Journal of Chromatography, 121 (1976) 285–294

CHROM. 8997

ANALYSIS OF TRACE POLLUTANTS IN THE AIR BY MEANS OF CRYOGENIC GAS CHROMATOGRAPHY

JOSEPH A. GIANNOVARIO*, ROBERT L. GROB and PETER W. RULON**
Chemistry Department, Villanova University, Villanova, Pa. 19085 (U.S.A.)
(First received September 22nd, 1975; revised manuscript received December 23rd, 1975)

SUMMARY

The utilization of a laboratory-constructed programmable, cryogenic gas chromatograph (KEDBOR$_1$OIR[1]) for use in air pollution studies is presented. The instrument (*J. Chromatogr.*, 89 (1974) 1) is modular in design and incorporates many commercially available components as well as a few "scratch-built" parts. A temperature control range of −100 °C to +300 °C, with five programmable rates, is possible using this particular instrument. The instrument is capable of dual-column and dual-detector operation. Data have been gathered from laboratory-prepared samples as well as from samples obtained from an air pollution study in the Philadelphia area. Small amounts (ppm or less) of the gaseous hydrocarbons and the common inorganic gases (NO_x, SO_x, CO, CO_2, H_2S, COS) are detected and quantitated. Calibration curves for each gaseous component have been constructed and the analyzed samples compared to them for quantitative data. Data and information from the use of several different columns, sampling sites and their locations are presented. Experimental data agreed favorably with the current findings and discussions of air pollution problems.

INTRODUCTION

A number of techniques have been described for separating atmospheric pollutants such as hydrocarbons, sulfur gases and oxides of carbon and nitrogen. At first, these separations were confined to a limited range of compounds, either all organic or all inorganic. Hodges and Matson[1] separated COS, H_2S, SO_2 and CS_2 on a 20% Benzocellosolve column at 30 °C. Guerrant[2] and Bellar *et al.*[3] separated a wide range of hydrocarbons on activated silica gel. Herbert and Holding[4], in 1972, reported separating mixtures of inorganic and hydrocarbon gases on Porapak R, Molecular Sieve 5A, and silica gel. There are many other techniques, including multiple columns[5–8] and/or back flushing[9,10]. An excellent reference for separations of gases on various packings is a study conducted in 1969 by Bethea and Meador[11].

* Present address: General Electric Space Center, King of Prussia, Pa., U.S.A.
** Present address: Norwich Pharmacal Co., Norwich, N.Y., U.S.A.

It was the aim of this project to develop a technique allowing the analyst to determine the maximum number of organic and inorganic gases in the most straightforward manner possible. This paper describes the use of Chromosorb 102 and 104 as column packings and a research cryogenic gas chromatograph constructed for this type of analysis.

EQUIPMENT AND APPARATUS

The instrument used in this study is a KEDBOR$_1$OIR[1] programmable cryogenic gas chromatograph, built in this laboratory and recently reported in the literature[12]. Two modifications have been made since our last publication. The original flame ionization detector (FID) has been replaced by a GOW-MAC FID and amplifier (Model No. 42-700 detector, Model No. 40-700 amplifier). An extra set of heaters have been installed in the base of the column compartment, giving a total heating power of 900 W.

Initial data were collected using a hot wire detector due to the low response of some inorganic gases with a FID. All the chromatograms were recorded on a Leeds and Northrup Speedomax H recorder.

All gases used in the study were obtained from Matheson Gas Products (E. Rutherford, N.J., U.S.A.) in lecture-size bottles. Individual gas samples were kept in Vacutainers, Type 4710, red tops (Becton-Dickinson, Rutherford, N.J., U.S.A.). Aliquots were removed from these containers by means of gas-tight syringes (Hamilton, Reno, Nev., U.S.A.).

Operating parameters for the two detectors were as follows: thermal conductivity detector (TCD): current, 250 mA; attenuation, 16×; carrier gas (helium) flow-rate, as stated; temperature, 150 °C. FID: hydrogen flow-rate, 38 ml/min; oxygen flow-rate, 154 ml/min; helium flow-rate, as stated; temperature, 150 °C.

