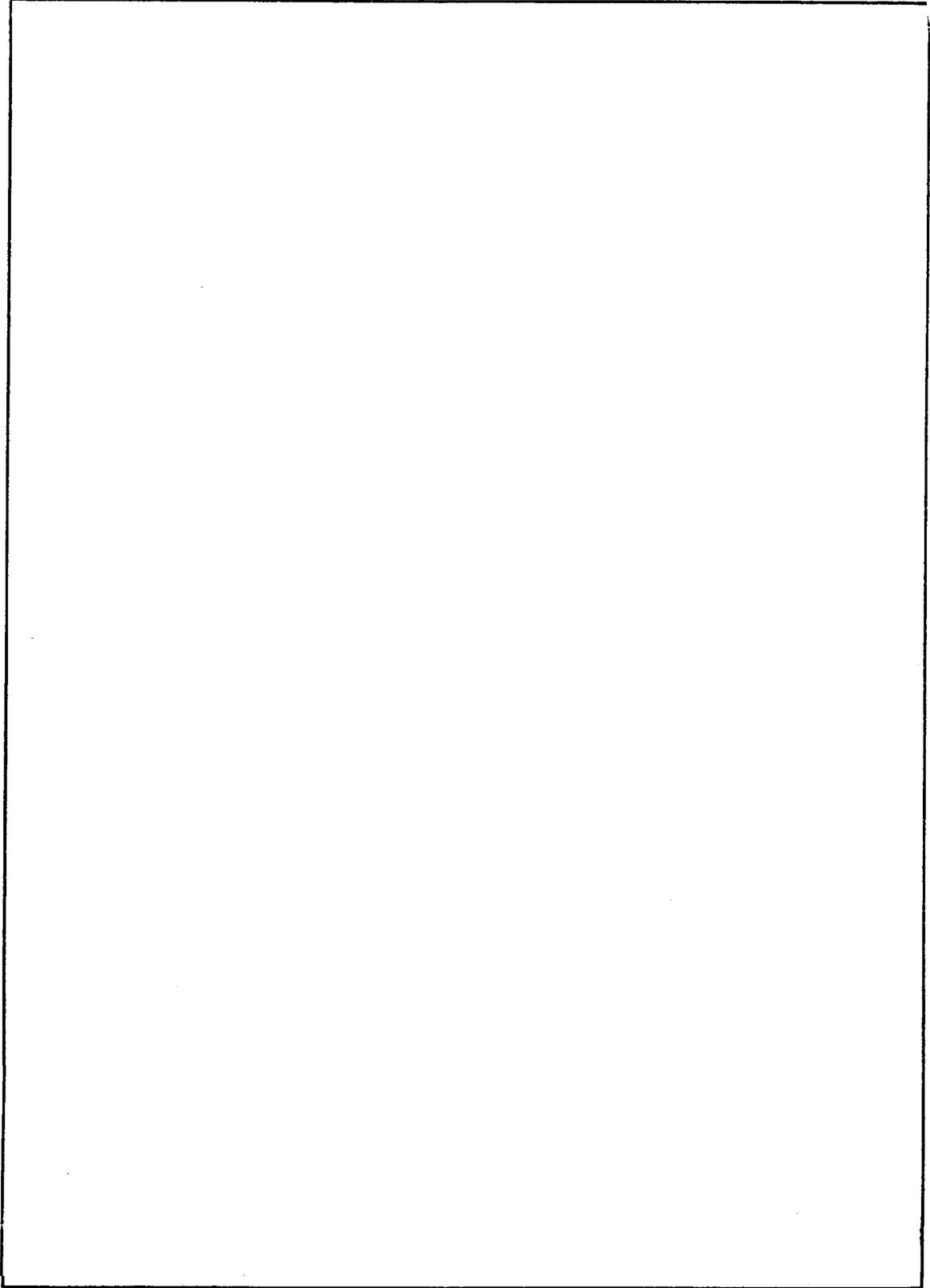


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PERSONAL ATMOSPHERIC GAS SAMPLER WITH A CRITICAL ORIFICE

PART 1 — DEVELOPMENT AND EVALUATION

INTRODUCTION

Although people have long been subjecting themselves knowingly and unknowingly to noxious fumes, not until May 29, 1971, were environmental occupational safety and health standards promulgated by the Federal Government. The National Institute for Occupational Safety and Health (NIOSH) was given scientific and technical responsibility for determining compliance with standards set forth by the Labor Department's Occupational Safety and Health Administration (OSHA). As part of this responsibility, NIOSH is tasked to develop sampling and analytical methods for various chemical compounds which may be deemed hazardous by OSHA. The Naval Research Laboratory, having the capability of performing this task, submitted a proposal to do so which was accepted by NIOSH.

