used to calibrate the Dasibi UV photometer (S/N 003061) used for the chamber and field studies. The UV photometer was calibrated weekly and prior to all field studies. Ozone concentrations were monitored with a strip chart recorder.

Before each test, the chamber was conditioned and equilibrated overnight with target ozone concentrations. At the beginning of each test, the ozone concentration would drop slightly when the chamber was opened to place the PSD's inside, but would recover to target values within approximately 30 minutes. To determine ozone loss in the chamber, a check of the ozone concentration at the inlet line versus that measured from within the chamber was conducted. In one case, the ozone at the inlet was 187-214 ppb compared to 195 ppb within the preconditioned chamber.

2.3 Experimental Design

Cassinelli et.al, have described protocols for the evaluation of passive monitors, and the experimental design of this study was patterned after those recommendations (3,4). The PSD's were evaluated for temperature and humidity effects, storage stability, use at concentrations of 0.5 - 2X the current REL of 100 ppb, minimum detection limits, interferences from H_2O_2 , $NaClO$ (bleach), and HCl , loss of sample from exposed filters, accuracy and precision when compared to the Dasibi UV photometer, and in two field studies. An attempt was made to determine the effect of velocity extremes but this data is suspect since a wind tunnel was not used, only a round chamber. The experimental design is summarized on Table 1.

2.4 Quantification of Interference Compounds

Concentrations of H_2O_2 , $NaClO$, and HCl were generated by passing the clean air stream on top of a solution of the target species. A nominal 1% solution of each compound was used, and the air concentration within the manifold was measured using a Draeger tube. Draeger tube #JS 7365 with a range of 0.1-3.0 ppm was used for H_2O_2 , tube #JS 4629 with a range of 0.25-25 ppm was used for HCl and $NaClO$. The nominal concentrations achieved were 0.75 ppm H_2O_2 , 1 ppm HCl and 8 ppm $NaClO$. Ozone was not used during the interference tests.

2.5 Field Studies

Two field studies were conducted. The first was located in the basement area of a microcomputer center (MCNC in RTP, N.C.) where ozone is used to disinfect water. The second field study was in a welding shop (Research Triangle Institute in RTP, N.C.) where Aluminum inert gas shielded arc welding was ongoing. Both field studies offered the opportunity to monitor a stationary source with the PSD and the Dasibi UV photometer. The PSD was used to sample multiple areas of the room and personnel.

Table 1 Summary of Experimental Approach

Factor	Experiment
Temperature and Humidity	Expose PSD's to 10, 25, & 40°C at both 20% and 80% relative humidity
Sampling Limitations/ Minimum Detection	Expose PSD's to levels between 180-1700 ppb-h where NIOSH criteria is 400 to 1600 ppb-h
Degradation / Clean Air Effects	Expose 6 PSD's to O ₃ , remove 3, expose remaining 3 plus 3 fresh PSD's to ozone-free air
Stability of Extracts	Expose PSD's to O ₃ , analyze 3 immediately, 3 after 2 wk at 25°C, 3 after 2 wk at 5°C
Interference	Expose PSD's to H ₂ O ₂ , NaClO, and HCl
Accuracy and Precision	Comparison of PSD's to Dasibi UV photometer
Velocity Effects	Expose PSD's to O ₃ under velocity extremes of 25 and 150 fpm
Field Tests	Comparison of PSD's to Dasibi UV photometer in two indoor field studies

RESULTS

3.0 Quality Assurance and Quality Control Activities

Two solutions of known NO_3^- concentrations prepared by the U.S. EPA were subsequently analyzed, and results of these tests can be used to quantify analytical laboratory precision. In addition, by comparing measured results with theoretically expected, assessments of analytical accuracy can be made. Results are summarized in Table 2 and displayed in Figures 4 and 5. The recovery/accuracy of the IC determination of NO_3^- was 99.5 and 98.6% for two solutions. The precision or relative standard deviation (RSD) was less than 2% for 16 samples of each solution.

The results of the blank filter analysis are included on Table 2. For $n=12$ filters the average blank was 0.018 ± 0.031 $\mu\text{g}/\text{ml}$ NO_3^- . Results of these blanks were used to correct the actual sample results ranging from 0.106 to 0.945 $\mu\text{g}/\text{ml}$ NO_3^- .

Solutions of known NO_3^- concentrations were loaded onto the Ogawa filters and were subsequently analyzed along with the samples. The recovery of the low spike (0.4 $\mu\text{g}/\text{ml}$) was $111 \pm 11\%$, and the recovery of the high spike (1.0 $\mu\text{g}/\text{ml}$) was $104 \pm 5\%$. The RSD was 9.8 and 4.5% respectively for $n=6$ each.

Several samples ($n=12$) were selected for replicate same-day analysis of NO_3^- . The precision was good with a median RSD of 2.5% and an average RSD of 3.8%.

The variability of the samplers can be assessed by looking at the precision of sampler sets. Each experimental condition subjected between 3- 7 samplers to identical chamber conditions. This measure of precision will represent the variability of sample preparation, sampling operations (location in the chamber), sample handling, extraction, and chemical analysis. For 18 laboratory experiments (excluding the experiments for minimum detection and velocity effects) the median RSD

Summary of Analysis of Quality Assurance Solutions

Solution	Theoretical (ug/ml)	Measured X	n	Percent X	Recovery SD
QA low	0.45	0.448	16	99.5	1.8
QA 1756	0.496	0.489	16	98.6	1.3
Low spike	0.40	0.445	6	111.3	9.8
High spike	1.00	1.038	6	103.8	4.5

