# Halogenated Compounds as Gaseous Meteorological Tracers

## Stability and Ultrasensitive Analysis by Gas Chromatography

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**▶ Tracer compounds added to moving air masses are useful for demonstrating the transfer of pollutants from one local area or city to another. A study of gaseous compounds resulted in the selection of three suitable materials: sulfur hexafluoride, bromotrifluoromethane, and octafluorocyclobutane. These materials are nontoxic, are rare in the atmosphere, and can be readily dispersed from weighed tanks containing them in liquid form under pressure. Good stability was demonstrated in the presence of common atmospheric pollutants and irradiation equivalent to sunlight; losses by washout with water were negligible. An ultrasensitive gas chromatographic procedure with an electron-capture detector was developed which utilized carefully purified carrier gas and optimized columns, detectors, and operating parameters. Sensitivity of $10^{-5}$ p.p.m. was achieved for sulfur hexafluoride without concentration of the sample. Convenient procedures for sampling and calibration were established. The components in air can be determined in a single 10-minute run.**

DISPERSION of pollutants by atmospheric diffusion and transport is an important fundamental process that has received considerable theoretical study (*2, 8, 10, 17*). There is a need for improved techniques for experimental dispersion measurements. Tracer aerosols have been employed for such measurements. Among these are smoke plumes (*8*), oil fogs (*1*), spores (*7*), dyes (such as uranine) (*13*), antimony oxide (which can be determined with high sensitivity by neutron activation analysis) (*6*), and inorganic fluorescent particles such as zinc silicates, zinc sulfides, and zinc cadmium sulfide with added small amounts of activator elements (*5, 8, 11*). Operational considerations with aerosol tracers include the need for proper dispersion and sampling equipment, possibility of atypical diffusion with reference to that of gaseous pollutants or of particulate pollutants of different size distributions, losses by fallout and impaction, washout by rainfall, instability in the atmosphere (such as partial loss of fluorescent activity of small particles after exposure to sunlight), statistical sampling errors, and time and cost of collecting and analyzing the large number of samples needed (*5, 11*).

Efforts have been made to overcome some of these difficulties by use of gaseous tracers such as ammonia and sulfur dioxide (*11*), radioactive xenon-133 (*5*), difluorodichloromethane (Freon 12) (*4, 16*), and sulfur hexafluoride (*4, 15*). Many halogenated gases are promising as tracer materials. Some early analytical measurements were made with a modified halogen leak detector (*16*). Recently available gas chromatographic instrumentation makes possible much more precise and sensitive analysis (*4*). Responses to a variety of compounds, many of which appear suitable as tracer materials, have been obtained by use of electron-capture detection techniques (*3*).

For the present study three candidate materials were selected: sulfur hexafluoride, bromotrifluoromethane, and octafluorocyclobutane. Properties of these substances are given in Table I. All are inert, nontoxic, colorless, odorless, tasteless, nonflammable, and noncorrosive gases that can be stored in liquid form under moderate pressure in tanks and can be determined with high sensitivity. They have high thermal stability; $SF_6$ and $CBrF_3$ are stable at temperatures as high as 600° C., but $c\text{-}C_4F_8$ decomposes. These combinations of properties closely approach that of the ideal tracer material (*11*). Sulfur hexafluoride, which can be determined with the highest sensitivity, is so nontoxic that a mixture of 80% of this gas with 20% of oxygen produced no harmful effects when breathed by rats for 24 hours (*12*). The toxicities of the other materials also are extremely low. These materials can be dispersed from a weighed tank simply by opening a valve. In the rare cases in which atmospheric blanks might be a problem, mixtures can be employed. Composition of such a mixture may be held constant by drawing the mixture from the bottom of the liquid layer in the cylinder.

Simple sampling techniques and an ultrasensitive gas chromatographic method were developed and tested. Collateral laboratory studies indicated that these substances should exhibit no losses in the atmosphere because they were shown to be chemically inert to some of the most reactive atmospheric pollutants. These materials also resist decomposition by solar irradiation and removal by washout or rainout. These techniques should be very useful both for tracing local emissions of pollutants and for long-range meteorological studies of movements of air masses.

### ANALYTICAL METHOD

**Gas Chromatographic Apparatus.** To achieve the extraordinary sensitivity possible with an electron capture detector, a study was made to optimize a variety of parameters. Various detectors were evaluated. The electrode spacings, operating voltages, temperatures, composition and flow rate of carrier (with and without scavenger gases), and performance with different strength tritium foils were examined. It was found that careful removal from the system of water, oxygen, and other electron-capturing impurities was required. Baymal, a fibrillar colloidal alumina has been recommended (*9*) for halogenated compounds as providing high separation factors, short retention times, and sharp peaks. It was found to be suitable as a column packing for the rapid analysis of all three tracer substances in air.