It is not enough to evaluate the general environment and from that extrapolate a total daily exposure of an individual. Instead, a realistic total exposure within a person's breathing zone as he goes about his tasks, whether from room to room or building to building, is required. Design criteria for such a sampling system encompass weight and size small enough that an individual may conveniently carry the sampler on his person. In addition the method must be (a) on a personal basis; that is, the immediate environment of an individual must be sampled; (b) time integrating for periods up to 8 hours to measure the total exposure; (c) capable of detecting concentration transients which might cause hazardous exposures for short times; and (d) quantitative, so that reliable time-weighted averages can be determined for individual exposures.

Current samplers which fulfill these requirements are the adsorptive type [1]. They usually consist of a small pump and some type of adsorptive material to trap atmospheric components. Activated carbon is widely used as a general adsorbent [2]. However, low-molecular-weight gases such as carbon monoxide (CO) cannot be collected, since the affinity of carbon for these compounds is low. When the affinity of a compound is high, adsorption techniques afford good sensitivity, because large volumes of air are processed. For quantitative results the adsorptive and desorptive efficiencies of a particular compound must be known.

The ideal way to evaluate the environment that an individual encounters is to transfer a portion of the whole gas back to the laboratory. This is done frequently by short-term samples collected in less than a minute. These samples are known as *grab samples*, but do not fulfill the criterion of a time-integrated sample.

This report will be concerned with the development and the coupling of gas-sampling technique with a critical orifice to give a sampling device which samples constantly for extended time periods. The techniques for analyzing and handling such a system will be discussed in NRL Report 7980 [3].

COMPONENT DEVELOPMENT

Gas Sampler

The maximum sampling interval depends on the size of the orifice and the volume of the evacuated sample bottle. A gas flow remains constant through a small orifice as long as a critical flow pattern exists [4]. To maintain a critical flow pattern, the internal pressure of a previously evacuated container must remain less than 1/2 of the external pressure during the sampling interval.

The equation that governs the gas flow across a critical orifice [4] is

$$\dot{m} = 10^{-5} \text{ CAP} \left[\frac{\gamma M}{RT} \left(\frac{2}{\gamma + 1} \right)^{(\gamma + 1)/(\gamma - 1)} \right]^{1/2},$$

where

\dot{m} = mass flow rate, $g \text{ s}^{-1}$,

A = orifice throat area, cm^2 ,

P = external pressure, $N \text{ cm}^{-2}$,

γ = specific heat ratio C_p/C_v ,

M = molecular weight, g ,

T = ambient temperature, K ,

R = gas constant, $8.31 \text{ joule mole}^{-1} \text{ K}^{-1}$,

C = discharge coefficient (accounts empirically for the boundary layer effect and has a range of 0.8 to 0.95 for small orifices).

By use of this critical orifice equation with the discharge coefficient of 0.8, some typical sampling intervals were determined for various orifice sizes and sample bottle volumes (Table 1).

Table 1 — Maximum Sampling Intervals (Times for Attaining 1/2 Atmosphere Within the Sampler) for Various Orifice Diameters and Sample Bottle Volumes

(Gas = Air, molecular weight = 28.95, $C_p/C_v = 1.400$, ambient pressure = 1.000 atm, ambient temperature = 298.0 K, discharge coef. = 0.8)

Sampler Volume at STP (cm^3)	Sampling Intervals For Various Orifice Diameters (hr)					
	1 μm	2 μm	3 μm	5 μm	7 μm	10 μm
50	44.2	11.0	4.9	1.8	0.9	0.4
100	88.3	22.1	9.8	3.5	1.8	0.9
150	132.5	33.1	14.7	5.3	2.7	1.3
200	176.6	44.2	19.6	7.1	3.6	1.8
500	441.5	110.4	49.1	17.1	9.0	4.4

The personal gas sampler (Fig. 1) is 6.35 cm wide by 7.32 cm high (less valve stems) by 2.54 cm deep and weighs 0.22 kg. The sampler body is fabricated from 0.1-cm stainless steel with reinforcing in the middle to avoid volume changes at reduced pressures. The internal volume is approximately 100 cm³.