Summary of Replicate Same-Day Analysis of Filter Solutions

n = 12

Median RSD 2.5 %

Average RSD 3.8 %

Summary of Precision of Paired Samples

n = 18 experiments, (3-7) per set

Median RSD 9.9 %

Average RSD 12.8 %

Summary of Blank Data

n = 12

Average Blank 0.018

Std Deviation 0.031

Quality Control Chart

QA LOW

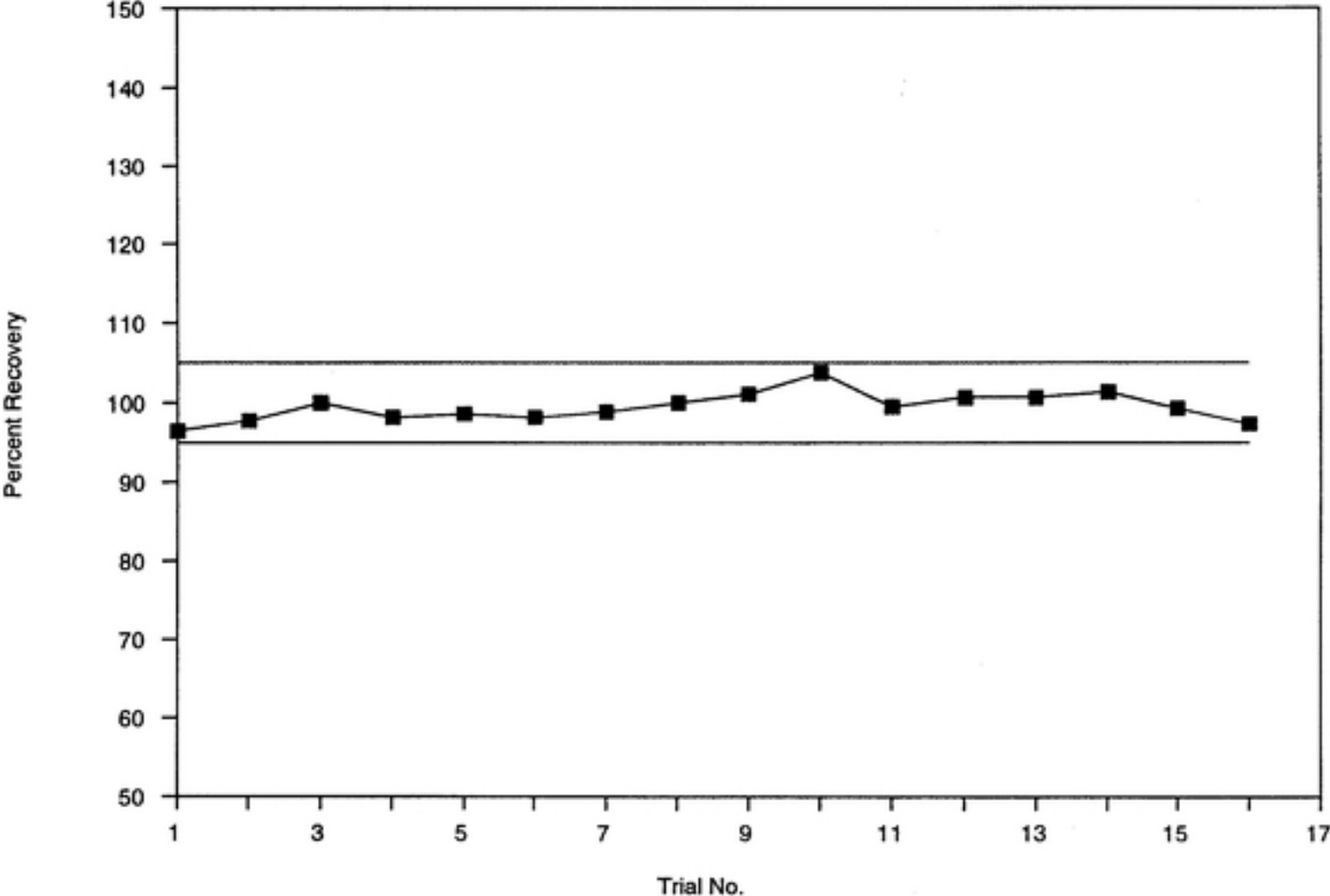


Figure 4 Quality Control Chart QA Low

Quality Control Chart

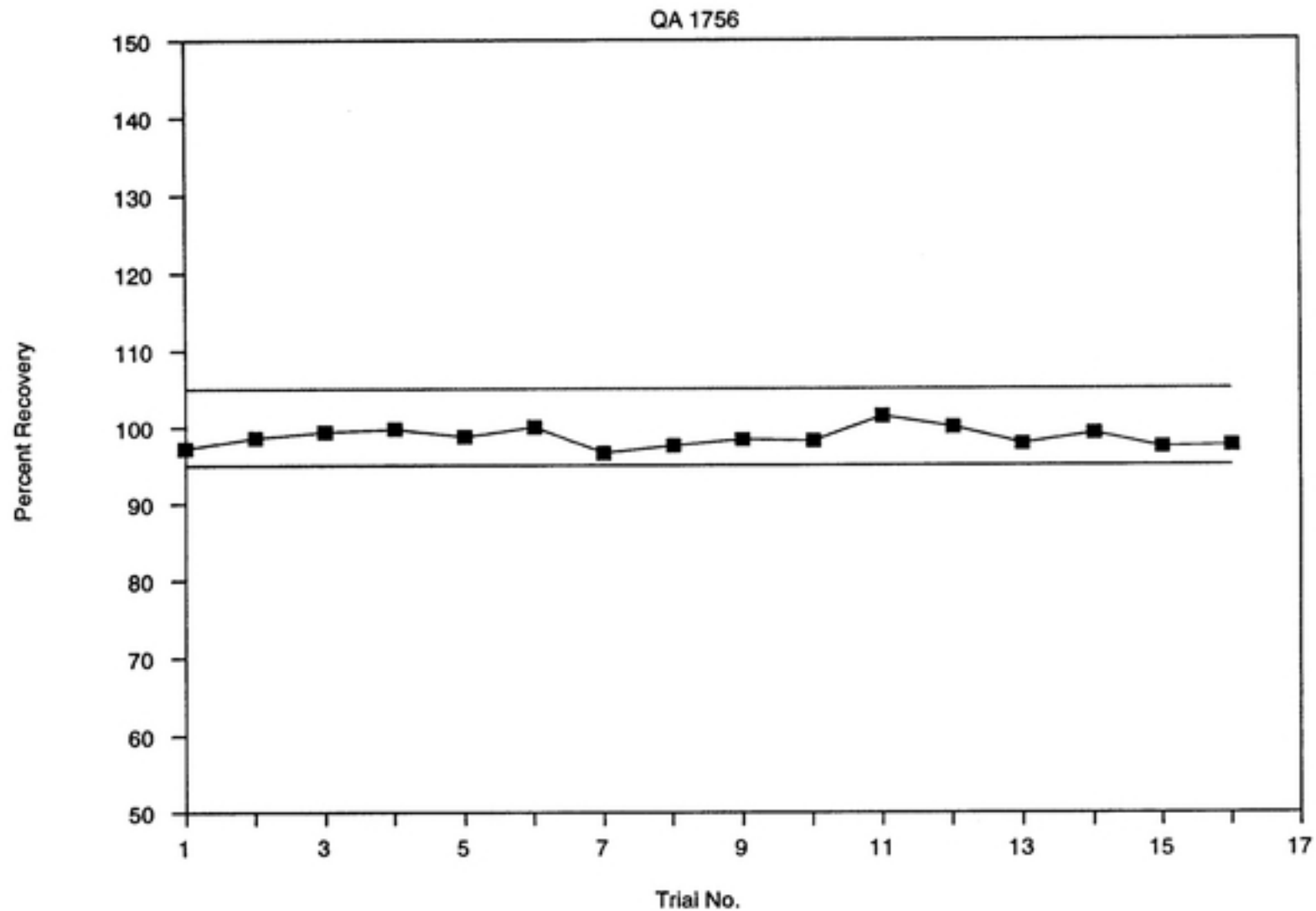


Figure 5 Quality Control Chart QA 1756

was 9.9% and the average RSD was 12.8%. No trends were observed for sampling location within the chamber.

The NIOSH criteria for evaluation of passive monitors requires a precision of less than 10.5% for n=25 per set (3). The testing reported here is for precision of n=3 to n=7 samplers per set so it is unknown if the NIOSH criteria for precision would be met.

3.1 Bias

The difference between the sample mean and the "known" value of ozone from the Dasibi UV photometer can be referred to as the accuracy or the bias in the method being evaluated. The bias of the ozone PSD was calculated for all laboratory experiments by the following formula:

$$\text{bias} = (X - X_0 / X_0) * 100 \quad (8)$$

where X = mean of sample data set

X₀ = "known" value at level tested (Dasibi UV photometer)

NIOSH criteria for the validation of a passive monitor requires a bias within $\pm 25\%$ of the true value for values at 0.5, 1, and 2 times the REL of 100 ppb, for n=25 samplers per set (3). Converting these concentrations to an eight hour average exposure would encompass concentrations between 400 to 1600 ppb-h. Results that follow, show the Ogawa ozone PSD to perform within the NIOSH criteria of $\pm 25\%$ bias, for all experiments within 400 to 1600 ppb-h and with velocities of nominally 60-70 fpm; for n=3 to n=7 per set (Figure 6). Exceptions include a bias of +58.2% when the total loading was 195 ppb-h, a bias of -38.2 and -40.5% for low velocity conditions, and a bias of -34.7% for one of the high velocity experiments (Table 3, Figure 6).

Table 3 Summary Data Passive Dosimeter

Exp No.	Conditions	Passive Mean O ₃ (ppb)	RSD (%)	Continuous Dasibi (ppb)	Dasibi Total ppb-h	Bias %
179a	25° C dry 2h	146	30.7	92	195	58.2
179b	25° C dry 3h	77	18.0	93	279	-17.6
164	25° C dry 2h	135	30.7	153	306	-11.8
190	25° C dry 7h	57	9.0	55	382	4.0
163	25° C dry 2h	203	25.4	238	476	-14.9
167	25° C dry 4h	103	8.9	132	526	-21.9
175a	25° C dry 7h	86	1.8	100	700	-11.6
165	25° C dry 8h	118	5.9	133	1064	-14.1
159	25° C dry 6h	190	8.3	203	1218	-6.6
166	25° C dry 8h	201	3.2	217	1734	-7.3
168	25° C dry 3h	143	8.9	162	486	-11.6
168	25° C dry 3h+3hClean	134	6.8	162	486	-17.5
168	25° C dry 3h Clean	0	0	0	0	
176	10° C humid 6h	100	16.6	106	671	-5.7
170	25° C humid 5h	150	6.2	177	953	-15.5
171	40° C humid 5h	101	22.1	131	676	-22.7
195	40° C humid 5h	127	8.4	107	813	19.1
174	10° C dry 5h	119	6.1	150	751	-20.6
173	40° C dry 6h	142	9.8	160	960	-11.2
177	25° C dry 6h 150FPM	58	21.4	89	549	-34.7
192	25° C dry 6h 150FPM	147	6.4	140	980	5.1
178	25° C dry 6h 25FPM	67	29.7	109	656	-38.2
191	25° C dry 6h 25FPM	72	5.0	121	787	-40.5
182	NaClO bleach	313	7.4			
183	HCl	0	0			
184	H2O2	59	64.3			