Two systems were finally set up, one to provide as much sensitivity as possible and another to study the stability of the materials at higher concentrations under simulated atmospheric conditions. Both systems utilized Micro-Tek 7-port sampling valves with Teflon inserts. These valves exhibited no detectable contamination effects from prior samples. The volume of the sample loop was $^1/_4$ ml.; larger atmospheric samples were avoided because of the consequent increased size of the resulting oxygen peak, which slightly overlapped the sulfur hexafluoride peak. Samples were contained in plastic bags, which, at the time of analysis, were attached to a ₮ 12/5 joint on the sampling-valve inlet. The sample was drawn through the loop at a rate of about 100

**Table I. Properties of Selected Tracer Gases**

| Name | Sulfur hexafluoride | Bromotrifluoromethane | Octafluorocyclobutane |
|---|---|---|---|
| Synonyms |  | Freon 13B1 | Freon-C318, Perfluorocyclobutane |
| Formula | $SF_6$ | $CBrF_3$ | $CF_2CF_2CF_2CF_2$ |
| Molecular weight | 146.07 | 148.93 | 200.04 |
| Vapor pressure at 70° F., p.s.i.g. | 310 | 190 | 25 |
| Boiling point at 1 atm., ° F. | −82.8[a] (−63.8° C.) | −72.0 (−57.8° C.) | 21.1 (−6.04° C.) |
| Freezing point at 1 atm., ° F. | −59.4 (−50.8° C.) | −270.4 (−168° C.) | −42.5 (−41.4° C.) |
| Heat of vaporization at normal b.p., cal./g. | 38.61[b] | 28.38 | 27.67 |
| Critical temperature, ° F. | 114 (45.5° C.) | 152.6 (67.0° C.) | 239.5 (115.3° C.) |
| Critical pressure, p.s.i.a. | 545.5 (37.1 atm.) | 574.8 (39.1 atm.) | 393 (26.7 atm.) |
| Uses | gaseous insulating medium | chemical intermediate, fire-extinguishing agent | gaseous dielectric, foam-producing agent, propellant |

[a] Sublimes.
[b] Heat of sublimation.

ml./min. by adjustment of a needle valve downstream from the loop connected to a vacuum source. After a few moments the vacuum was disconnected and the samples injected into the column. In both systems Keithley Model 417 picoammeters were used. The outputs were recorded on 1-mv. recorders (Honeywell Series 153). The power supplies used were MicroTek GC 0000272 polarizing sources 0 to 50 volts d.c., calibrated in 0.05-volt increments.

SYSTEM A. System A was developed for calibration and interference studies at the highest possible sensitivity. The carrier gas consisted of 5% hydrogen in argon, flowing at 75 ml./min. The gas was purified by passage through a series of five 200-ml. cylinders. The first contained silica gel; the next two contained BTS Catalyst (a special catalyst for oxygen removal, containing 30% copper in finely dispersed form stabilized on a carrier, available from Badische Anilin- & Soda-Fabrik AG, Ludwigshafen am Rhein, Germany); and the last two cylinders each contained 5A Molecular Sieve. For removal of accumulated water, which lowered the sensitivity of the system, the silica gel and molecular sieve were reactivated every 2 months by heating in an oven for 36 hours at 325° C. The BTS Catalyst was reduced with hydrogen, according to the manufacturer's recommendations, at intervals of several months.

The column consisted of 14 feet of $^1/_8$-inch o.d. stainless steel tubing packed with 40- to 60-mesh Baymal. This column exhibited a pressure drop of 46 p.s.i. under operating conditions. It was maintained at 50° C. in a MicroTek Model 2500 gas chromatograph oven. This column was stable and had a long life. After several days of operating the system, the standing current decreased slightly, probably because of the accumulation of water in the column. The standing current was restored by raising the oven temperature to 150° C. and purging the column overnight with carrier gas.

The electron-capture detector was a Barber-Colman Model 5120 with adjustable anode spacing. This device was modified by capping the scavenger gas connection to the cathode and bypassing the linearizing resistor. To provide a convenient connection for flow measurement, a piece of $^1/_{16}$-inch tubing was brazed to the gas outlet on the anode. A locking nut was used to maintain the electrode spacing, which was set at 1.5 cm. The original 300-millicurie tritiated foil was replaced with a 550 millicurie foil, 0.8 × 1.1 cm., selected for high activity and uniformity. This yielded a maximum standing current of 18 namp. A standing current of 11 namp. was obtained at the selected operating voltage of 17.5 volts.