EXPERIMENTAL

Previous work on this instrument[12] involved the use of 33% DC-550 on 60–80 mesh Chromosorb W AW DMCS for the separation of organic and inorganic gases. Two papers, one by Mieure and Dietrick[13] and another by Dravnicks *et al.*[14] brought attention to porous polymer supports.

Samples of 60–80 mesh Chromosorb 102 and 104 were obtained from Johns-Manville (Denver, Colo., U.S.A.). Each was packed into a 6 ft. × 6 mm O.D. glass column. These columns were conditioned overnight at 200 °C under a helium flow of 40 ml/min. The gases used in this investigation were CO, NO, CO_2, N_2O, H_2S, COS, SO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, and iso-C_4H_{10}. Individual gas samples were run at a variety of isothermal temperatures ranging from −60° to +130 °C. Retention data were utilized to aid in the identification of component peaks during a programmed-temperature separation.

During the study involving DC-550, the column compartment temperature was never lower than −30 °C and the temperature program never operated above 0 °C. However, in this case, initial temperatures of −50 °C and −60 °C, and final temperatures of +120 °C to +130 °C were necessary.

The coolant exhaust into the compartment caused a cold spot to form on one

column. This greatly affected the flow-rate of this column and caused serious baseline drift when temperature programming was used with TCD. The problem was overcome by baffling the exhaust port into the compartment.

Gas samples were prepared by removing aliquots from lecture bottles with a gastight syringe and injecting 10 ml into a Vacutainer. This provided easy access to each gas and variation in sample size at any time. Mixtures of gases were prepared by taking a volume of gas from an individual sample tube and then transferring each to another tube until the desired number of components was achieved. This mixture was then immediately injected onto the chromatographic column. H_2S and SO_2 were always added last to the mixture, since they tend to form a redox couple whose product is elemental sulfur[15].

RESULTS AND DISCUSSION

Chromosorb 104 using TCD

It was originally thought that Chromosorb 104 would provide the desired separation because of information provided by the manufacturer. However, the separation achieved was much poorer than expected. Several factors contributed to this poor performance; retention data changed drastically with small temperature changes, and isobutane, *n*-butane and SO_2 could not be eluted at this temperature. Fig. 1 shows the results of this program. Chromosorb 104 was found to be totally unsuited as a chromatographic packing in this application. However, a possible use for this packing will be suggested later in this paper.

Chromosorb 102 using TCD

Data obtained at above-ambient, isothermal temperatures indicated that both

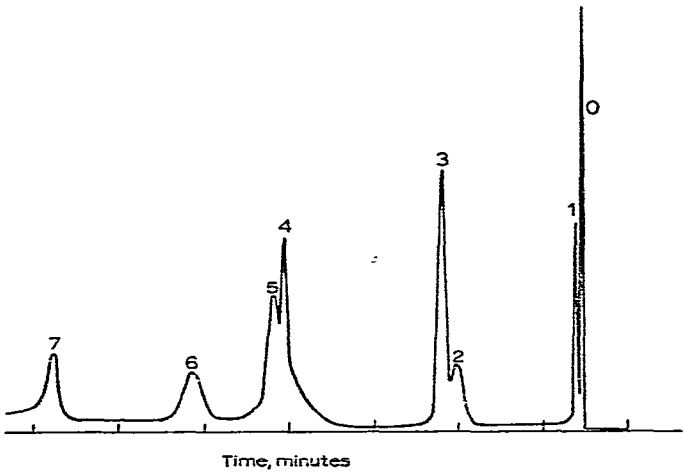

Fig. 1. Separation of gaseous hydrocarbons and inorganic gases by programmed-temperature gas chromatography on Chromosorb 104. Initial temperature, 20 °C, isothermal for 100 sec, then programmed at 10 °C/min up to 130°C; flow-rate, 40 ml/min; TCD, 250 mA; attenuation, 16 ×. 0 = Air; 1 = CH_4; 2 = C_2H_6; 3 = CO_2 + NO_2; 4 = H_2S; 5 = COS; 6 = iso-C_4H_{10} + *n*-C_4H_{10}; 7 = SO_2.