Passive Sampler vs Continuous Analyzer

25 C, dry conditions, 70 fpm velocity

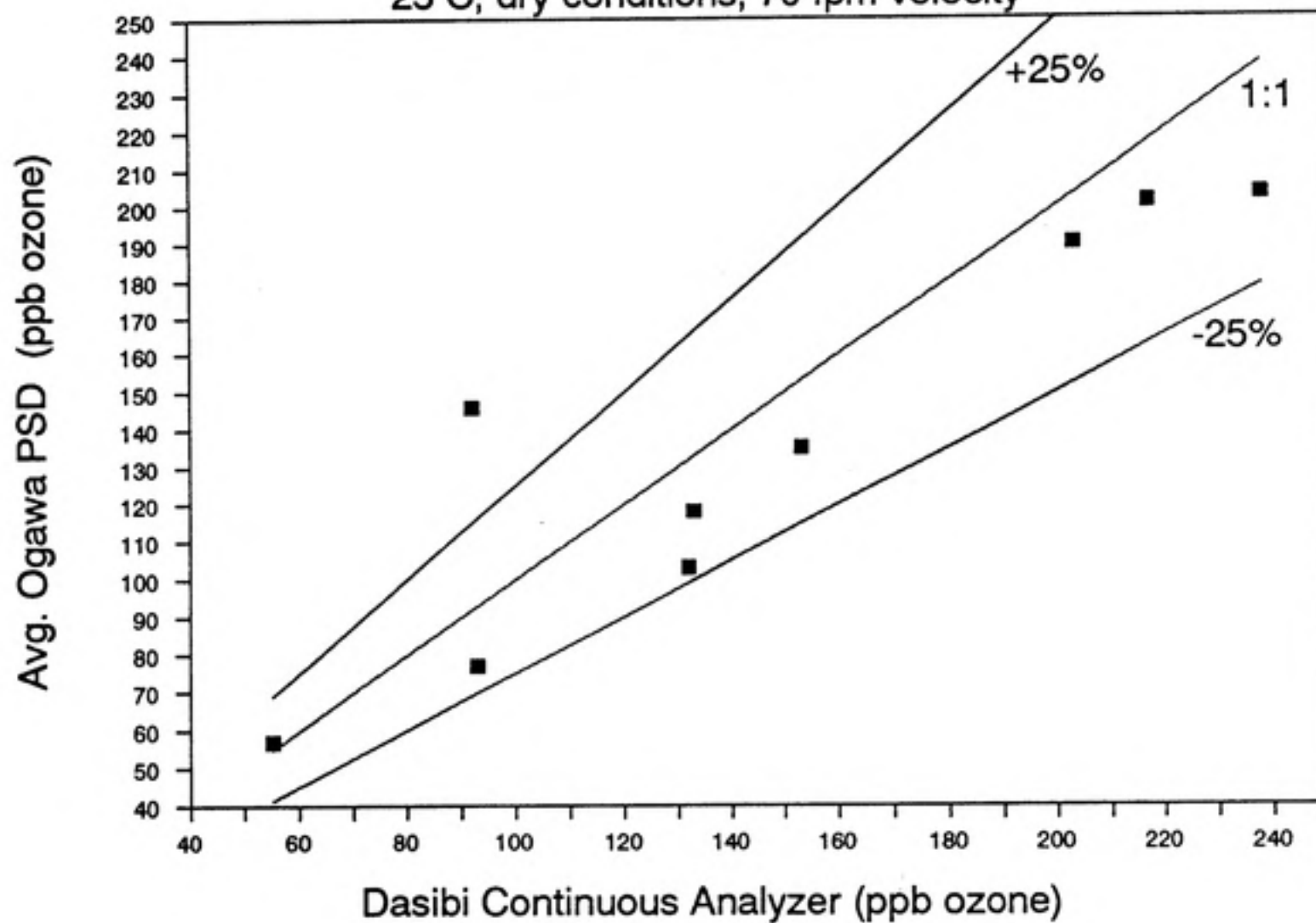


Figure 6

Passive Sampler vs Continuous Analyzer

10 - 40 C, dry and humid conditions, 70 fpm velocity

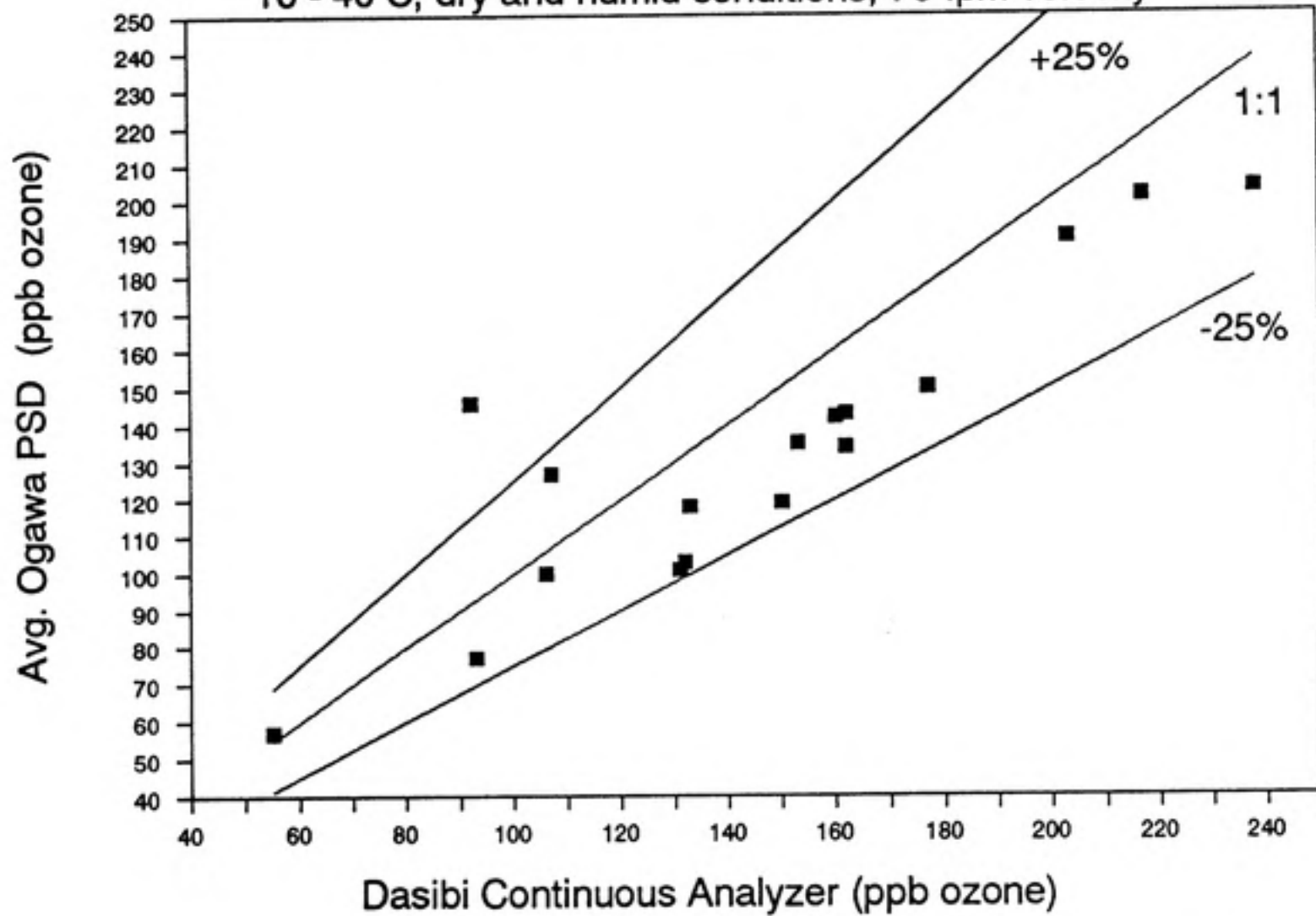


Figure 7

3.2 Temperature and Humidity Effects

The PSD was evaluated for use at temperatures of 10^o, 25^o and 40^o C under both dry (20% relative humidity) and humid (80% relative humidity) conditions (Table 3, Figure 7). The nominal ozone concentration in the manifold was 150 ppb and the average test lasted 5 hours for a total of approximately 750 ppb-h. The 750 ppb-h can be compared to 800 ppb-h expected if the exposure were 100 ppb for 8 hr (the current PEL and TLV). The conversion factor (k), used in the calculation of ozone concentration (Eqn. 6), was corrected for the temperature and k= 0.0409 at 25^oC, 0.0431 at 10^oC, and 0.0389 at 40^oC.

The PSD bias for the dry conditions was -20.6, -11.6, and -11.2% for 10^o, 25^o and 40^o C respectively. The precision (RSD) was 6.1, 1.8 and 9.8% respectively.

Under humid conditions the bias was -5.7, -15.5, and -22.7% respectively, suggesting a trend of increasing negative bias with increasing temperatures at high humidity conditions. The 40^o C experiment was repeated and the second trial demonstrated an average bias of +19.1%, thus disputing the trend. The precision for these four experiments was 16.6, 6.2, 22.1, and 8.4%.

3.3 Limit of Detection

In an effort to quantify the detection limits in terms of total ppb-h sampled, the PSD was exposed to concentrations of ozone ranging from 50-213 ppb for 2-8 hours, for total exposures ranging from 179 ppb-h to 1600 ppb-h. The bias was less than 25% for levels greater than 279 ppb-h and 58% at a level of 195 ppb-h (Table 3, Figure 8). The blank corresponded to 32 ppb-h. The precision of the 179 ppb-h experiment was 31% and the bias ranged from +14 to +148%.

The experimental limit of detection of 279 ppb-h corresponds well with the HSPH reported limit of detection of 200 ppb-h (12), and meets the NIOSH criteria for validation.