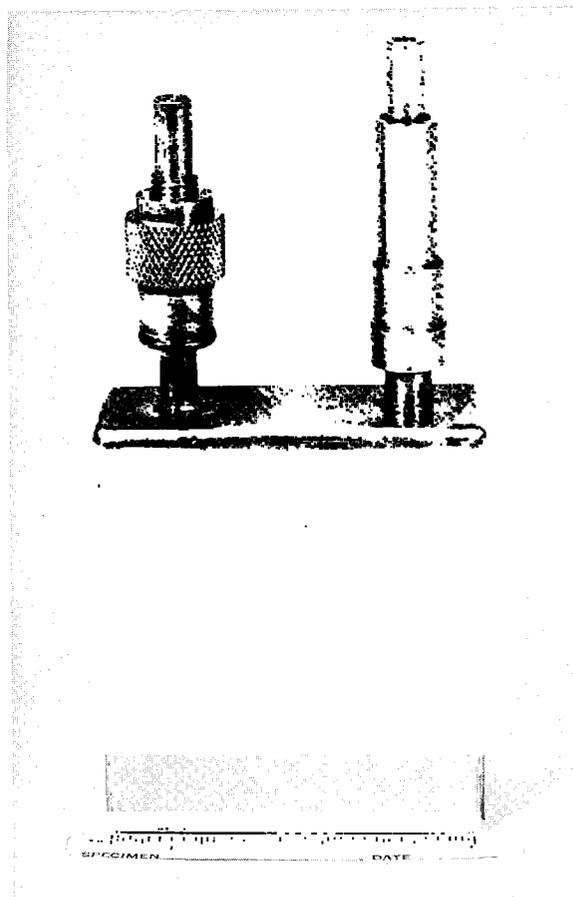


Fig. 1 — Pocket-size personal gas sampler

The left valve, 5.41 cm high, is a simple off-on type and is either used to evacuate the sampler when connected to a vacuum system or used to connect to a gas chromatograph for evaluation of the contaminants entrapped after a sampling period. The right valve, 6.35 cm high, houses the critical orifice and protective filters through which the atmospheric sample enters. This valve is actuated by one complete counterclockwise turn.

Figure 2 shows details of the right valve. As shown, the valve is closed, with threads of the cover (B) fully engaging those of the body (G). In this position, closure between the cover and the center O ring* (F) blocks the flow. To open, the cover is rotated

counterclockwise. As the cover and body threads disengage, the two cover notches (broached 3.2 mm long and 0.8 mm deep with a grooving tool and 180 degrees apart) bridge the center O ring; flow through the unit from left to right is indicated by arrows. A disk (D) with a critical orifice is held between two O rings (E) in a double-O-ring gland normal to the unit axis: one groove is machined in the body, and the other is machined in the cap (A). The disk is chosen from among a set of disks 4.62 mm in diameter and as thin as 0.025 mm and having axial orifice holes ranging from 2 to 20- μ m in diameter[†]. On either side of a disk, filters[‡] (C) 1.27 mm in diameter are centered over the orifice hole and axial body and cap holes. Minimal application of organosiloxane high-vacuum lubricant to the O rings affords system integrity and is compatible with trace-contaminant analysis, particularly for low-molecular-weight gases to which whole-air sampling is well suited.

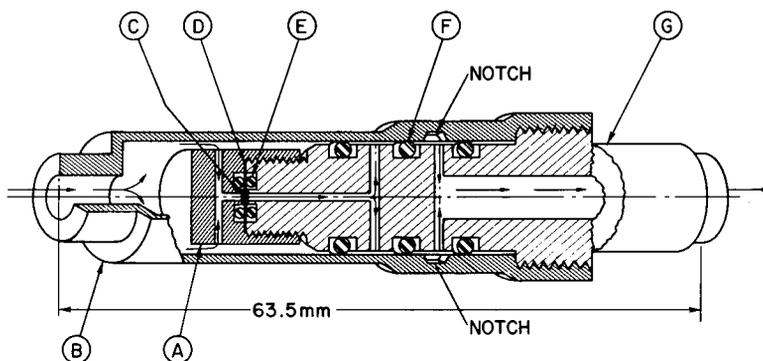


Fig. 2 — Critical-orifice valve: (A) brass cap, (B) brass cover, (C) filter, (D) orifice disk (stainless steel, type 303), (E) O ring (Parker size 2-002), (F) O ring (Parker size 2-009), (G) body (stainless steel, type 304)