inorganic and organic gases might be separated using temperature programming. Fig. 2 shows a temperature-programmed chromatogram of a mixture of hydrocarbons and inorganic gases. All the peaks are sharp and well formed with good resolution. There are two characteristics shown here which are worth noting. H_2S causes a baseline shift, possibly due to reduction of the oxide film formed on the detector filaments, and SO_2 exhibits tailing. These characteristics were found to be useful in identifying these peaks during a programmed run.

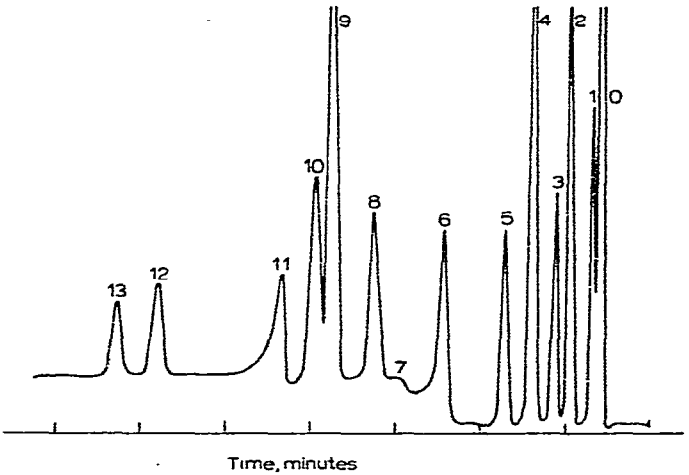

Fig. 2. Separation of gaseous hydrocarbons and inorganic gases by programmed-temperature gas chromatography on Chromosorb 102. Initial temperature, 60°C, isothermal for 100 sec, then programmed at 10°C/min up to 140°C; flow-rate, 30 ml/min; TCD, 250 mA; attenuation, 16 ×. 0 = Air; 1 = CH_4; 2 = CO_2; 3 = N_2O; 4 = C_2H_4; 5 = C_2H_6; 6 = H_2S; 7 = H_2O; 8 = COS; 9 = C_3H_6; 10 = C_3H_8; 11 = SO_2; 12 = iso-C_4H_{10}; 13 = n-C_4H_{10}.

Although these separations are excellent, the stated goal was the separation of the maximum number of component gases. Therefore, the temperature was gradually decreased (10° at a time) in an effort to include CO and NO in the gas mixture separation. Fig. 3 shows the results obtained at an initial temperature of −60 °C. The CO peak is well separated from both the air peak and the NO peak. The slow initial rate was used because it was found that the column compartment had a tendency to heat up quickly at lower temperatures.

Chromosorb 102 using FID

After achievement of the separation shown in Fig. 3, it was decided to investigate the response of the inorganic gases with the FID. The response of the detector was maximized using methane as a standard. The inorganic gases used in the mixture were then individually injected onto the column. CO and CO_2 gave little or no response whereas NO and NO_2 showed minimal response in the flame. H_2S, COS and SO_2 all gave negative response in the flame. A search of the literature revealed an article by Schaefer[16] which discussed this phenomenon. The author proposed mechanisms to account for the negative response and described the conditions under which they