Passive Sampler vs Continuous Analyzer

10 - 40 C, dry and humid conditions, 70 fpm velocity

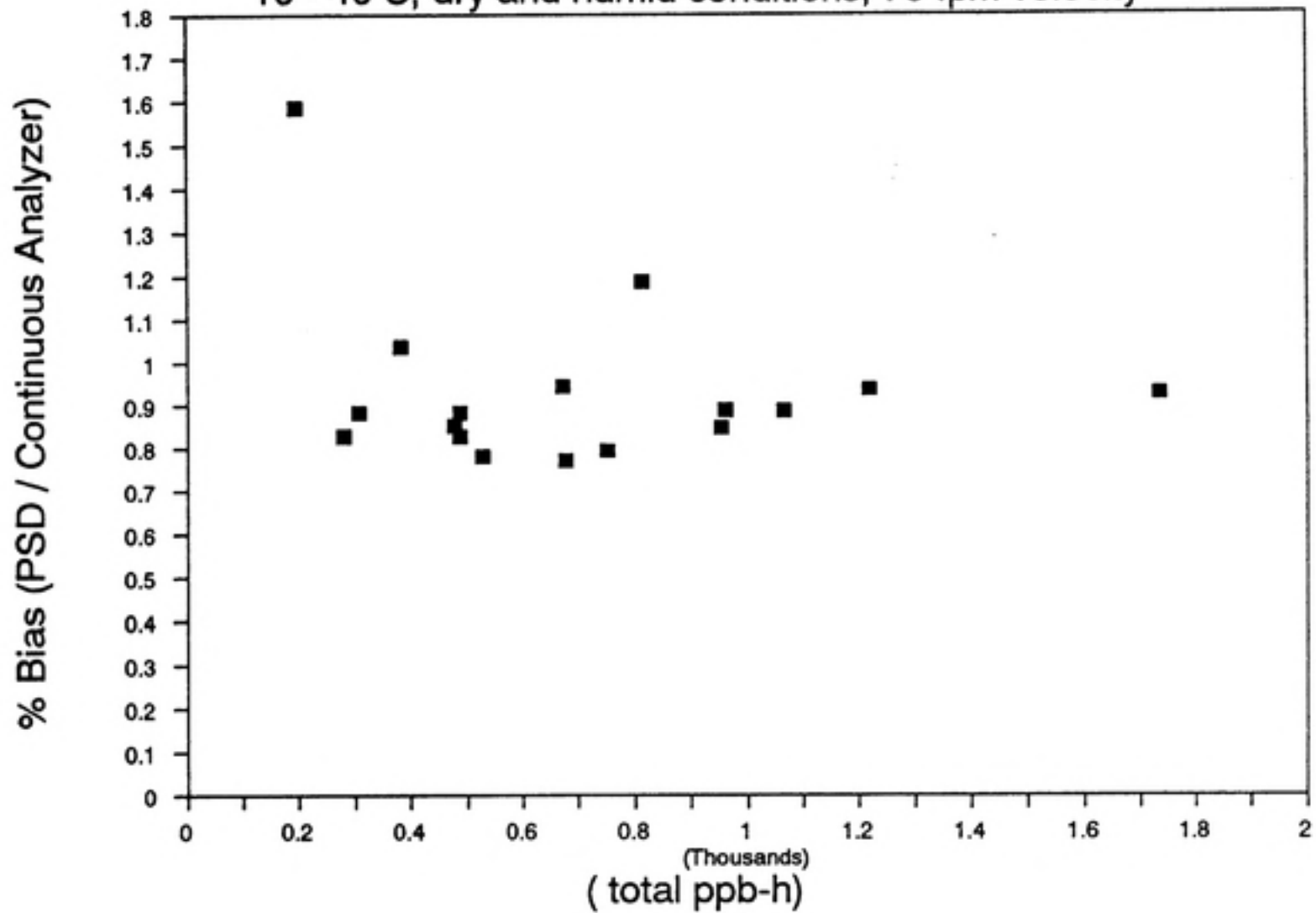


Figure 8

3.4 Degradation

The effects of clean (ozone-free) air exposure on the PSD was assessed by loading six filters with ozone, removing three for analysis and exposing the remaining three to an ozone-free atmosphere in the sampling chamber for two additional hours. The ozone-free atmosphere was verified by placing three previously unexposed PSD's in the chamber as well using the Dasibi UV photometer. Results demonstrated minimal to no loss of detectable ozone after exposure to an ozone-free atmosphere. The first set showed an average ozone concentration of 143 ± 12.8 ppb, while the set exposed to ozone followed by clean air showed 134 ± 9.1 ppb. The Dasibi UV photometer showed 162 ppb. The bias was -11.6% for the first set and -17.5% for the second set. No ozone was detected by the third set exposed to clean ozone-free air.

The second assessment of degradation evaluated the stability of the extracts (Table 4). A set of 9 filters was simultaneously exposed and extracted. One third was analyzed immediately, one third was stored at 25°C for two weeks prior to analysis, and one set was stored at 5°C in the refrigerator for two weeks prior to analysis. There was a substantial difference in the recovery of the three sets of PSD's. The mean ozone recovered was 86, 70 and 60 ppb respectively (a change of -16 and -26 ppb). This experiment suggested that the extracts are not stable, so two additional sets of filters were analyzed for storage stability. Three filters from a field study were reanalyzed after storage at 5°C for two weeks. This reanalysis for three filters showed ozone concentration differences of +2, +5, and -13 ppb (out of 33, 60 and 40 ppb).

The third evaluation of storage stability included reanalysis of solutions after storage at 5°, and 25° C for two weeks. The recovered ozone differed by +13 and +39 ppb out of 147 ppb.

In contrast to the instabilities noted here, HSPH reported stable extracts with a maximum change of ± 4 ppb, 10 weeks after filter extraction when stored at 5°C (11,12). This 4 ppb corresponds to ± 0.5

Table 4 Storage Stability of Extract Solutions

Sample ID	Initial ppb O ₃	2wk @ 5°C ppb O ₃	(diff)	2wk @ 25°C ppb O ₃	(diff)
-----	-----	-----	-----	-----	-----
175 (n=3)	86	70	-16	60	-26
188-3	33	35	+2		
188-4	60	65	+5		
188-5	40	27	-13		
192 (n=3)	147	160	+13	186	+39

ppm nitrate, or nominally 400-10,000 ppb-h (17 to 62 ppb for 24-167 h), much higher than the 200-1700 ppb-h tested here.

3.5 Interference Tests

The basic nitrite solution which is impregnated on the filter in the PSD may react with other strong oxidizers in addition to ozone. HSPH reported that the rate reaction of the nitrite to nitrate conversion is pH dependant and that the potassium carbonate used to keep the collection solution alkaline would prevent peroxides from causing a positive reaction with the Ogawa PSD (12,13). In an effort to determine if a positive bias was possible, five PSD's were exposed to three strong oxidizers in the absence of ozone.

The first trial exposed the PSD's to 0.75 ppm H₂O₂, (the NIOSH/OSHA REL/PEL is 1.0 ppm). The Dasibi UV photometer read 110 ppb initially then quickly dropped to below zero, indicating no response. The average recovery on the PSD's was 59 ± 38 ppb. Recovery ranged from 0 to 102 ppb.

In the presence of 1 ppm HCl (the NIOSH/OSHA REL/PEL is 5 ppm), no ozone could be quantified from the PSD's. The chlorine caused a peak that interfered with with the nitrite/nitrate recovery. The Dasibi UV photometer went off scale, indicating a positive response.

When the PSD's were exposed to an atmosphere of 8 ppm bleach (NaClO) (there is no REL/PEL), some conversion of nitrite to nitrate was observed. The recovery of nitrate expressed as ozone was 312 ± 23.3 ppb. The Dasibi UV photometer went off scale, indicating a positive response.

The hydrolysis of peroxyacetyl nitrite (PAN) on the collection media may present an overestimation of the average ozone concentrations (12,13). PAN as a strong oxidant, could oxidize nitrite to nitrate; and it includes nitrate as a component. Typically PAN concentrations are 10 to 20 times smaller than ozone concentrations. If PAN were to be

generated in the same atmosphere as the ozone, a positive interference would be anticipated, but it was not evaluated in this study.

3.6 Velocity Effects

The average velocity maintained in the exposure chamber was 70 fpm. To determine the effect of velocity extremes; the fan was regulated to 25 fpm (12 cm/sec) and 150 fpm (75 cm/sec), and two sets of PSD's were exposed to each condition while sampling a nominal 100 ppb ozone for 5-8 hours.

The PSD's showed the effects velocity starvation as the bias for the low velocity was -38 and -41% with precisions of 30 and 5%. The developers of the Ogawa PSD recommend using the PSD in an area where air stagnation will not occur (i.e. not in a corner of a room) (9). The average air velocity surrounding a person in an air conditioned workspace will be 60 fpm (28), sufficient to use the PSD.

The other extreme of high velocities was reported by HSPH to effect the ozone PSD collection rate, and HSPH recommends placing the PSD in a protective cup when using outside where strong winds may occur (9,10,12). HSPH reported an exponential increase in the collection rate from 21-46 cm³/min when used at velocities up to 540 fpm. When the PSD's were tested at RTI in high velocity conditions of nominally 150 fpm, the first trial found a negative bias of -35%. The high velocity conditions should theoretically overcome the resistance presented by the diffusion barrier and cause a positive bias. The experiment was repeated and the second trial demonstrated a positive bias of +5.1%. The precision was 21 and 6% respectively for the two experiments.

3.7 Field Studies

Two field studies employing the Dasibi UV photometer and the Ogawa ozone PSD were conducted (Table 5). The first field study was conducted in the basement of a microelectronics center (MCNC in RTP, N.C.) where a Welsbach Ozone Generator, Model T-816, is used to disinfect water. The floorplan of MCNC is attached as Figure 9. The room was approximately 34 x 68 ft. The Dasibi UV photometer inlet was located very close to the ozonator where employees stated that they could smell ozone. A PSD was attached to the inlet to allow a direct comparison. Additionally two other areas in the basement and two employees were sampled. The ozone concentration at the location of the Welsbach Generator averaged 19 ppb over 24 hours as determined by the Dasibi UV photometer. The strip chart recorder attached to the Dasibi recorded periodic spikes of ozone rising as high as 800 ppb for approximately 30 seconds. During these peak episodes the average hourly concentration was between 60-80 ppb. If the peaks were excluded from the data, the average ozone concentration is 12.6 ppb for a 24 hour average.

The PSD, which was placed adjacent to the Dasibi inlet, showed the average 24 hour ozone concentration to be 9 ppb, about half of the 19 ppb integrated from the UV photometer. The other two areas sampled with the PSD's contained 0 and 3 ppb ozone for 24 hour samples. These areas were located up to 20 feet away from the source of ozone.

The two employees who work in the basement area left after the ozonator had been on for 4 hours. The average ozone concentration calculated from the UV photometer during those 4 hours the employees were present, was 40 ppb with the spikes included in the integration and 16 ppb excluding the spikes. The personal exposures as measured by the Ogawa PSD were nominally 4 ppb and 9 ppb. The passive badges were clipped to the employees collars and would be expected to be lower than the real time monitor since the Dasibi UV photometer was located near the source of the ozone, while the employees were moving around the basement and the building, thus diluting their exposures.