Environmental Test Chamber

The environmental test chamber used to evaluate the sampler is shown in Fig. 3. This system is a modified chamber used by Woods et al. [5]. Before the sampler is placed in the chamber, the sampler is evacuated to less than 133 N/m² (1 torr). Atmospheres containing various contaminants are prepared in the 175-liter steel chamber by evacuating it and then injecting the compounds of interest. Calculated quantities of liquid and gaseous components are injected with a syringe into the evacuated chamber through a rubber system housed in the sampling port.

*The O rings are Viton, which is less absorptive than Buna-N.

†The disks, with laser-drilled critical orifices, were obtained from the New England Laser Corp., Lowell, Mass. 01852.

‡The filters are Gelman glass fiber, type E, which have a retentivity of 99.8 ± 0.3% for 0.3- μ m particles.

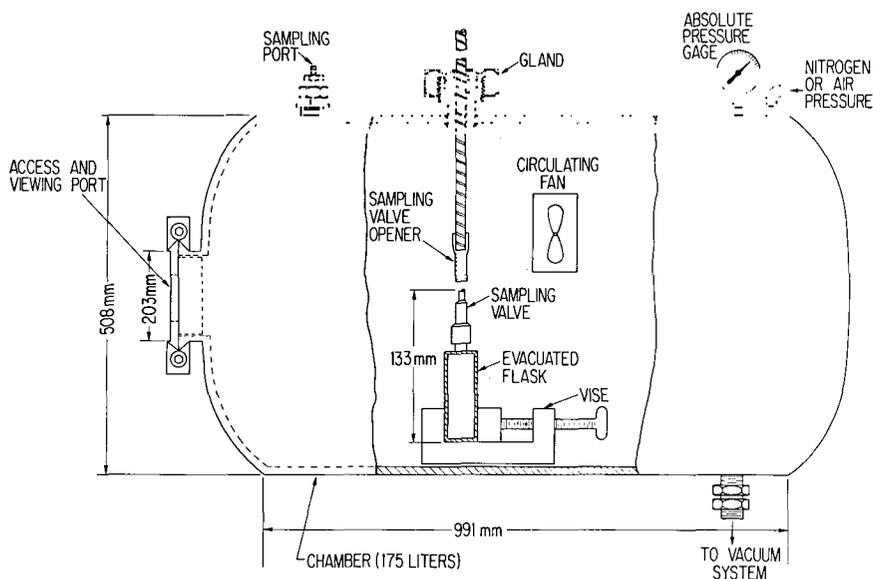


Fig. 3 — Environmental chamber

In most cases compressed air is used to pressurize the chamber to 138 kN/m^2 (20 psi) for evaluation of the sampler. However, in evaluating possible sampling bias across the small orifice for different molecular weight components, hydrogen and hexane, nitrogen was used to pressurize the chamber to facilitate analysis. A ventilating fan is used to mix the gases in the chamber.

The chamber is analyzed by withdrawing a sample by means of a gas-tight syringe from the port housing the rubber system and injecting the sample into the gas chromatograph. Following chamber atmospheric analysis, the sampler is opened to the environment by connecting the rod passing through the chamber to the sampler and turning the sampler valve counterclockwise one complete turn.

At the completion of the testing interval the sampler is closed and removed from the chamber. The pressure in the sampler is measured with a small-volume vacuum-pressure measuring system to insure that the resultant pressure is not greater than $1/2$ of the testing atmosphere and thus did not exceed the pressure limit for linear flow into the sampler during the sampling period.