SYSTEM B. System B was developed for studies of the reactivities of the various tracers with atmospheric pollutants; this system was operated at somewhat higher tracer gas concentrations than System A. The carrier was prepurified nitrogen at a flow rate of 75 ml./min. This gas was purified by passage through a 150-ml. cylinder containing 5A Molecular Sieve adsorbent. The column consisted of two sections of $^1/_8$-inch o.d. stainless steel tubing. The first section, 3.9 feet long, was packed with 40- to 60-mesh 3A Molecular Sieve to remove the relatively large quantities of interfering water vapor from some samples. The second section, 10 feet long, was packed with 50- to 60-mesh Baymal. This column was maintained at 58° C. in a Barber-Colman column bath, Model 5060. For removal of accumulated water, which lowers the sensitivity of the system, the molecular sieve column was reconditioned every 2 to 3 months by raising the oven temperature to 300° C. and purging the column with carrier gas for a few hours. The Baymal section of the column was removed prior to this step so that it would not be exposed to the liberated water vapor.

The electron-capture detector for System B was also a Barber-Colman Model 5120 with the electrode spacing set at 1 cm. Scavenger gas (5% hydrogen in argon) was utilized at a flow rate of 50 ml./min. With 14 volts applied across the detector circuit (which included the linearizing resistor), the operating standing current was 5.3 namp.

**Calibration Procedures.** Primary standards for calibration were prepared from the pure gases which were purchased in liquid form in small cylinders under pressure. Dilution techniques were used, often in two steps, utilizing small glass syringes and making to volume in 100-liter plastic bags. In some of the initial work (*3*) the first dilution was made by injecting the material through a septum on the side of a 500-ml. glass gas-collecting tube fitted with stopcocks at each end. Later, plastic bags were found less subject to contamination from prior use. Since these tracers are relatively inert, good results were obtained with bags made of Mylar, Saran, and fluorinated ethylene propylene copolymer (FEP). Dilution air was metered accurately by a precision dry test meter.

More convenient secondary mixtures were prepared in 1A steel cylinders. The cylinder was first evacuated with a vacuum pump and the cylinder valve closed. A hose fitting with a rubber septum in the opening was attached to the outlet. The cylinder valve was then opened and the tracer gases were injected by means of syringes of various sizes (20 µl. to 1 ml.). The septum was partially pulled out of the hose fitting to flush the gas charge into the cylinder with air. The cylinder was then closed, and a high-pressure gas-transfer apparatus with an armored line was used to connect it to a second cylinder containing high-pressure pure air. For some mixtures nitrogen was used as a diluent. The cylinder was then charged to a pressure of about 1000 p.s.i.g. over a $2^1/_2$-hour period. These mixtures showed no detectable changes in concentrations in a 4-month period. They were useful for routine daily calibration checks of the instruments; however, they could not be used as primary standards because the absolute concentrations were not known precisely. At these trace concentrations adsorption-desorption effects were very serious. When these mixtures were connected to the sampling valve, the vacuum connection to the sampling loop was disconnected.

Figure 1 shows the recorder responses for one standard mixture analyzed by the two systems. The standing currents were 10.9 namp. for System A and 5.23 namp. for System B. For this mixture, the $SF_6$ and $C_4F_8$ peaks exceeded the calibration range in System A, which ordinarily was operated with lower concentrations at a more sensitive current scale.

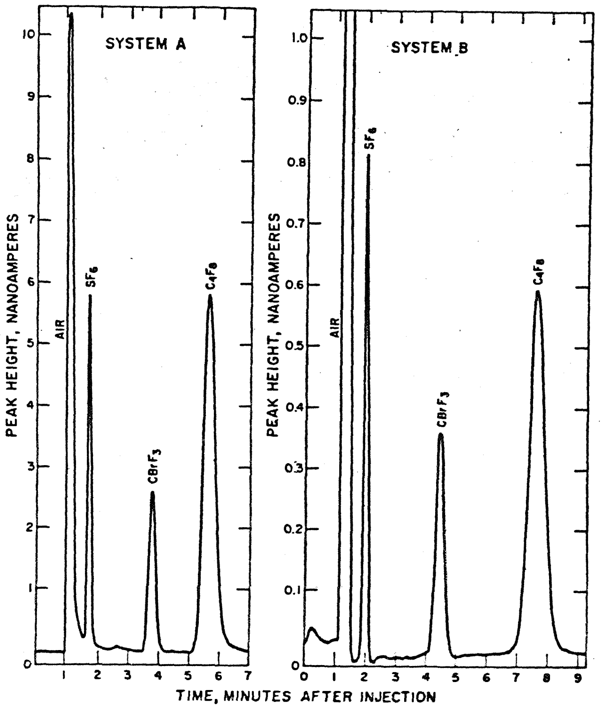

Figure 1. Responses of System A (left) and System B (right) to a 1/4-ml. sample of ternary tracer mixture in air