Table 5
Summary of Field Studies with the Ogawa Ozone PSD

Field Study #1 at MCNC

<u>Location</u>	<u>ppb Ozone</u>
Area 1 Dasibf UV photometer	19
Area 1 PSD	9
Area 2 PSD	0
Area 3 PSD	3
Employee 1 PSD	4
Employee 2 PSD	9

Field Study #2 at RTI Welding Shop

<u>Location</u>	<u>ppb Ozone</u>
Area 1 Dasibf UV photometer	41
Area 1 PSD	41
Area 2 PSD	37
Area 3 PSD	33
Employee 1 PSD	60
Employee 2 PSD	40

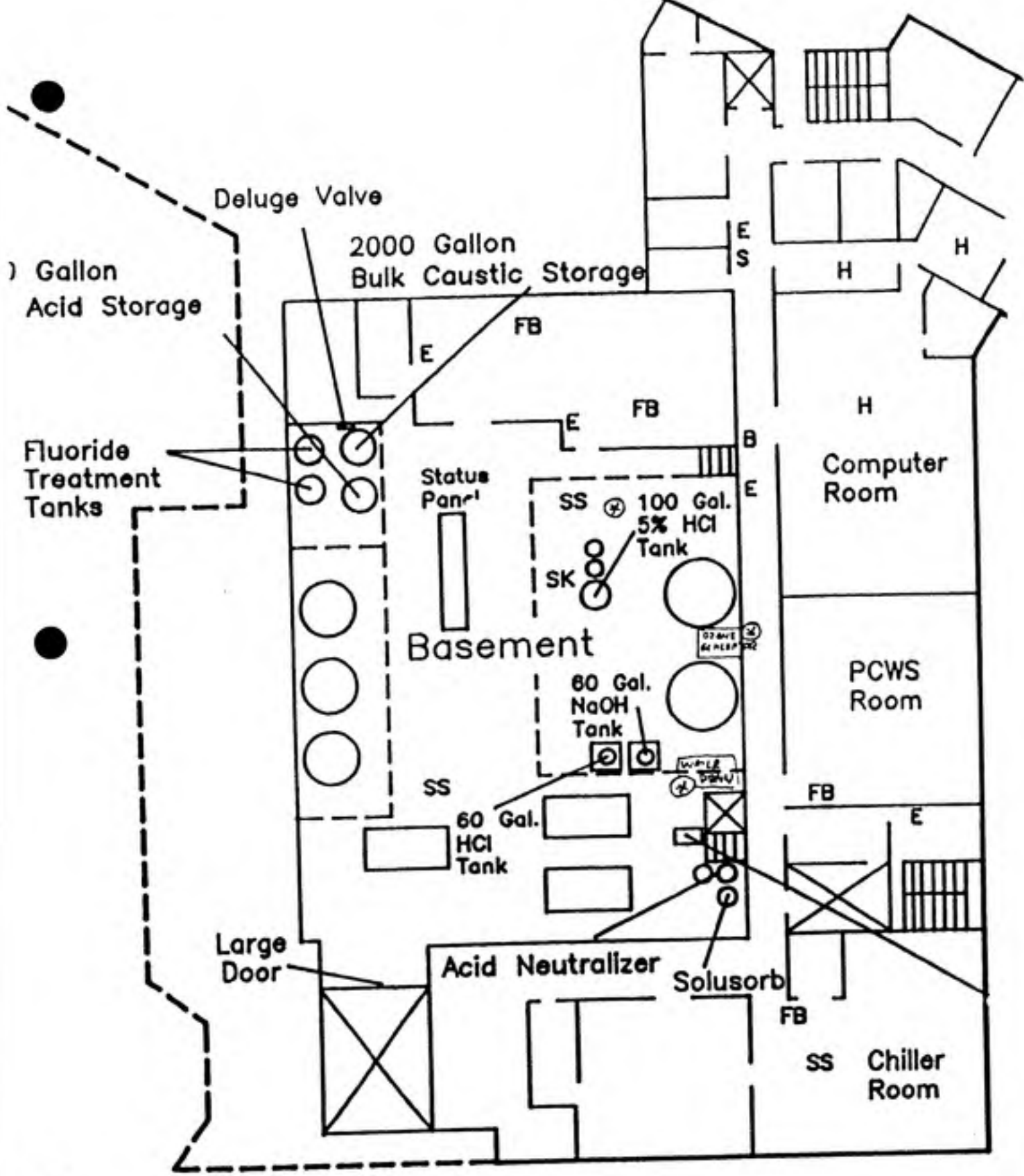


Figure 9 MCNC Floorplan

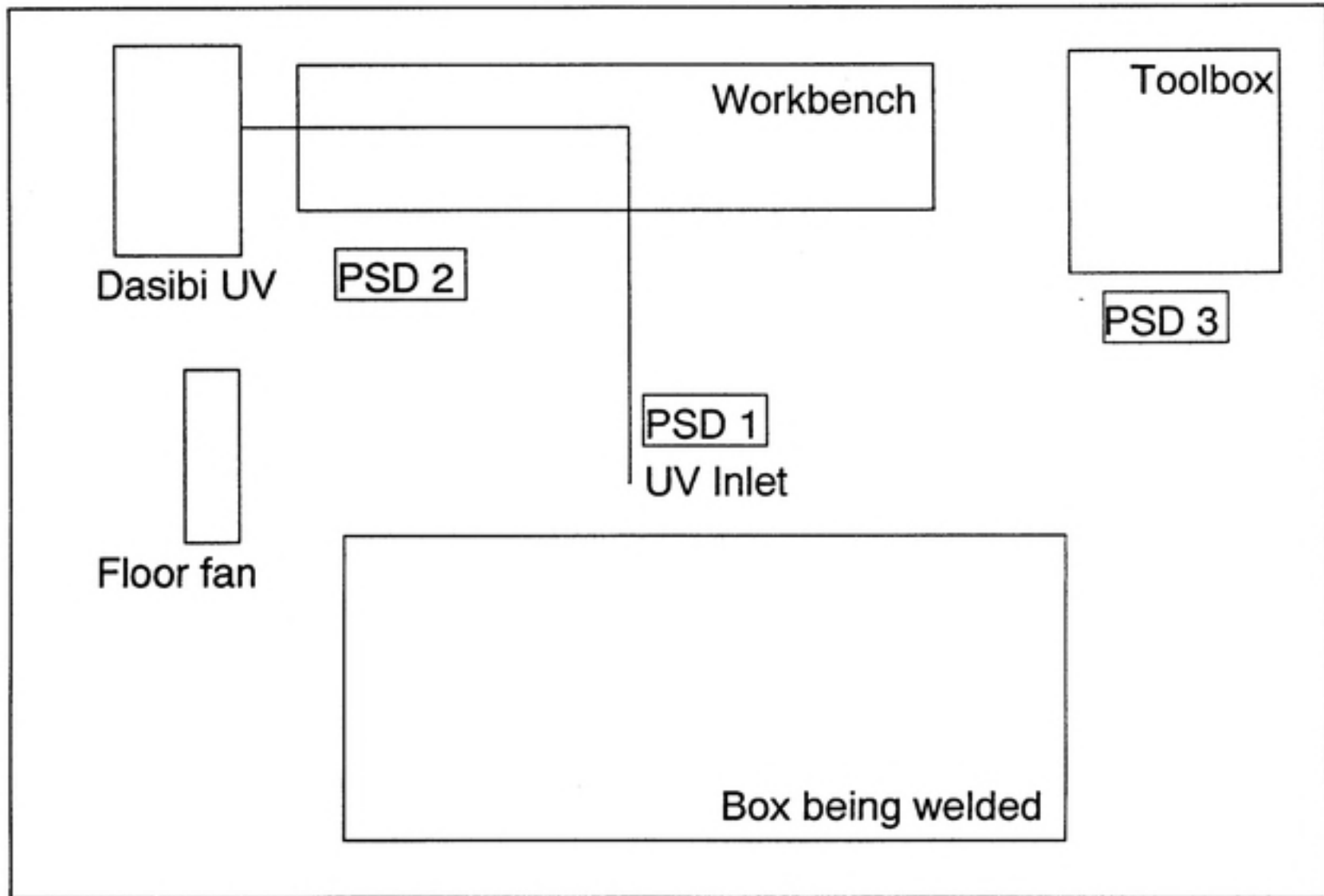


Figure 10 RTI Welding Shop Floorplan

The second field study was conducted in a welding shop at the Research Triangle Institute, RTP, N.C., while aluminum arc welding was ongoing (Figure 10). The welding shop is a room approximately 12 x 18 feet. An axial fan was used on the floor at one side of the room blowing across the welding surface. The fan was located approximately 2 feet off the floor while the welding was occurring at a level of 3 to 4 feet from the floor. For this study, three area PSD's were employed, along with two personal PSD's, and the Dasibi UV photometer. The average ozone in the room from the Dasibi, as averaged over 24 hours, was 41 ppb, and no spikes similar to those observed in the first field study were noted. The PSD that was attached directly to the Dasibi inlet showed 41 ppb. The other two area PSD's were located about 4 ft away in either direction from the Dasibi inlet and from the welding process. The ozone concentration at these locations as determined by the PSD were 37 and 33 ppb. The 37 ppb value was measured closest to the floor fan.

Two employees were monitored; the principle welder's exposure was 60 ppb while the second persons exposure was 40 ppb. The second person was not welding but was working on the same piece of equipment and was shaping and cutting the aluminum. The average exposure for the working hours that the employees were present was integrated to be 54 ppb from the Dasibi UV photometer.

CONCLUSIONS

The results indicate that the ozone PSD is well suited for IH purposes to assess exposures near the current REL, PEL and TLV of 100 ppb, when sampling for a minimum of 6 hours. If the TLV were lowered to 50 ppb then a sampling time of 6 hours would yield a total of 300 ppb-h, very near the limit of detection. If the PSD is used in areas of low (<50 ppb) ozone concentrations, it should be used for longer duration sampling.

The ozone PSD demonstrated equivalent quantification of ozone as compared to the Dasibi UV photometer within the NIOSH recommended bias of $\pm 25\%$, for the required concentration range of 0.5 to 2 times the regulation limit for average indoor room velocities. The PSD generally underestimated the ozone concentration by 11%. This underestimation of ozone is probably due to an inaccurate collection rate. If the PSD data were adjusted to be equivalent to the UV photometer in the laboratory tests presented here, the effective collection rate would be 16.2 cm^3/min , not 18.2 cm^3/min as reported by the inventors. The effective collection rate is lower than the theoretical for the following probable reasons; the collection efficiency of the coating solution, the high reactivity of ozone with the sampling badge material including the stainless steel screen, and the fluid mechanics involved i.e. the starvation effects noted by HSPH.

The PSD can not be used to determine peak ozone episodes since it is a time weighting device. If real time monitoring of ozone is required, the Dasibi UV photometer should be used. The PSD could not be used to determine compliance with a short term exposure limit (STEL) of 0.3 ppm for a 15 minute average.

Velocity extremes affected the use of the PSD's but the work was not conducted in a wind tunnel and is considered suspect. The use under velocity starvation resulted in a negative bias of 38-40%; suggesting that the PSD should be used in areas free from air stagnation and not placed in the corner or a closet. The results were conflicting for two

assessments of high velocity effects, in general the average air currents encountered indoors should not be high enough to effect the PSD use. For outdoor use the inventors suggest the use of a protective shield.