A schematic of a small-volume vacuum-pressure-measuring system is presented in Fig. 4. This system is designed for measuring the pressure of the sampler prior to metering the contents into the gas chromatographic sample loops, transferring the contents to the sample loops, and evacuating the sampler after analysis is completed. The tubulation is 3.175-mm-OD 303-type stainless steel. The stainless steel (316) valves are ball type manufactured by Hoke, Inc. (Cresskill, N.J.), the pressure transducer is from Validyne Corp., (Northridge, Calif.) rated at 0 to 11 MN/m^2 (0 to 1600 torr), the digital panel meter is from Analogic (Wakefield, Mass.), and the 12-volt power supply is from Lafayette (Syrosset, N.Y.). The vacuum pump used is a small direct-drive Vac Torr 20 pump (GSA/Precision Scientific Corp., Chicago, Ill.).

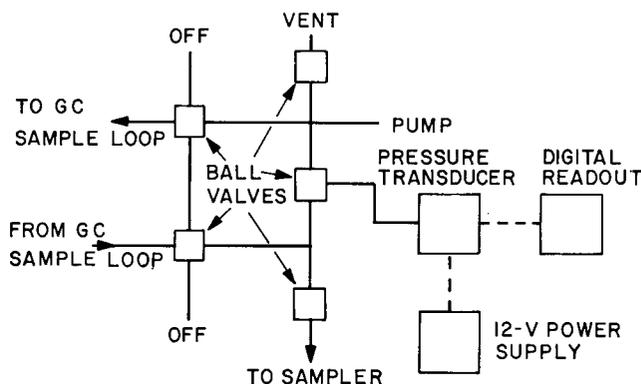


Fig. 4 — Vacuum-pressure-measuring system (at right) gas-handling system (at left connecting with a gas chromatograph (GC))

Analytical System

The analytical system used to evaluate the performance of the gas sampler was a modified Beckman GC-5 gas chromatograph. The valving arrangement for the gas chromatograph is shown in Fig. 5. This analyzer was equipped with a thermal-conductivity cell and dual hydrogen flame ionization detectors.

System I was designed for the detection of ethane (C_2H_6), Freon-12 (CF_2Cl_2), vinyl chloride ($CH_2=CHCl$), Freon-11 ($CFCl_3$), vinylidene chloride ($CH_2=CCl_2$), hexane (C_6H_{14}), benzene (C_6H_6), and "total hydrocarbons." The column used was 10% DC-200 (200 centistokes) on Chromosorb G, 45/60 mesh, 3.05 m by 6.35 mm (10 ft by 1/4 in.) stainless steel tubing.

System II was designed for the detection of methane (CH_4) and carbon monoxide (CO). The column used was a Molecular Sieve 5A, 70/80 mesh, packed in 1.83 m by 6.35 mm (6 ft by 1/4 in.) stainless-steel tubing.

The detailed description of sampler preparation for analysis, sequence of injecting the subambient pressured sample, and proposed alternatives is quite involved and will be presented as a separate NRL report [3].

PERFORMANCE EVALUATION OF THE GAS SAMPLER

Critical Flow Test

Although the two concepts, gas sampling and critical orifice, are well known, they have never been tested together for the application considered in this study. To test the ability of the orifice to remain critical when tested with the sampler, the sampler was first evacuated. The change in pressure versus time was monitored through the off-on valve while the valve containing the orifice was open and sampling.