Approximate mixture concentrations (p.p.b.) were: SF$_6$, 6.9; CBrF$_3$, 62; C$_4$F$_8$, 183. Note the differing electrometer scale settings (vertical scales)

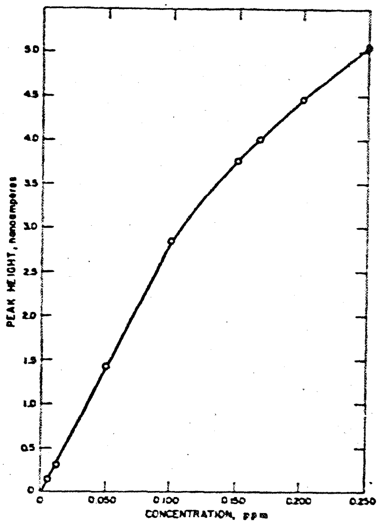

Figure 2. Calibration curve for System A

Conditions were adjusted so that the identical calibration applied for both CBrF$_3$ and C$_4$F$_8$. The same calibration applied for SF$_6$ with the concentration scale reduced by a factor of 30

The retention times for air and these tracer substances and the sensitivity of the detector responses are given in Table II. Retention times are similar for the two systems. Note, however, that sensitivity is appreciably higher with System A. This advantage is partially offset by the fact that the sulfur hexafluoride peak in System A is not completely resolved from the oxygen peak, which might cause some uncertainty about the baseline.

A small peak occurred probably as a result of the flow pulse caused by operating the sampling valve. In System A this peak occurred at about 2$^1/_2$ minutes, whereas in System B it occurred within $^1/_4$ minute. In neither case did this artifact interfere with the measurement of the tracer substances. Any difficulties with this spurious peak could be readily eliminated by slight changes in flow rate of the carrier gas.

A calibration curve for System A is shown in Figure 2. Response approximates linearity up to about 30% of the standing current, after which it falls off at an accelerating rate, as theoretically expected. It was extremely difficult to check the validity of the calibrations at low concentrations because of the possibilities of contamination in the preparation of extremely dilute mixtures. Best results were obtained by use of a flow system designed to dilute a mixture with clean air turbulently in a 3.8-liter polyethylene bottle. The outlet from the top of the bottle was connected to the ball joint of the gas sampling valve. A flow of 0.36 l.p.m. was drawn through the sampling loop by a vacuum source. The polyethylene bottle was initially charged with tank gas mixture. When a few analyses indicated that constant composition had been attained, a wet test meter open to the outdoor air was connected to the inlet to the bottom of the bottle. The mixture thus was flushed out with air (free from tracer materials). If complete mixing in the bottle is assumed, the concentration would be expected to follow the following relationship:

$$\frac{C}{C_o} = e^{-x}$$

Where: $C$ is the concentration at a given time,
$C_o$ is the initial concentration, and
$x$ is the number of air changes (total air volume passed through divided by volume of the bottle)

This equation indicates that a plot of the natural logarithm of the concentrations *vs.* the number of air changes should yield a straight line of slope −1. A semilogarithmic plot of detector responses is given in Figure 3, which shows linear relationships over a range of three decades of peak height. The slopes of these lines agreed closely with that given by the theoretical relationship. The detector response deviated from linearity at currents exceeding 2 namp. The linearity of the plots for all three components at lower currents was evidence of the validity of the calibrations at the lower limit of measurable concentrations.

## STABILITY OF TRACERS IN THE ATMOSPHERE

To investigate the stability of the materials as tracers in the atmosphere, laboratory studies were conducted by introducing mixtures of the materials in air from a cylinder into plastic bags with added amounts of some of the more common reactive pollutants found in the atmosphere. The pollutant concentrations were at least twice those of a high normal atmospheric value. Since moisture is a possible factor in these reactions, a small amount of liquid water was injected into each bag before introduction of the gas mixture. The quantity

Table II. Calibrations of Gas Chromatographic Systems

| | System A | | System B | |
|---|---|---|---|---|
| Substance | Retention time, min. | Detector response, amp./ml.[a] | Retention time, min. | Detector response, amp./ml.[a] |
| Air | 1.0 | | 1.2 | |
| SF$_6$ | 1.7 | 3.40 | 1.9 | 0.46 |
| CBrF$_3$ | 3.75 | 0.11 | 4.3 | 0.023 |
| C$_4$F$_8$ | 5.6 | 0.11 | 7.6 | 0.013 |

[a] Equivalent to nanoamperes/(ml. × p.p.b.). Based on measurements of peak heights.

was sufficient to saturate the mixture and leave an excess of a few drops in the bag. In appropriate cases these mixtures were subjected to ultraviolet irradiation from fluorescent black-lights (General Electric F42T6BL) at an intensity somewhat greater than that of sunlight for 16 hours each day; this was done to determine whether irradiation would cause consumption of tracer gas. Most of the studies were conducted with mixtures in 100-liter FEP bags, since FEP has good transparency in the ultraviolet region. For work with ozone, however, Mylar bags of the same size were used.