The PSD extract solution should be analyzed as soon as possible after extraction, no longer than two weeks, as instability of the extract solution was observed.

The ozone PSD was influenced by other strong oxidizers. NaClO , and H_2O_2 were positive interferences while HCl interfered with any determination of the nitrite/nitrate by ion chromatography. The Dasibi UV photometer also exhibited a positive interference from NaClO and HCl and interpreted these oxidizers as ozone.

The results from the second field study in a welding shop were very encouraging and showed good agreement between the PSD's and the Dasibi UV photometer for both area and personnel sampling. The first field study proved difficult to compare since there were many peak episodes detected by the Dasibi, and the employees monitored did not stay nearby the source of ozone.

The results of this testing agree well with validation tests published by Koutrakis et.al. at the Harvard School of Public Health (HSPH) (12,13,16,17). They reported 15 out of 16 chamber tests predicting ozone concentrations to $\pm 20\%$ of actual concentrations when exposed to 17 to 62 ppb for 24-167 hours (400-10,000 ppb-h). HSPH reported no effects from humidities ranging from 20-80%, and no effects from temperatures ranging from 0° to 40° C. A slope of 0.88 was reported (a negative bias of 12%) for one set of experiments conducted in a human exposure chamber with the PSD's attached to human subjects. This 12% negative bias agrees well with the average 11% negative bias observed in this testing. HSPH used a collection rate of $18.2 \text{ cm}^3/\text{min}$ for the chamber tests (12,13,16,17).

It is noteworthy that for outdoor field tests, HSPH uses a higher collection rate of 29.0 cm³/min, and when sampling 10 to 50 ppb for 7 days was able to predict ozone levels within 20% for 40 out of 43 sampling weeks.

Caution should be used in the interpretation of the HSPH data as the collection rate of the ozone PSD was set for each condition (laboratory versus field), to produce the most accurate comparison of ozone concentrations with the UV photometer. The collection rate applied in this study of 18.2 cm³/min, can only be applied to laboratory chamber and indoor settings. HSPH suggested the use of a small fan with the ozone PSD to insure steady state velocity conditions. The use of a fan with the ozone PSD may not stabilize the collection rate if the fans were not all blowing (or pulling) exactly the same velocity. Additionally, the use of a fan would yield a more cumbersome badge and it would no longer be classified as a "passive" device.

The Ogawa ozone PSD proved a useful tool for screening ozone. It is inexpensive, (\$45 for the filter holder and \$4 worth of filters for every PSD), portable and easy to use. By contrast the Dasibi UV photometer is not easily portable, it requires a movable cart, a strip chart recorder, and a source of electricity. The Dasibi requires frequent calibration. The disadvantage of the Dasibi is that only one area can be monitored at a time and it cannot be conveniently used to sample a persons breathing zone. The Ogawa ozone PSD is a useful alternative for industrial hygienist's to use in screening ozone exposure.

RECOMMENDATIONS

Since the collection rate of 18.2 cm³/min results in an 11% negative bias, future research should focus on achieving a more appropriate collection rate and understanding the fundamental reasons for the disparity between the theoretically generated (24.5 cm³/min) and the experimentally determined effective collection rate.

It is recommended that future research include field studies where more than one UV photometer could be collocated with the ozone PSD within areas of a room. This would allow a better representation of ozone gradients across the work space and ozone concentration versus distance from the source could be represented.

Future research should also include more tests into the storage stability of the extract solutions and storage of the dry/exposed filters prior to extraction.

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Appendix A

Ogawa Ozone PSD Laboratory Data

Quality Control Ogawa PSD's

Replicate Analysis for Nitrate

I.D.	Initial (ug/ml)	Replicate (ug/ml)	Diff (ug/ml)	Avg (ug/ml)	SD	RSD %
159 7	0.587	0.636	-0.049	0.612	0.035	5.7
163 1	0.334	0.321	0.013	0.328	0.009	2.8
164 2	0.155	0.134	0.021	0.145	0.015	10.2
165 3	0.534	0.526	0.008	0.530	0.006	1.1
166 4	0.887	0.899	-0.012	0.893	0.009	1.0
167 5	0.226	0.239	-0.013	0.233	0.009	3.9
168 6	0.235	0.237	-0.002	0.236	0.001	0.6
171 1	0.355	0.347	0.008	0.351	0.006	1.6
174 2	0.326	0.34	-0.014	0.333	0.010	2.9
175-4	0.274	0.266	0.008	0.270	0.006	2.1
182-5	0.241	0.202	0.039	0.222	0.028	12.4
190-5	0.234	0.231	0.003	0.233	0.002	0.9
Avg			0.001			3.8

Spikes	Low 0.4 ug/ml	Percent Recovery	High 1.0 ug/ml	Percent Recovery
1	0.452	113.0	0.985	98.5
2	0.471	117.7	1.121	112.1
3	0.435	108.8	1.011	101.1
4	0.364	91.0	1.042	104.2
5	0.488	122.0	1.053	105.3
6	0.46	115.0	1.017	101.7
Avg	0.445	111.3	1.038	103.8
S.D.	0.044	10.9	0.047	4.7
RSD	9.8	9.8	4.5	4.5

Blank Data Ogawa PSD Filters

Trial No.	NO3 µg/ml
1	0.00
2	0.00
3	0.00
4	0.067
5	0.00
6	0.00
7	0.00
8	0.00
9	0.057
10	0.00
11	0.086
12	0.00
Avg.	0.018
S.D.	0.031

Sample ID	N03 µg/ml	O3 Total ug	Exposure min	PSD Ozone ppb	Dasibf Ozone ppb	PSD / Dasibf %	ppb h

Field Study MCNC							
2477	0.182	0.45	1440	8.7	19	45.5	27360
2478	0.105	0.15	1440	2.9	19	15.0	27360
2479	0.115	0.19	1440	3.6	19	19.0	27360
2480	0.086	0.07	240	8.6	19	45.1	4560
2481	0.067	0.00	240	0.0	19	0.0	4560
2482blank	0.067	0.00	0				
Field Study Herbert Welding Area							
188-1	0.623	2.18	1485	41.1	41	100.2	60885
188-2	0.565	1.95	1485	36.8	41	89.9	60885
188-3	0.509	1.74	1485	32.8	41	79.9	60885
188-4	0.426	1.42	665	59.6	54	110.4	35910
188-5	0.305	0.95	665	39.9	54	73.9	35910
188-blank	0.060						
188-3	0.536	1.84	1485	34.7	41	84.7	2wk @5C
188-4	0.459	1.54	665	65.0	54	120.4	2wk @5C
188-5	0.225	0.64	665	26.9	54	49.8	2wk @5C

Ogawa Ozone PSD Data

Sample ID	NO3 ug/ml	O3 Total ug	Exposure min	Ozone ppb	Mean Ozone	S.D.	RSD
159 1	0.624	2.37	360	184.2	189.8	18.6	9.8
159 2	0.615	2.33	360	181.5			
159 3	0.632	2.40	360	186.6			
159 4	0.635	2.41	360	187.5			
159 6	0.764	2.91	360	226.3			
159 7	0.587	2.23	360	173.0			
159 7 dup	0.636	2.42	360	187.8			
163 1	0.334	1.25	120	290.7			
163 2	0.241	0.89	120	206.7			
163 3	0.245	0.90	120	210.4			
163 4	0.165	0.59	120	138.1			
163 5	0.197	0.72	120	167.0			
163 1 dup	0.321	1.20	120	279.0			
164 1	0.172	0.62	120	144.5	134.9	46.3	34.4
164 2	0.155	0.55	120	129.1			
164 3	0.238	0.87	120	204.0			
164 4	0.146	0.52	120	121.0			
164 5	0.096	0.33	120	75.8			
164 2 dup	0.134	0.47	120	110.1			
165 1	0.549	2.08	480	121.2			
165 2	0.552	2.09	480	121.9			
165 3	0.534	2.02	480	117.8			
165 4	0.473	1.78	480	104.1			
165 5	0.556	2.11	480	122.8			
165 3 dup	0.526	1.99	480	116.0			
166 1	0.945	3.61	480	210.6	201.1	7.1	3.6
166 2	0.928	3.55	480	206.7			
166 3	0.879	3.36	480	195.7			
166 4	0.887	3.39	480	197.5			
166 5	0.875	3.34	480	194.8			
166 4 dup	0.899	3.43	480	200.2			
167 1	0.225	0.82	240	96.2			
167 2	0.279	1.03	240	120.5			
167 3	0.242	0.89	240	103.8			
167 4	0.23	0.84	240	98.4			
167 5	0.226	0.83	240	96.6			
167 5 dup	0.239	0.88	240	102.5			

Ogawa Ozone PSD Data

Sample ID	Dasibi Ozone ppb	ppb h	PSD / Dasibi %	Bias %	Exp. Cond.
159 1	203	1218	93.4	-6.6	6h 25°C dry
159 2					
159 3					
159 4					
159 6					
159 7					
159 7 dup					
163 1	238	476	85.1	-14.9	2h 25°C dry
163 2					
163 3					
163 4					
163 5					
163 1 dup					
164 1	153	306	88.2	-11.8	2h 25°C dry
164 2					
164 3					
164 4					
164 5					
164 2 dup					
165 1	133	1064	88.4	-11.6	8h 25°C dry
165 2					
165 3					
165 4					
165 5					
165 3 dup					
166 1	217	1734	92.7	-7.3	8h 25°C dry
166 2					
166 3					
166 4					
166 5					
166 4 dup					
167 1	132	526	78.1	-21.9	4h 25°C dry
167 2					
167 3					
167 4					
167 5					
167 5 dup					