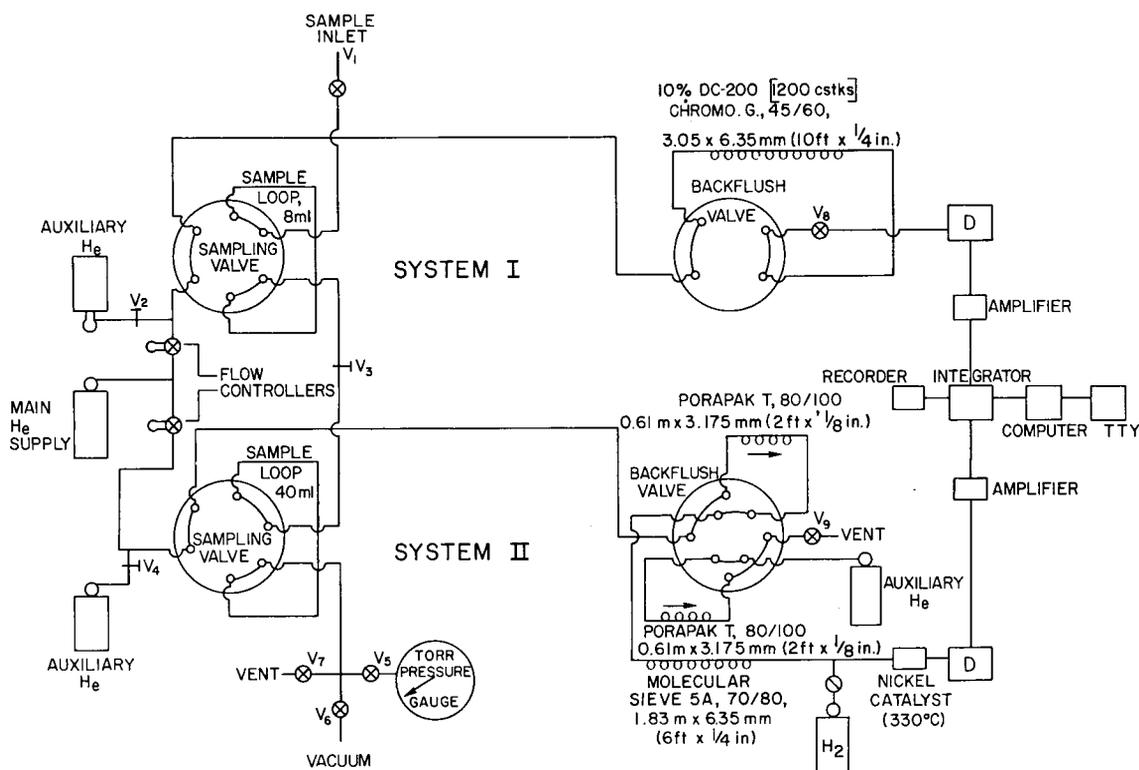


Fig. 5 — Gas-handling and analytical systems

These tests were conducted and comparison made with and without a protective filter needed to protect the orifice from clogging with airborne particles. Ideally such a filter should not alter the flow into the sampler. One filter tested was a Gelman membrane, pore size $0.80 \mu\text{m}$. The result of testing the sampler with a $10\text{-}\mu\text{m}$ orifice first without the filter is shown in Fig. 6. As can be seen, the plot of pressure versus time produces a constant linear sampling rate (critical flow) until the pressure reaches $1/2$ atmosphere; then the rate begins to decrease (noncritical) as predicted from theory. However, when the membrane-type filter was used, the flow rate was greatly altered. This was due to the close proximity of the filter to the orifice and the constricting nature of the membrane. This problem was rectified by using a Gelman glass-fiber-type filter as indicated in Fig. 7 in testing a $4\text{-}\mu\text{m}$ orifice. As can be seen there is no difference in the flow rate with or without the filter.

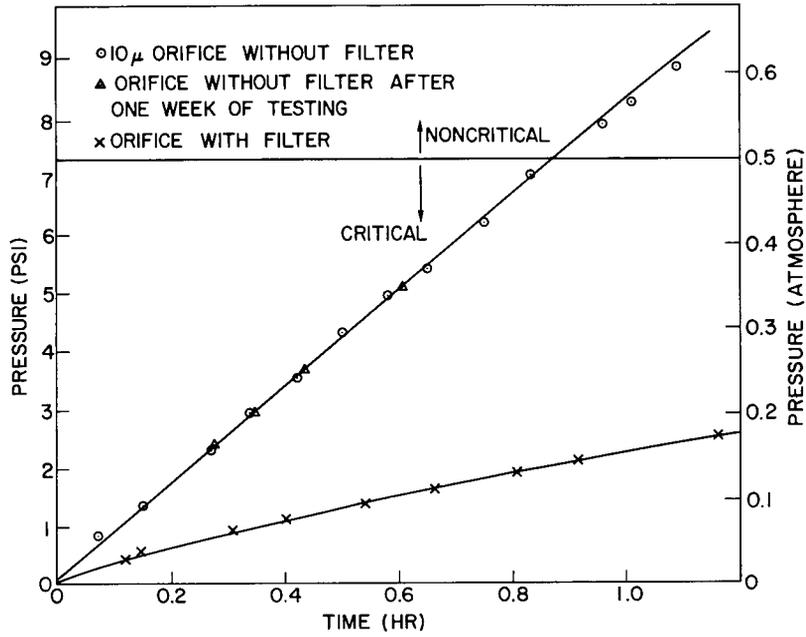


Fig. 6 — Critical gas flow through a 10- μ m orifice with and without a Gelman-membrane-type filter