Results of all of these studies are given in Table III. As controls in these experiments, other mixtures were stored in bags at the same time without the addition of pollutants. Sulfur hexafluoride and bromotrifluoromethane were lost at the rate of about 1% per day, whereas octafluorocyclobutane was lost at the rate of 0.4% per day. Since these losses probably were caused by diffusion through the 0.002-inch thick plastic film, it is reasonable that the losses would be least for the substance with the largest molecule ($C_4F_8$).

The bag mixtures were analyzed initially and after aging for various periods up to 2 weeks. The differences between the control values and the initial values could be a measure of either instantaneous reaction or negative interference from the pollutants in the analysis. These differences were negligible. The differences between the rate of loss in the controls and in the bags containing pollutant air were a measure of the chemical decomposition of the tracer materials due to reaction with the pollutants. The data in Table III indicate no significant reaction with automobile exhaust, hydrogen sulfide, ozone, nitrogen dioxide, sulfur dioxide, or water vapor, either with or without ultraviolet radiation.

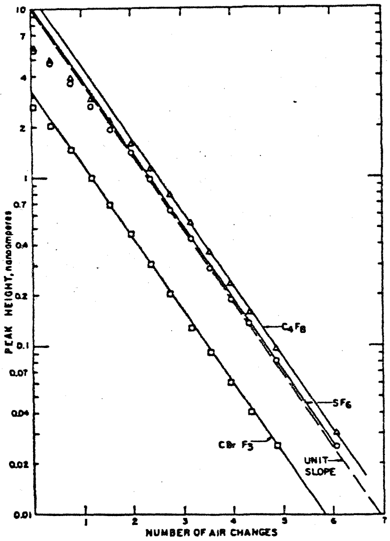

Figure 3. Check of calibrations of System A at low concentrations approaching the detection limits

A turbulent dilution of the initial ternary mixture contained in a 3.8-liter bottle was arranged by admitting pure air at a flow rate of about 0.36 liter per minute

Solubility data indicate that these tracers would not be readily washed out by rainfall. For experimental confirmation, a quantity of liquid water was added to the bag mixtures; the bags were shaken vigorously for a few minutes and the contents analyzed. Studies of possible losses by rainout were conducted by putting a bag containing tracer mixture saturated with water vapor into a refrigerator at 3° C. This was done to cause condensation of the water vapor; condensate was visually observed. A sample was then drawn from the cold bag into a small Saran bag and an analysis run. The experiments confirmed that losses caused by both static and dynamic contact with water were negligible. The small drop in concentration observed when liquid water was introduced into a bag containing a dry mixture could be wholly explained by its dilution with water vapor. These results indicate that the materials should be suitable for practical use as tracers in the atmosphere.

### ATMOSPHERIC SAMPLING PROCEDURE

**Sampling Apparatus.** Because of inertness of the tracer gases, a wide variety of sampling equipment should be suitable. Earlier field sampling studies (*4*) indicated that dry polyethylene bottles could be used merely by squeezing them several times to flush them with ambient air. Another technique reported in the same study was the use of a 1000-cu.-in. evacuated stainless steel tank with a constant-differential-type needle-valve flow control. Losses on the surfaces of the steel tank resulted in contamination difficulties at low concentrations.

Table III. Stability of Ternary Mixtures of Tracer Gases in Air in Presence of Common Atmospheric Pollutants