Ogawa Ozone PSD Data

Sample ID	NO3 ug/ml	O3 Total ug	Exposure min	Ozone ppb	Mean Ozone	S.D.	RSD
168 1	0.28	1.04	180	161.3	143.2	15.6	10.9
168 2	0.234	0.86	180	133.6			
168 3	0.236	0.87	180	134.8			
168 4	0.252	0.93	180	144.5	133.6	11.1	8.3
168 5	0.215	0.79	180	122.2			
168 6	0.235	0.86	180	134.2			
168 7							
168 8							
168 9							
168 6 dup	0.237	0.87	180	135.4			
170 1	0.486	1.83	320	160.5	149.6	10.4	7.0
170 2	0.468	1.77	320	154.4			
170 3	0.461	1.74	320	152.0			
170 4	0.451	1.70	320	148.6			
170 5	0.404	1.52	320	132.7			
171 1	0.355	1.33	310	126.0	101.3	25.8	25.5
171 2		-0.05	310				
171 3	0.338	1.26	310	119.8			
171 4	0.25	0.92	310	87.5			
171 5	0.208	0.76	310	72.0			
171 1 dup	0.347	1.30	310	123.1			
173 1	0.527	1.99	360	163.0	142.0	15.6	11.0
173 2	0.489	1.85	360	150.9			
173 3	0.406	1.53	360	124.7			
173 4	0.46	1.73	360	141.8			
173 5	0.422	1.59	360	129.7			
174 1	0.361	1.35	305	117.6	119.1	8.1	6.8
174 2	0.326	1.22	305	105.8			
174 3	0.381	1.43	305	124.4			
174 4	0.371	1.39	305	121.0			
174 5	0.387	1.45	305	126.4			
176 1	0.368	1.38	305	120.0	100.0	18.5	18.5
176 2	0.225	0.82	305	71.8			
176 3	0.323	1.20	305	104.8			
176 4	0.339	1.27	305	110.2			
176 5	0.288	1.07	305	93.0			

Ogawa Ozone PSD Data

Sample ID	Dasibf Ozone ppb	ppb h	PSD / Dasibf %	Bias %	Exp. Cond.
168 1	162	486	88.4	-11.6	3h 25°C
168 2					
168 3					
168 4		486	ERR	ERR	3h + CA
168 5					
168 6					
168 7					Clean Air
168 8					
168 9					
168 6 dup					
170 1	177	953	84.5	-15.5	5h 25°C humid
170 2					
170 3					
170 4					
170 5					
171 1	131	676	77.3	-22.7	5h 40°C humid
171 2					
171 3					
171 4					
171 5					
171 1 dup					
173 1	160	960	88.8	-11.2	6h 40°C dry
173 2					
173 3					
173 4					
173 5					
174 1	150	751	79.4	-20.6	5h 10°C dry
174 2					
174 3					
174 4					
174 5					
176 1	106	671	94.3	-5.7	6h 10°C humid
176 2					
176 3					
176 4					
176 5					

Ogawa Ozone PSD Data

Sample ID	NO3 ug/ml	O3 Total ug	Exposure min	Ozone ppb	Mean Ozone	S.D.	RSD
177 1	0.184	0.67	370	50.4	58.2	13.9	23.9
177 2	0.227	0.83	370	63.0			
177 3	0.193	0.70	370	53.0			
177 4	0.285	1.06	370	79.9			
177 5	0.164	0.59	370	44.5			
192 1	0.289	2.14	420	142.9	147.2	10.3	7.0
192 2	0.321	2.39	420	159.4			
192 3	0.268	1.98	420	132.1			
192 4	0.315	2.35	420	156.3			
192 5	0.305	2.27	420	151.2			
192 6	0.286	2.12	420	141.4			
192 1	0.371	2.78	420	185.2	186.4	14.7	7.9
192 2	0.403	3.03	420	201.7			
192 3	0.346	2.59	420	172.3			
192 4	0.343	2.56	420	170.8	159.8	9.8	6.1
192 5	0.315	2.35	420	156.3			
192 6	0.307	2.28	420	152.2			
178 1	0.327	1.22	364	93.8	67.3	22.4	33.2
178 2	0.225	0.82	364	63.4			
178 3	0.231	0.85	364	65.2			
178 4	0.282	1.05	364	80.4			
178 5	0.126	0.44	364	33.9			
179 1	0.136	0.48	128	105.0	145.6	50.0	34.4
179 2	0.282	1.05	128	228.5			
179 3	0.196	0.71	128	155.7			
179 4	0.153	0.55	128	119.3			
179 5	0.153	0.55	128	119.3			
179 6	0.16	0.57	182	88.1	76.7	15.4	20.1
179 7	0.135	0.48	182	73.2			
179 8	0.131	0.46	182	70.8			
178 9	0.172	0.62	182	95.2			
179 10	0.106	0.36	182	56.0			
190 1	0.234	0.86	420	57.3	57.2	5.7	10.0
190 2	0.215	0.79	420	52.4			
190 3	0.27	1.00	420	66.6			
190 4	0.216	0.79	420	52.6			
190 5	0.234	0.86	420	57.3			
190 5 dup	0.231	0.85	420	56.5			

Ogawa Ozone PSD Data

Sample ID	Dasibi Ozone ppb	ppb h	PSD / Dasibi %	Bias %	Exp. Cond.
177 1	89	549	65.3	-34.7	150 FPM
177 2					
177 3					
177 4					
177 5					
192 1	140	980	105.1	5.1	150 FPM
192 2					
192 3					
192 4					
192 5					
192 6					
192 1	140	980	133.2	33.2	2wk @25°C
192 2					2wk @25°C
192 3					2wk @25°C
192 4	140	980	114.1	14.1	2wk @5°C
192 5					2wk @5°C
192 6					2wk @5°C
178 1	109	656	61.8	-38.2	25 FPM
178 2					
178 3					
178 4					
178 5					
179 1	92	195	158.2	58.2	Min Detection
179 2					25°C dry
179 3					
179 4					
179 5					
179 6	93	279	82.4	-17.6	Min Detection
179 7					25°C dry
179 8					
178 9					
179 10					
190 1	55	382	104.1	4.0	Min Detection
190 2					25°C dry
190 3					
190 4					
190 5					
190 5 dup					

Ogawa Ozone PSD Data

Sample ID	NO3 ug/ml	O3 Total ug	Exposure min	Ozone ppb	Mean Ozone	S.D.	RSD
175 1	0.911	3.48	420	231.9	85.9	2.2	2.5
175 2	0.351	1.31	420	87.4			
175 3	0.339	1.27	420	84.4			
175 4	0.274	1.01	420	67.6	69.6	5.8	8.3
175 5	0.264	0.98	420	65.0			
175 6	0.307	1.14	420	76.1			
175 7	0.26	0.96	420	64.0	60.0	3.9	6.5
175 8	0.244	0.90	420	59.8			
175 9	0.23	0.84	420	56.2			
182 1	0.288	1.07	90	332.2	312.5	26.0	8.3
182 2	0.261	0.96	90	299.7			
182 3	0.295	1.10	90	340.7			
182 4	0.273	1.01	90	314.2			
182 5	0.241	0.89	90	275.7			
183 1	0	-0.05	60	-21.7	-21.7	0.0	-0.0
183 2	0	-0.05	60	-21.7			
183 3	0	-0.05	60	-21.7			
183 4	0	-0.05	60	-21.7			
183 5	0	-0.05	60	-21.7			
184 1	0	-0.05	120	-10.8	58.5	42.0	71.9
184 2	0.096	0.33	120	75.8			
184 3	0.125	0.44	120	102.0			
184 4	0.077	0.25	120	58.7			
184 5	0.086	0.29	120	66.8			
194 1	0.284	1.05	390	75.6	71.9	5.1	7.1
194 2	0.258	0.95	390	68.3			
195 1	0.578	2.19	455	141.7	127.4	13.1	10.3
195 2	0.475	1.79	455	115.9			
195 3	0.51	1.93	455	124.7			

Ogawa Ozone PSD Data

Sample ID	Dasibf Ozone ppb	ppb h	PSD / Dasibf %	Bias %	Exp. Cond.
175 1	100	700	85.9	-14.1	24h
175 2					24h
175 3					24h
175 4	100	700	69.6	-30.4	2wk 25°C
175 5					2wk 25°C
175 6					2wk 25°C
175 7	100	700	60.0	-40.0	2wk 5°C
175 8					2wk 5°C
175 9					2wk 5°C
182 1	0	0			HC104
182 2					
182 3					
182 4					
182 5					
183 1	0	0			HC1
183 2					
183 3					
183 4					
183 5					
184 1	0	0			H202
184 2					
184 3					
184 4					
184 5					
194 1	121	787	59.5	-40.5	Low Velocity
194 2					25°C dry
195 1	107	813	119.1	19.1	7.5h 40°C
195 2					humid
195 3					

Appendix B

Calibration Procedure For Dasibi UV Photometer

APPENDIX B

ULTRAVIOLET PHOTOMETRIC PROCEDURE FOR PRIMARY OZONE STANDARDS*

CALIBRATION PROCEDURE

1. Principle. The calibration procedure is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 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 O_3 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 O_3 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 O_3 at 254 nm = 308 ± 4
 $\text{atm}^{-1} \text{cm}^{-1}$ at 0°C and 760 torr. (1,2,3,4,5,6,7)

C = O_3 concentration in atmospheres

l = optical path length in cm

*Extracted from the Code of Federal Regulations, Title 40, Part 50, Appendix D, as amended February 8, 1979 (Federal Register, 44:8221-8233).

APPENDIX B ULTRAVIOLET PHOTOMETRIC PROCEDURE/Principle

In practice, a stable O_3 generator is used to produce O_3 concentrations over the required range. Each O_3 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,

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

or,

$$c(\text{ppm}) = -\frac{10^6}{\alpha l} (\ln I/I_0) \quad (2b)$$

The calculated O_3 concentrations must be corrected for O_3 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 O_3 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 O_3 generator should be of glass, Teflon, or other relatively inert material. 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 O_3 , the transfer standard may replace the O_3 generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

APPENDIX B ULTRAVIOLET PHOTOMETRIC PROCEDURE/Apparatus

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 O_3 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 O_3 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 O_3 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 O_3 concentration.