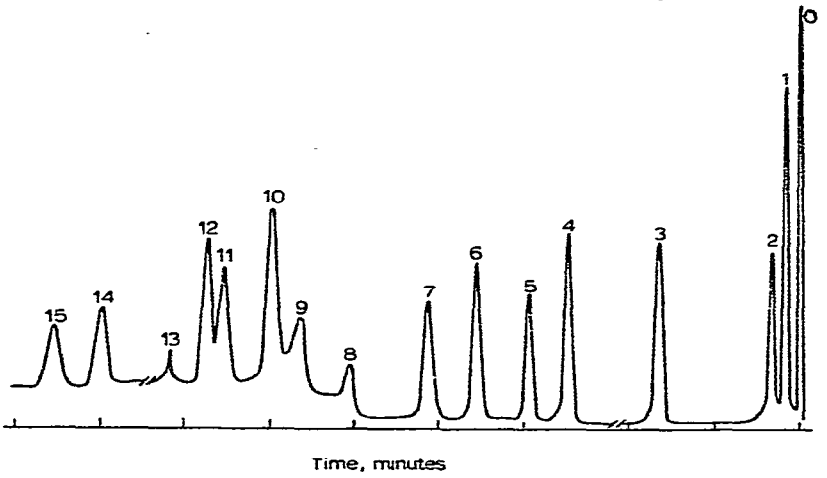

Fig. 3. Separation of gaseous hydrocarbons and inorganic gases by programmed-temperature gas chromatography on Chromosorb 102. Initial temperature, −60°C, isothermal for 200 sec, then programmed at 5°C/min for 500 sec, then program changed to 10°C/min up to 130°C; flow-rate, 40 ml/min; TCD, 250 mA; attenuation, 16 ×. 0 = Air; 1 = CO; 2 = NO; 3 = CH_4; 4 = CO_2; 5 = N_2O; 6 = C_2H_4; 7 = C_2H_6; 8 = H_2S; 9 = H_2O; 10 = COS; 11 = C_3H_6; 12 = C_3H_8; 13 = SO_2; 14 = iso-C_4H_{10}; 15 = n-C_4H_{10}.

occurred. It was found that by changing from breathing air to oxygen as the support gas, our negative peaks were inverted to positive peaks.

Fig. 4 shows a temperature-programmed chromatogram of the gas mixture using the modified FID (oxygen support gas). Note that the response for the hydro-

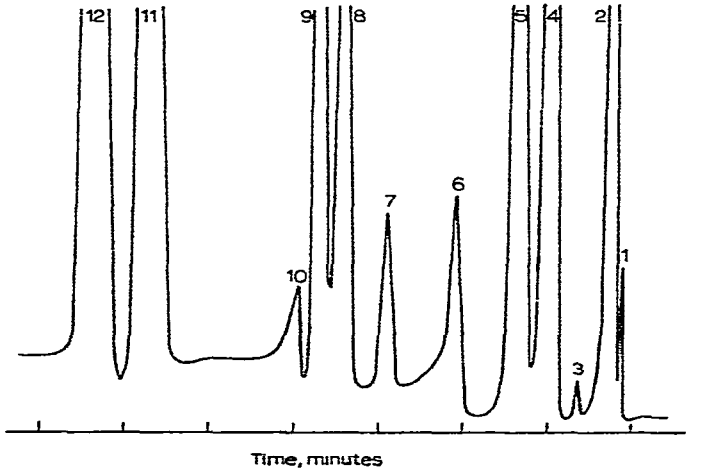

Fig. 4. Separation of gaseous hydrocarbons and inorganic gases by programmed-temperature gas chromatography on Chromosorb 102. Initial temperature, 40°C, isothermal for 100 sec, then programmed at 10°C/min up to 130°C; flow-rate, 43 ml/min; FID, 10^{-12} A; attenuation, 16 ×; oxygen flow-rate, 154 ml/min; hydrogen flow-rate, 38 ml/min. 1 = NO; 2 = CH_4; 3 = N_2O; 4 = C_2H_4; 5 = C_2H_6; 6 = H_2S; 7 = COS; 8 = C_3H_6; 9 = C_3H_8; 10 = SO_2; 11 = iso-C_4H_{10}; 12 = n-C_4H_{10}.

carbons is very much greater than that for the inorganic gases. However, the separation between components is good enough for the hydrocarbons not to mask the inorganics.

ANALYSIS OF REAL AIR SAMPLES

National air quality standards

The Clean Air Act as amended in 1967 recognized, at that time, that most of the instrumentation available for measurement of air quality was deficient in sensitivity, or ease of operation and maintenance. As such, the act provided for a research and development effort to provide air pollution monitoring instruments that would be reliable and accurate[17].