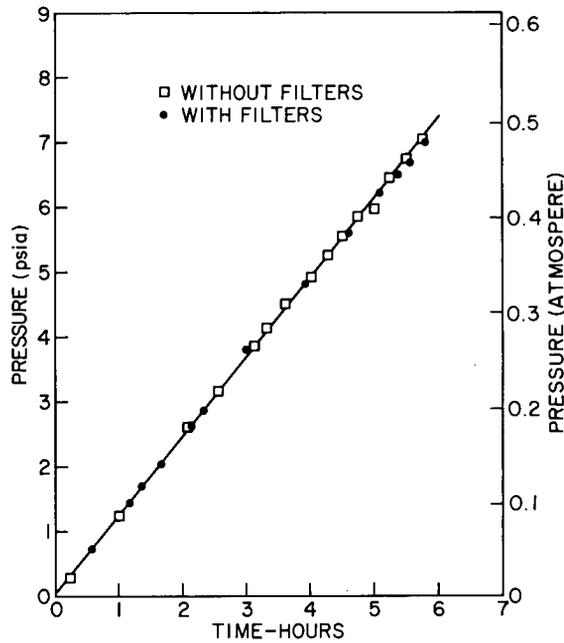


Fig. 7 — Critical gas flow through a 4- μ m orifice with and without a Gelman glass-fiber-type E filter

Accuracy Determination

To determine the accuracy of the sampler, three concentrations of CO were established in the chamber. The concentrations of CO was determined based on partial pressures, direct sampling, and evaluation with the whole gas sampler. The results are given in Table 2. As seen in the table, the personal sampler, in this case equipped with a 12.5- μ m orifice, is accurate over a 40-fold concentration range.

Table 2 — Accuracy of the Personal Sampler for Determining CO

Run	CO Concentration (ppm)		
	Calculated	Direct Analysis From Chamber	Sampler
1	4	4 \pm 0.8	4 \pm 0.8
2	84	80 \pm 4	85 \pm 4
3	168	168 \pm 8	164 \pm 8

Precision of Sampling

The precision of the whole gas sampler equipped with a 7- μ m orifice was determined by attaching the sampler to a gas flow system. This flow system contained a calibrated 18.3-ppm concentration of CO, obtained from Matheson Co., Inc. This sampling procedure was conducted four times, and the precision was calculated from the measurements. Each of the four samples was analyzed three times, and the average is recorded in Table 3. The precision, 11 parts per thousand, is excellent considering the low concentration and multiple gas handling.

Table 3 — Sampling Precision of the Personal Sampler

Run	CO Concentration (ppm)	Mean Deviation
1	18.6	0.3
2	18.3	0.0
3	18.1	0.2
Av	18.3	0.2
Precision = $\frac{0.2}{18.3} = 11$ parts per thousand (ppt)		

Dynamic Test for Variable CO Concentrations

To test the ability of the sampler to integrate a changing CO concentration, pure CO was metered throughout the test into the environmental chamber while being mixed with a fan. At the same time the sampler was operating, direct analyses of the chamber were obtained at the times indicated in Fig. 8. Since the concentration-vs-time relationship was not linear, the curve was integrated with a planimeter, and the area under the curve was used to calculate the time-weighted averages. The integrated time-weighted average for run 1 was 138 versus 140 ppm found in the sampler. Run 2 gave an integrated value of 438 versus 446 ppm found in the sampler. These values are in excellent agreement.

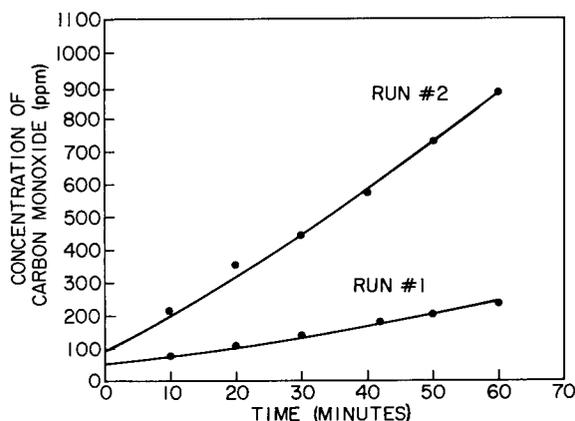


Fig. 8 — Variable carbon monoxide concentration used in a dynamic test of a $7.5\text{-}\mu\text{m}$ -orifice sampler. The data points are direct analyses of the chamber concentration. The integrated time-weighted concentrations given by the curves through the points are 138 ppm for run 1 and 438 ppm for run 2.