APPENDIX B. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Apparatus

3.6 Temperature indicator. Accurate to $\pm 1^\circ\text{C}$.

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 O_3 analyzer, and it should be free of NO , C_2H_4 , and other species which react with O_3 . 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 I_0 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

APPENDIX B. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Procedure

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 O_3 concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and reassay 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

A_1 = assay of the original concentration

A_2 = 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.

APPENDIX B. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Procedure

5.2.4 Intercomparison: When possible, the photometer should be occasionally intercompared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 Ozone losses: Some portion of the O_3 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 O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 Assay of O_3 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_p , 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.

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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.

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

where: $[O_3]_{OUT}$ = O_3 concentration, ppm
 α = absorption coefficient of O_3 at 254 nm = $308 \text{ atm}^{-1} \text{ cm}^{-1}$ 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 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

APPENDIX B. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Procedure

term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O_3 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 O_3 analyzer and the photometer or transfer standard to warm up and stabilize.

5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 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 O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

5.5.4 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{\text{OUT}}}{\text{URL}} \times 100 \right) + Z \quad (5)$$

where: URL = upper range limit of the O_3 analyzer, ppm

Z = recorder response with zero air, % scale

Record the O_3 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 O_3 concentration standards (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 concentration and the corresponding analyzer response.

5.5.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.5.7 Option 1: The various O_3 concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O_3 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 O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_0) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]_{\text{OUT}}' = [O_3]_{\text{OUT}} \left(\frac{F_0}{F_0 + F_D} \right) \quad (6)$$

APPENDIX B ULTRAVIOLET PHOTOMETRIC PROCEDURE/Procedure

where: $[O_3]_{OUT}$ = diluted O_3 concentration, ppm
 F_{O_3} = flowrate through the O_3 generator, liter/min
 F_D = diluent air flowrate, liter/min

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APPENDIX B. ULTRAVIOLET PHOTOMETRIC PROCEDURE/References

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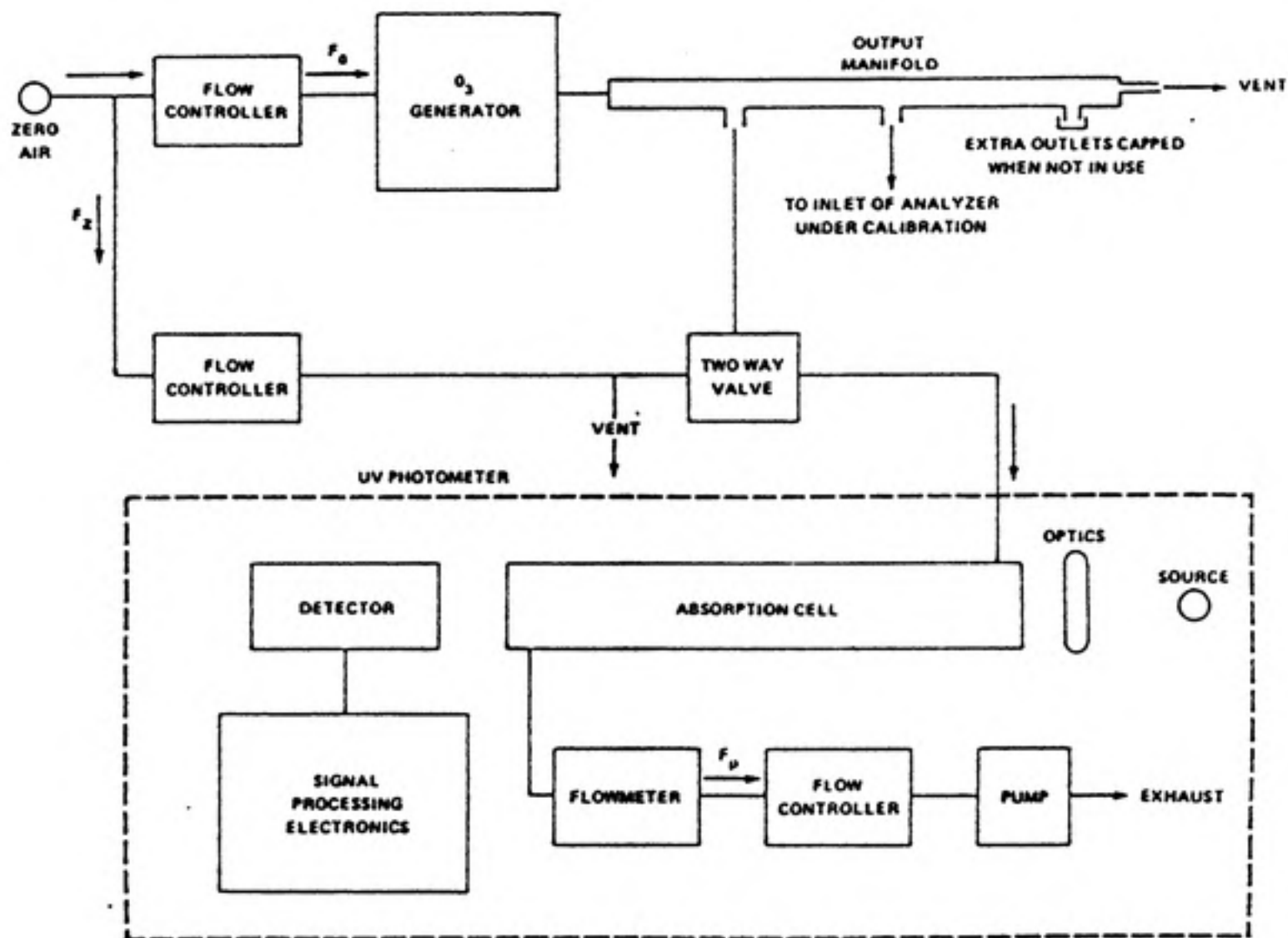


Figure 1. Schematic diagram of a typical UV photometric calibration system.

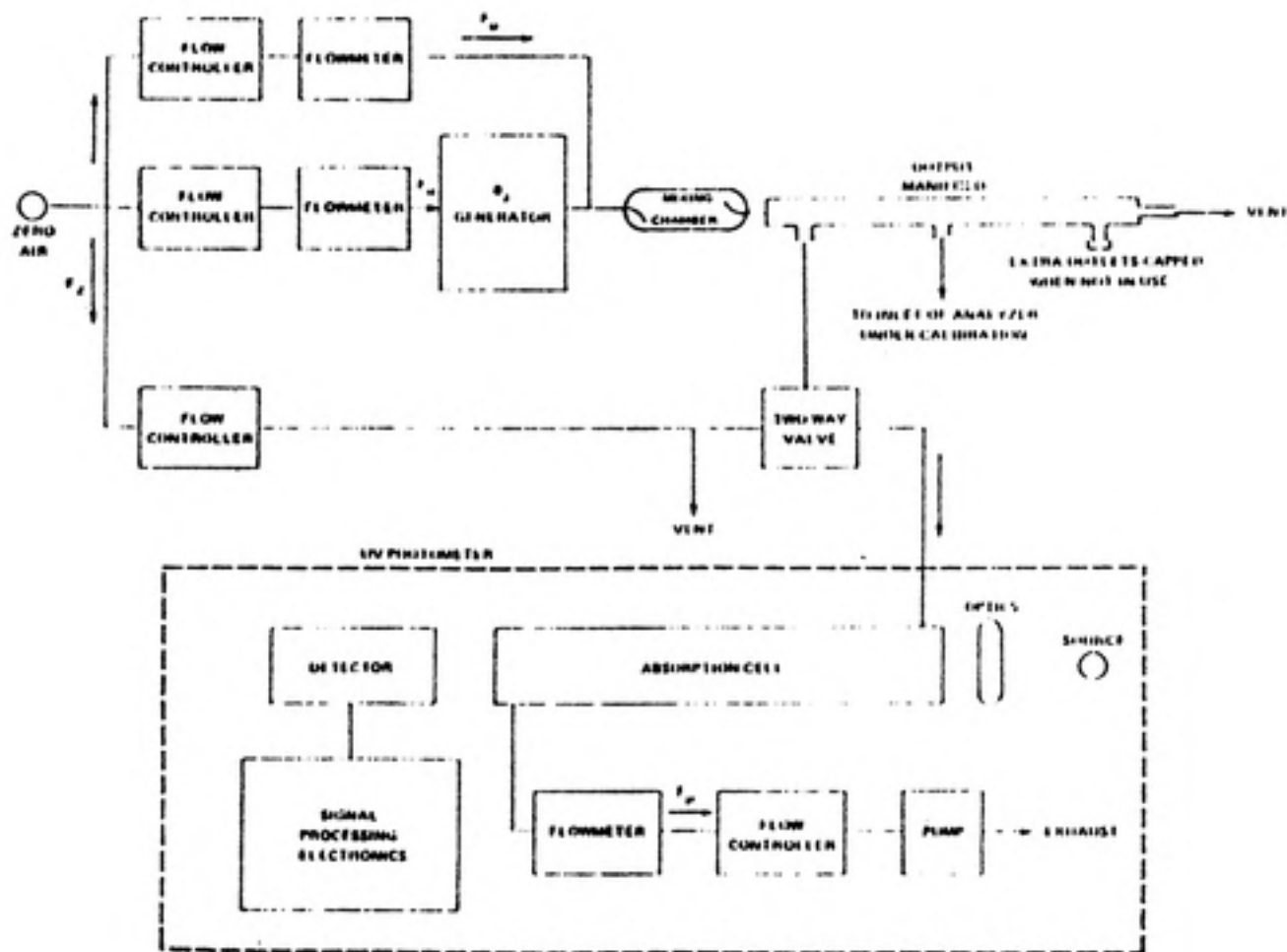


Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).