| | | | | | Sulfur hexafluoride | | | Bromotrifluoromethane | | | Octafluorocyclobutane | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Analysis, p.p.b. | | | Analysis, p.p.b. | | Loss, | Analysis, p.p.b. | | Loss, |
| Bag no. | Pollutants added | Bag material | Initial pollutant concentration | Contact time, days | Initial | Final | Loss, %/day | Initial | Final | %/day | Initial | Final | %/day |
| 1 | None | FEP Teflon | | 8 | 8.0 | 7.5 | 0.9 | 100 | 91.8 | 1.1 | 250 | 248 | 0.1 |
| 2 | None | FEP Teflon | | 8 | 5.0 | 4.8 | 0.6 | 100 | 92.5 | 1.0 | 500 | 483 | 0.4 |
| 3 | Water, no agitation[a] | Saran | Excess liquid water | 3 | 7.4 | 7.3 | 0.5 | 66.9 | 67.0 | −0.03[d] | 194 | 184 | 1.7 |
| 4 | Water, agitation[a] | Saran | Excess liquid water | 3 | 7.4 | 7.3 | 0.5 | 67.8 | 68.4 | −0.03[d] | 192 | 196 | −0.7[d] |
| 5 | Water, agitation[a] | Saran | Excess liquid water | 3 | 7.0 | 7.0 | nil | 62.4 | 64.3 | −0.1[d] | 186 | 186 | nil |
| 6 | None | Mylar | | 5 | 3.8 | 3.9 | −0.5[d] | 35.3 | 32.0 | 2.0 | 96.3 | 95.7 | 0.1 |
| 7 | Ozone | Mylar | 5.9 p.p.m.[b] | 5 | 3.9 | 3.9 | nil | 35.6 | 31.9 | 2.2 | 99.1 | 97.6 | 0.3 |
| 8 | None | FEP Teflon | | 5 | 7.3 | 7.5 | −0.5[d] | 66.4 | 63.9 | 0.8 | 181 | 196 | −1.6[d] |
| 9 | $SO_2$ | FEP Teflon | 5 p.p.m. | 5 | 7.4 | 7.6 | −0.5[d] | 68.7 | 65.0 | 1.1 | 179 | 193 | −1.5[d] |
| 10 | $SO_2$, irradiated | FEP Teflon | 5 p.p.m. | 5 | 7.3 | 7.5 | −0.5[d] | 67.6 | 63.7 | 1.2 | 187 | 193 | −0.6[d] |
| 11 | None | FEP Teflon | | 2 | 6.7 | 6.8 | −0.7[d] | 60.3 | 61.8 | −1.2[d] | 172 | 182 | −2.8[d] |
| 12 | Automobile exhaust (diluted with $N_2$) | FEP Teflon | 2.8%[c] | 2 | 7.0 | 6.8 | 1.4 | 64.9 | 64.5 | 0.3 | 183 | 180 | 0.8 |
| 13 | Automobile exhaust (diluted with $N_2$), irradiated | FEP Teflon | 2.8%[c] | 2 | 7.0 | 7.0 | nil | 64.2 | 63.5 | 0.5 | 174 | 186 | −3.3[d] |
| 14 | Automobile exhaust | FEP Teflon | 9.1%[c] | 2 | 7.0 | 6.9 | 0.7 | 64.2 | 61.7 | 2.0 | 183 | 174 | 2.5 |
| 15 | $H_2S$ | FEP Teflon | 5 p.p.m. | 3 | 8.0 | 8.1 | −0.3[d] | 110 | 107.3 | 0.8 | 116 | 115 | 0.3 |

[a] With cyclic cooling to 3° C. and warming to 26° C. on the first and second days.
[b] Final concentration, 1.1 p.p.m.
[c] Average analysis of exhaust (vol. %): nitrogen oxides, 0.14; hydrocarbons (as carbon), 0.56; $CO_2$, 12.35; CO, 2.03; $O_2$, 1.8.
[d] Slight increase in concentration shown is within analytical error.

A technique recommended by Schaffer, Stolpe, and Hoyle (*15*) utilizing a simple, inexpensive, commercially available apparatus, was found to be satisfactory. The device is a vacuum-cleaner clothes brush (Pilot Star brand), available at department stores, which contains a centrifugal pump made of plastic. The cloth dust bag was removed and a one-hole rubber stopper cut to fit the pump outlet. Constant flow for a half hour was obtained when the pump was driven by two size D heavy current (alkaline type) batteries.

The pump outlet was connected to the sample bag by means of a glass tube. Inexpensive Saran bags (commercially available from Vilutis & Co., 10855 South Michigan, Chicago, Ill.), were obtained in the 1- by 2-foot size, capacity 14 liters. The air pump produced a sampling flow rate of 7 liters per minute. When sampling was desired over a longer period than 2 minutes, a suitable orifice was inserted in the pump outlet tube or a larger bag was used. No appreciable decrease in the sampling flow rate occurred until the bag was filled; however, it was not necessary to fill a bag completely. After the bag was filled, an ordinary cork was inserted into its inlet tube. All bags were checked for leaks before use by noting whether they showed any visible signs of collapsing within a day when filled with air.

Studies with synthetic tracer mixtures showed no significant losses in these bags over periods of several days. The 0.004-inch wall thickness of Saran sufficed to eliminate diffusion losses. After analysis of the contents, the bags were evacuated and flushed out with air. Tests showed no contamination from the walls, even from prior high concentrations of tracer materials. Simple flushing sufficed to clean the bags. For example, in one test a mixture at relatively high concentrations ($SF_6$-10 p.p.m., $CBrF_3$-250 p.p.m., $C_4F_8$-250 p.p.m.) was stored for 24 hours in a bag and then withdrawn. The bag was partially refilled with nitrogen. No tracer gases were detected in the final contents.