Sample Bias Test

Two possible types of sample bias are of concern in a collection system of this nature: low-molecular-weight-compound bias from diffusion across a small orifice, and sample adsorption from high-molecular-weight, polar, or reactive compounds.

To evaluate possible low-molecular-weight orifice bias, a $5\text{-}\mu\text{m}$ -diameter orifice was tested with a gas mixture of hydrogen and hexane at relatively high concentrations of 0.5% with no indication of bias. The hydrogen concentration found in the sampler was $0.68 \pm 0.01\%$ versus $0.66 \pm 0.01\%$ in the chamber. The sampler concentration of hexane was $0.36 \pm 0.01\%$ versus $0.35 \pm 0.01\%$ in the chamber. It was necessary to operate at this concentration due to the poor response of hydrogen in a thermal-conductivity detector.

In evaluating the performance of the sampler with less volatile contaminants, such as n-decane, it was obvious that adsorption did occur, not only within the sampler but in the environmental chamber as well. As seen in Table 4, a sample mixture containing 70 ppm of n-decane was prepared. During the period of sampling this value decreased to 64 ppm within the chamber. The initial analysis of the sampler indicated 21 ppm. The sampler was warmed with air and the resulting concentration was 55 ppm. Fabrication of a sampler lined with Teflon may relieve this problem.

Table 4 — Results of Test of 5- μ m Orifice for Bias Toward Methane, Hexane, and n-Decane Samples

Compound	Concentration (ppm)		
	Calculated	Direct Analysis From Chamber	Sampler
Methane	50	55 \pm 3	58 \pm 3
Hexane	10	11 \pm 0.6	11 \pm 0.6
n-Decane	70	64 \pm 3	21*, 55

*Sampler was then warmed and reanalyzed to obtain 55 ppm.

Test of Ability to Store the Sample

When the whole-gas sampler is used in the field, it will not be feasible to analyze the contents immediately. To test the effect of storage in the sampler, a gas mixture of hydrogen and hexane was stored for 20 days with no loss of either contaminant.

Eight-Hour Sampling Test

One objective of this investigation was to test the sampler with an orifice suitable for at least an 8-hour exposure to an environment. This test was conducted with a 3- μ m orifice, and as seen in Table 1 for a 100-cm³-volume sampler, a critical flow is maintained for 9.8 hours. The result of this test is shown in Table 5. As indicated, a comparison of the direct analysis versus that from the sampler is excellent.

Table 5 — Results of 8-Hour Test of a 3- μ m Orifice

Component	Concentration (ppm)		
	Calculated	Direct Analysis From Chamber	Sampler
Methane	10.0	8.55	8.52
Carbon monoxide	10.0	7.41	7.81
Vinyl chloride	5.0	4.33	4.47
Hexane	10.0	10.18	13.27

DISCUSSION

A personal gas sampler has been designed, fabricated, tested, and proven capable of collecting accurate time-integrated air samples over an interval up to 9 hours. As discussed, the collection of the more volatile contaminants and subsequent analyses presents no unsolved problems. For the analysis of the less volatile contaminants, such as n-decane, adsorption on the walls of the sampler and, quite possibly, the walls of the sample loops of the gas chromatograph must be considered.

This adsorption characteristic might be obviated, or at least minimized, by using a Teflon-lined sampler, or by warming the sampler prior to analysis, and by installing the sample loops in a heated compartment (in this study, the gas-chromatograph sample loops were at room temperature).

The valves are equipped with Viton O rings, and it has been found that after repeated use these O rings need to be replaced. Otherwise, the sampling rate will be much faster than the system is designed for. Thus the leak rate through the small orifice should be checked after the sampler is used in the field. Another factor that influences the sampling rate is the filter. If it becomes clogged with dirt or small particles, too little sample would be collected as the criticality of the orifice would be lost. Both of these factors can be determined prior to analysis by measuring the pressure in the sampler first if the sampling time is known.

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