The Clean Air Act of 1970 charged the administrator of the Environmental Protection Agency (EPA) with establishing national primary and secondary air quality standards for six major pollutants. These standards were published by the EPA on April 30, 1971[18]. Table I shows these data. The standards included reference analytical methods for the six pollutants and instrument specifications, to provide a basis for the evaluation of new instruments. Of the six methods described, only the method for total hydrocarbons involves gas chromatography.

TABLE I

NATIONAL AIR QUALITY STANDARDS[18]

Pollutant	*Averaging time*	*Primary standard*,***	*Secondary standard****	*Reference method*
SO_2	Annual arithmetic mean	80 $\mu g/m^3$ (0.03 ppm)	60 $\mu g/m^3$ (0.02 ppm)	Pararosaniline
	24 h	365 $\mu g/m^3$ (0.14 ppm)	260 $\mu g/m^3$ (0.1 ppm)	
	3 h	—	1300 $\mu g/m^3$ (0.5 ppm)	
Hydrocarbons (corrected for methane)	3 h	160 $\mu g/m^3$ (0.24 ppm)	Same as primary	FID using gas chromatography
Photochemical oxidants (corrected for NO_2 and SO_2)	1 h	160 $\mu g/m^3$	Same as primary	Gas phase chemiluminescence
CO	24 h	260 $\mu g/m^3$	150 $\mu g/m^3$	Non-dispersive infrared
	8 h	10 mg/m^3 (9 ppm)	Same as primary	
	1 h	40 mg/m^3 (35 ppm)	Same as primary	

* National standards other than those based on annual arithmetic means are not to be exceeded more than once a year.

** National Primary Standards: The levels of air quality necessary, with adequate margin of safety, to protect the public health.

*** National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.

EPA method for total hydrocarbons (corrected for methane)

A gas chromatograph equipped with a FID and two multi-port injection valves has been adapted to measure total hydrocarbons and methane[18].

The total hydrocarbon sample (THC) is swept by the carrier gas directly to the FID. Upon combustion, a signal is generated proportional to the THC concentration. Another air sample is swept onto a stripper column removing water vapor, carbon dioxide and hydrocarbons other than methane. The methane component is then directed to the FID and the signal recorded. The methane value is then subtracted from the THC value and the difference is calculated as ppm carbon, determined as methane.

This method is based on two assumptions, the first being that only hydrocarbons will generate a signal in the flame. This has been shown not to be the case. The second assumption is that one ethane molecule will yield twice the response of one methane molecule, propane three times, etc. Thus, the hydrocarbon content from one locale may differ significantly from another locale, although both might report the same corrected THC.

The method developed during this project takes into account the above conditions and allows for the calculation of individual hydrocarbon concentrations, while also obtaining some information about any inorganic gases present.

Of the inorganic gases studied during this project only two are considered to be air pollutants by the EPA at this time and thus have associated reference methods. They are carbon monoxide and sulfur dioxide. Carbon monoxide is determined by an infrared technique and sulfur dioxide by a colorimetric method. It is interesting to note that nitric oxide, nitrous oxide, hydrogen sulfide and carbonyl sulfide are not considered to be air pollutants.

Sampling procedures

Five sampling sites were chosen on the Villanova University campus and a sixth was chosen on a public road adjacent to a local steel mill. Each site was sampled three times.

The air samples were collected using glass sampling bulbs. Before sampling, each bulb was washed, rinsed with acetone, oven dried at 150 °C and then evacuated on a vacuum manifold to 0.5 torr. To collect an air sample, the stopcock on the bulb was opened and a sample was drawn into the bulb.