**Analytical Procedures.** A series of short range field tests were run, in which one or more of the tracer gases were released. The gases, in different amounts in each test, were disseminated at a constant rate during 15-minute intervals. Air samples were collected during one or several consecutive 15-minute periods.

To minimize the danger of contaminating the analytical system with very high concentrations, the field samples were first run at high dilution by means of a newly developed dilution device (*14*) connected to the multiport sampling valve of the gas chromatograph. The bag sample was connected at the device inlet. After the nitrogen dilution gas pressure was adjusted for the desired dilution ratio, a minute or two was allowed for flushing through the system. The diluted sample mixture was drawn through the calibrated $^1/_4$-ml. sample loop at the rate of about 100 ml./min. After sample injection, it was necessary to wait only a few minutes to observe whether a measurable peak appeared. If no peak showed, a lower dilution was tried. For work at higher sensitivity the dilution device was disconnected and the bag sample connected directly to the inlet of the sampling valve. It was possible to run an analysis about every 8 minutes for each trial dilution or direct sample.

**Sensitivity.** Adjustments in the electrometer attenuation can also be made to bring the sample peaks into a measurable range. Successful calibrations have been made by measurements of both peak height and peak area. With the former, the background variation of about 0.01 namp. limits the sensitivity for sulfur hexafluoride to about 0.01 p.p.b. and for bromotrifluoromethane and octofluorocyclopropane to about 0.3 p.p.b. In one test, release of only 6.3 lbs. of $SF_6$ yielded detectable concentrations of this gas at sites $1^1/_2$ miles downwind.

The limiting factor in sensitivity may well be the background levels of the tracer substances in the atmosphere. Ten samples of polluted air were collected at various points in Cincinnati in the vicinity of power plants, factories, traffic arteries, and other pollution sources. These samples were analyzed at the highest possible sensitivity; in no case were any peaks observed that could be interpreted as an indication of the tracer materials. Thus the blanks were negligible up to the limit of sensitivity of the analytical method. Since the procedure has been arranged so that one, two, or three components can readily be analyzed, contamination by any one of these tracers should cause no particular difficulty. If a mixture is used, contamination would be indicated when the ratio of concentrations deviates from that of the tracers dispersed in the atmosphere.

## DISCUSSION

In the work described, the analyses were conducted with unconcentrated samples of air. It has been suggested (*18*) that materials such as carbon could be used to concentrate the samples. This procedure would introduce additional problems of sample absorption efficiency and desorption efficiency. Further development may indicate that such an approach could extend the sensitivity of the determination by several orders of magnitude, in which event air masses could be traced over extended distances.

An important consideration in the analytical work is to keep the system free from electron-capturing contaminants. The cleaner the system, the fewer the problems due to minor variations in flow, temperature, and detector voltage. With System A, higher carrier flow rates did not affect the responses; also the detector was operable at room temperature. The BTS Catalyst was very effective in removing oxygen and possible traces of sulfur compounds, and resulted in an increase of 10 to 20% in standing current. Ordinarily, contamination of the detector should not cause difficulty. In the event of accidental contamination, which would be shown by a sudden drop in sensitivity, the detector can easily be disassembled and cleaned by one of the conventional methods.

After completion of the reactivity and stability studies, steps were taken to increase the sensitivity of System B to make it commensurate with that of System A. Replacing the tritiated foil in the detector with one of 550 millicurie strength doubled the standing current and resulted in the largest single increase in sensitivity (100%) of all the modifications made. Another 10% gain in sensitivity was achieved by the combined effects of the following: The linearizing resistor in the detector circuit was bypassed; the interelectrode spacing in the detector was increased to 1.5 cm. and the operating voltage raised to 29 volts; the scavenger gas was eliminated, and the carrier gas was changed to 5% hydrogen in argon. Later in the course of the work, extreme broadening of the composite air peak appeared, causing it to overlap that from the $SF_6$. This difficulty was eliminated by bypassing the sample injection port.

During the field tests some experimental measurements were made of discharge rates from size 1A cylinders at about 62° F. containing the pure gases. Approximate rates in lb./min. for various orifice sizes were as follows: $SF_6$- 3.5(0.083″); $CBrF_3$- 1.2 (0.045″), 2.0 (0.055″); c-$C_4F_8$- 0.2 (0.040″), 1.0 (0.147″), 1.7 (cylinder valve wide open, no orifice). A field test in 30° F. weather confirmed that the vapor pressure of c-$C_4F_8$ was too low at this temperature for unaided release from the cylinder. The analytical data obtained appeared reasonable, and no major difficulties were experienced with the procedures.