Gas standards

Hydrocarbon standards of both alkanes and alkenes were purchased from Supelco (Bellefonte, Pa., U.S.A.). These were 100 ppm of each hydrocarbon in helium. Inorganic gases were prepared in the laboratory by the following method. A clean, dry sampling bulb of known volume was evacuated to a few torr of mercury and then filled to a positive pressure with dry helium. The bulb was then equilibrated to atmospheric pressure by venting. The volume of sample gas remained constant. This procedure was checked by preparing a lab-made standard of 100 ppm methane and comparing it to a commercial standard of 100 ppm methane. Both standards were chromatographed under identical conditions using a FID. No difference could be detected between the two types of standards.

Separation and analysis of the sample

An analytical column containing 60–80 mesh Chromosorb 102 was prepared for the analysis. Since the carbon monoxide is not detectable, directly, by the FID, it was not necessary to begin the analysis at a very low temperature. Nitric oxide would be the next component of interest, although not likely to be present in ambient air. and an initial temperature of 0 °C would provide an acceptable separation of nitric oxide and methane. A 20-ml sample was removed from a sample bulb and injected onto the analytical column.

If the sample did not reveal traces of inorganic gases, the sample volume was reduced to 5 ml and the initial temperature was raised to 40 °C and a rate of 10 °C/min was used to allow rapid analyses (*ca.* 15 min). If traces of inorganics were detected, the initial temperature of 0 °C and the rate of 5 °C/min was used for subsequent analyses to insure complete separation of all components. Each sample was run at least twice and agreement between replicates was within the standard deviation of the calibration.

Determination of components

Two methods were used to calculate the hydrocarbon concentration.

1. Modified EPA method. After separation and identification of the components in the air sample, all of the hydrocarbon peak areas are summed (except methane) and the number of micrograms of carbon, as methane, is read from the methane calibration curve. This value is converted to mg/m^3 by dividing by the injection volume. A conversion factor of RT/molecular weight is used to obtain the concentration in ppm. In this case, R is the gas constant, T is taken as room temperature, 300 °K, and the molecular weight of methane is 16; therefore, the conversion factor is 1.53. The value thus obtained is reported as Total Hydrocarbons (THC) corrected for methane. The procedure is repeated for methane and the methane concentration is reported separately.

2. Calibration curve method. A calibration curve was prepared for each hydrocarbon of interest. After identification, the number of mg/m^3 is obtained for each component using the calibration curve of that component. The conversion to ppm carbon is accomplished using the factor RT/molecular weight of component. In this manner, the concentration values calculated are corrected for nonlinear response with respect to carbon number.

The inorganics present, if any, are determined in a manner similar to Method No. 2 for hydrocarbons, employing individual calibration curves.

RESULTS

Table II compares the data from these two methods. Note that the data from Method No. 1 are consistently higher than those from Method No. 2. This discrepancy is due to the assumption that one ethane molecule has twice the response of one methane molecule, etc. Additionally, even if this error were not present, another error is introduced into Method No. 1 by use of the factor 1.53 for conversion of mg/m^3 to ppm. As the molecular weight of the hydrocarbons increase this factor becomes <1.

A second area was chosen for additional sampling. This was an area in a suburban community near several industrial complexes. Appreciable amounts of

TABLE II

COMPARISON OF DATA: METHOD NO. 1 TO METHOD No. 2

	Total hydrocarbons (ppm) corrected for methane	
	Method No. 1 (EPA)	*Method No. 2 (calibration)*
Site 1		
July 15	5.63	1.72
July 18	5.99	1.38
July 22	8.99	2.70
Site 2		
July 15	8.92	2.70
July 18	4.12	1.47
July 22	1.44	1.96
Site 3		
July 15	5.36	2.10
July 18	4.71	1.67
July 22	3.04	1.19
Site 6		
July 24	2.26	1.15
October 3	6.81	1.70
October 4	6.93	2.12

hydrocarbons and very large quantities of inorganic gases (SO_2 and H_2S) were found. In addition, 0.21 ppm of ethanal and traces of methanal and propanal were also identified.

Table III summarizes the data from our second sampling area giving the high and low values obtained for each component. As one will note some of the samples exceeded the EPA Standards.

TABLE III

TRACE AIR POLLUTANT LEVELS (ppm)

Pollutant	*Maximum*	*Minimum*	*Pollutant*	*Maximum*	*Minimum*
Methane	15.9	0.154	Pentene	0.030	0.018
Ethane	1.20	0.015	Hexene	0.035	0.013
Propane	27.1	0.016	Ethyne		Trace
Butane	1.15	0.026	Methanal	3.45	0.884
Pentane	1.58	0.018	Ethanal	0.235	0.025
Hexane	0.939	0.033	Propanal	0.048	0.025
Ethene	0.102	0.005	H_2S	22.9	0.126
Propene	0.260	0.007	SO_2	215	6.21
Butene	0.139	0.008	Total hydrocarbons corrected for methane	27.3	0.078

CONCLUSIONS

It has been demonstrated that Chromosorb 102, when used with temperature-programmed cryogenic gas chromatography, has the necessary properties to perform the separation of a wide variety of gases which might be found as atmospheric pol-

lutants. If the hydrocarbons are of major interest, the cryogenic capability is not necessary and use with the FID will yield the best results. However, if CO and NO and other inorganic gases are important considerations, the entire programmed cryogenic separation takes only 30 min.

Chromosorb 104 was found to be unsuitable as a column packing in this application. However, our data substantiate its ability to retain both organic and inorganic gases at lower temperatures and thus its suitability as a collection column as noted previously[13,14].

A large difference is noted in the THC values when determined by the two methods described. The authors feel that Method No. 2 is more valid for evaluating air quality and hydrocarbon emissions. An advantage of this method is that it allows for identification of individual hydrocarbons and this may be important in trying to locate the source of emissions.

Overall the method presented is capable of measuring small amounts of both inorganic and organic gases in real air samples. Additionally, we have an instrumental system which is capable of precisely controlling conditions, one run to another.

REFERENCES

1 C. I. Hodges and R. F. Matson, *Anal. Chem.*, 37 (1965) 1065.
2 C. O. Guerrant, *Anal. Chem.*, 37 (1965) 516.
3 T. Bellar, J. E. Sigsby, C. A. Clemons and A. P. Altschuller, *Anal. Chem.*, 34 (1962) 763.
4 R. A. Herbert and A. J. Holding, *J. Chromatogr. Sci.*, 10 (1972) 174.
5 D. H. Bollman and D. M. Mortimore, *J. Chromatogr. Sci.*, 10 (1972) 523.
6 T. Doran and J. P. Cross, *J. Gas Chromatogr.*, 4 (1966) 260.
7 J. O. Terry and J. H. Futrell, *Anal. Chem.*, 37 (1965) 1165.
8 A. G. Kim and L. J. Douglas, *J. Chromatogr. Sci.*, 11 (1973) 615.
9 J. L. Marchio, *J. Chromatogr. Sci.*, 9 (1971) 432.
10 K. A. Smith and R. J. Dowdell, *J. Chromatogr. Sci.*, 11 (1973) 655.
11 R. M. Bethea and M. C. Meador, *J. Chromatogr. Sci.*, 7 (1969) 655.
12 J. A. Giannovario, R. J. Gondek and R. L. Grob, *J. Chromatogr.*, 89 (1974) 1.
13 J. P. Mieure and M. W. Dietrick, *J. Chromatogr. Sci.*, 11 (1973) 559.
14 A. Dravnicks, B. K. Krotoszynski, J. Whitfield, A. O'Donnell and T. Burgwald, *Environ. Sci. Technol.*, 5 (1971) 1220.
15 E. S. Gould, *Inorganic Reactions and Structure*, Holt, Rinehart and Winston, New York, Rev. Ed., 1962, p. 292.
16 B. A. Schaefer, *Anal. Chem.*, 42 (1970) 448.
17 S. Coloff, M. Cooke, R. Drago and S. Sleva, *Amer. Lab.*, 5, No. 7 (1973) 10.
18 *Fed. Regist.*, 36, April 30 (1971) 8195.