The technique should be valuable in tracing pollution from a single stack and in determining the movements of air masses over extended distances. Ultimately it may be applicable for demonstrating transfer of pollutants from one city to another over distances as great as 100 miles.

## LITERATURE CITED

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RECEIVED for review January 10, 1966. Accepted March 14, 1966. Division of Water, Air and Waste Chemistry, 150th Meeting, ACS, Atlantic City, N. J., September 13, 1965. Mention of commercial products does not constitute endorsement by the Public Health Service.

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# A Method for Binary Gas Analysis Utilizing Ultrasonic Velocity Detection

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**▶ A method for binary gas mixture analysis based upon a positive displacement gas mixing pump with ultrasonic velocity detection is described. The method is capable of achieving a precision of 0.05%. The accuracy is dependent upon the proper design of the mixing pump to ensure operation of the device in the linear response region of the ultrasonic detection system. Accuracies to four significant figures are attainable with most binary mixtures for the concentration range from 1 to 50%.**

GASES of known composition are used extensively in the calibration of a variety of gas analysis instruments, particularly instruments which are used for continuous monitoring and are specific for a single gas such as oxygen or carbon dioxide. The usual approach for calibration is to purchase certified or analyzed gas mixtures from suppliers and utilize the data supplied by the manufacturer for calibration. The gas manufacturers commonly use standard analytical equipment equivalent to that utilized by the purchaser. This means the manufacturer in turn must have standards for calibrating his own instruments. Normally the manufacturer prepares his own standard using techniques similar to those employed in preparing the high pressure mixtures, but at lower pressures where mixing effects and deviations from perfect gas law behavior are less pronounced. (At least one gas producer, Precision Gas Products, Westfield, N. J., utilizes gravimetric techniques to eliminate these problems and reports accuracies to 4 and 5 significant figures.)

Our own experience has shown that each specific analytical instrument or technique employed for analysis can provide reasonably precise results. When compared against a different approach, however, agreement may be to as few as one or two significant figures. We have attempted to circumvent the influence of operator competence through the development of a technique requiring little or no operator skill or experience and with only pure gases needed for single point calibration. The method as developed to this point utilizes the high precision inherent in the phase multiplier system of ultrasonic detection (*1*) with the simplicity of positive mechanical displacement and mixing of two gases. Although not required by this technique, the high reproducibility of the ultrasonic detection principle simplifies repetitive analyses performed over long time intervals.

## EXPERIMENTAL

**Basic Concept.** With a detection system which provides perfect linearity of response over the range of 0 to 100% for binary gas mixtures, calibration could consist of simply replacing the pure major component with the pure minor component, thereby determining the absolute difference in response. If the minor component were present at a concentration of precisely 10%, then the response difference between the pure major component and the mixture would be precisely 0.1 the calibration value.

Although the change in ultrasonic velocity with concentration is not linear over the entire 0 to 100% range, a system has been investigated which reproducibly dilutes binary mixtures with the major component. In this way the detector can be operated in its linear range regardless of sample concentration, thereby providing linear calibration.

Figure 1 shows a schematic flow diagram of the system. Although shown schematically as two separate syringes, the mixing pump consists of a concentric, flow-through syringe, both chambers of which are fully isolated to prevent cross-leakage. The input to each chamber is controlled by independent directional-flow valves. When actuated, these valves shut off the gas flow to each chamber. Simultaneously, a drive motor is actuated, continuously displacing the contents of the larger chamber through the detector (which is on the output of the mixer) to provide a baseline value. After a predetermined time interval to insure stabilization of the baseline, a mixing valve is actuated, thereby directing the flow of gas from the smaller chamber into the mixer. This results in a step change in response, the height of which is dependent upon the composition of gas in each chamber. The actual operating sequence, referred to Figure 1, is as follows:

Pistons in full out position, all power off, valves *A* and *B* open to piston, valve *C* open to vent. Reference gas flows through chamber *L* to detector cell, sample gas flows through chamber *S* and vents.

Motor drive and valves *A* and *B* actuated simultaneously. Both sample and reference gases vented. Pistons displace gases from chambers *S* and *L*. Gas from chamber *L* establishes baseline value while gas from chamber *S* vents.

Valve *C* actuated. Gas from chamber *S* is directed to mixing chamber. Mixed gas passes to detection cell and results in a step change in response.

Valve *C* shut off. Sample gas vents, baseline returns to previous value.

Limit switch 2 shuts off drive motor and valves *A* and *B*.

Drive motor reversed until stopped by limit switch 1. The unit is now ready for the next analysis.

Although we exclusively used an

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