CONTROLLED ENVIRONMENT PORTABLE GAS CHROMATOGRAPH FOR *IN-SITU* AIRCRAFT OR BALLOON-BORNE APPLICATIONS

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(Received August 25th, 1980)

SUMMARY

The construction of an electron-capture detector equipped gas chromatograph is described which is capable of *in-situ* ambient stratospheric halocarbon measurements. By enclosing the plumbing of the chromatograph in a sealed chamber, a system has been developed which is immune to changes in the ambient pressure and gas composition. This sealed chamber also provides a very clean system which is essential for the control of the ion chemistry in the detector associated with carrier gas doping techniques. Application of this instrument to some doping techniques is discussed briefly.

INTRODUCTION

Although various atmospheric sampling programs have been quite successful using grab-sampling techniques[1] for analysis of certain halocarbons, an instrument for the *in-situ* measurement of many substituents in the troposphere and in the stratosphere is highly desirable. Certain species of great interest in the field of atmospheric chemistry, 1,1,1-trichloroethane and carbon tetrachloride, for example, are difficult to measure accurately at ppt level concentrations with grab sampling methods because of surface adsorption at active sites on the container walls. Passivation with silane compounds appears to work well for some species[2], but is inadequate for others such as carbon tetrachloride and methyl chloroform.

Electron-capture–gas chromatography was chosen as the best method of analysis because of the high sensitivity of this relatively simple detector for many of the halogenated species of interest. Since it was necessary for the research program undertaken to measure atmospheric concentrations of these species from sea level to the middle stratosphere, an instrument whose sensitivity is independent of ambient pressure was required. At present, in all commercially available instruments, the effluent of the electron-capture detector (ECD) is vented directly to the ambient environment. Since the response of the ECD is strongly dependent on the gas density within its ionization chamber, these instruments did not meet our primary requirement as an atmospheric probe. In addition, our experiences have shown that all ECD

equipped gas chromatographs show some degree of sensitivity to the composition of the atmosphere surrounding the instrument. That is, entrainment of minor atmospheric constituents, such as halogenated species, in the carrier gas stream through the inevitable small leaks in the system plumbing result in measurable changes in sensitivity.

For these reasons we have undertaken the development of a small portable ECD equipped gas chromatograph in which the entire gas chromatographic stream: sample loop, column(s), detector and valving, is enclosed in an hermetically sealed, pressure stabilized housing that is purged with gas of controlled composition.

Other requirements for this instrument include electronic stability over a large temperature range, low power consumption from an easily available source, and low weight in a conveniently portable package. Also, the instrument must be capable of automatic operation, including remote determination of sample size. To a satisfactory extent, all of these requirements are met by the instrument described below.

CONSTRUCTION

The instrument was constructed in two compartments, one of which can be sealed, and contains most of the plumbing. The other compartment, which is not airtight, contains the electronics and all operating controls and connections. All components are screwed to a 2-cm thick aluminum plate, 36 cm², which is tapped with blind holes to preserve leak-tight integrity, and serves as a chassis. A leak-tight aluminum housing 34 × 34 × 27 cm seals to one side of this chassis through an O-ring, forming the sealed chamber. All components in the chromatographic gas stream, including the sampling valve, chromatographic column, detector, and associated plumbing, are mounted in this chamber (Fig. 1). Connections are made through the chassis with sealed fittings. Removal of the leak-tight housing allows easy access to these components.

The sampling valve is a Valco gas chromatographic multiport injection valve fitted with a pneumatic actuator, which, in turn, is actuated by small electro-pneumatic valves. This valve train allows the system to be operated remotely or automatically by a microprocessor.

The chromatographic column is contained in a temperature controlled oven, which is a "sandwich" composed of the column, wound in a spiral, and a similarly coiled long, flexible probe heater held between aluminum plates (Fig. 2). Thermocouples for reading and servoing the temperature are included between the plates, and the entire assembly is supported between panels of fiberglass insulation. The arrangement provides even heating and makes column changing relatively easy. Care must be taken to prevent packed regions of the column from extending beyond the heated zone, however. A continuously adjustable front panel control allows the selection of any temperature from ambient to 200°C with a temperature stability of ±1°C over a 48-h period.

The ECD, shown schematically in Fig. 3, is of our own design and is constructed to accommodate a standard ^{63}Ni radioactive foil of 10 mCi nominal activity[4]. The detector is a stainless-steel "spool" with the foil lining the interior wall of the detector body. A 1/16 in. stainless-steel inlet tube enters one end of the spool and is insulated from it by a ceramic adapter which is braized to both the spool and the inlet tube. This adapter serves the dual function of supporting the inlet tube and insulating
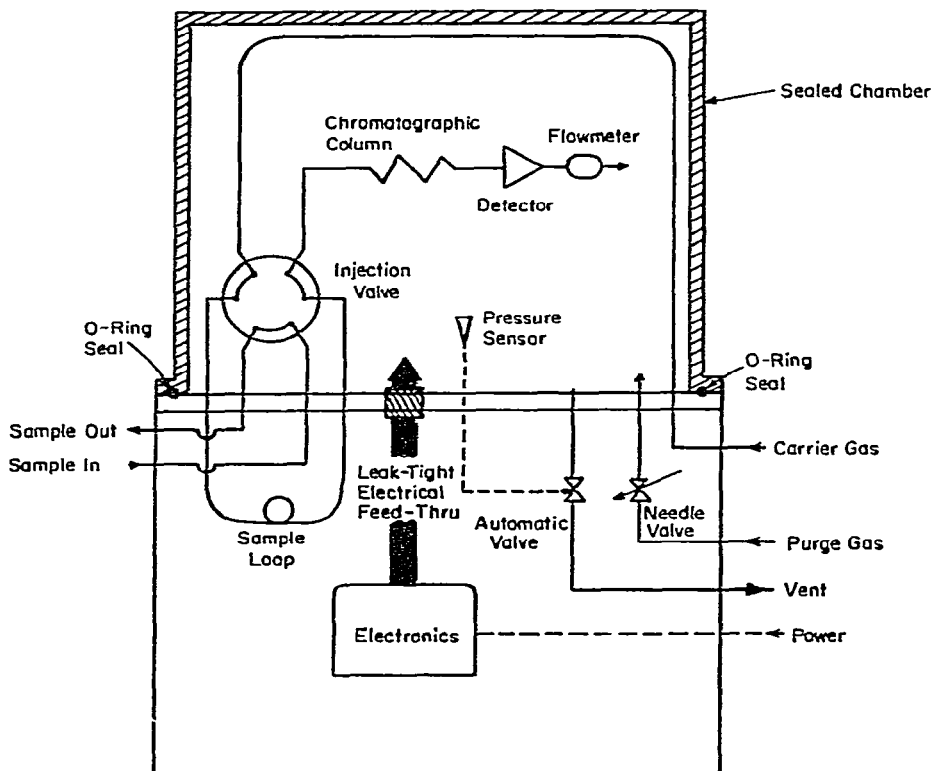
Fig. 1. Schematic diagram of gas chromatograph.

the tube electrically from the detector body. A "cap" with a similar ceramic adapter and outlet tube fits the other end of the spool. A gold O-ring between the spool and cap renders the detector leak-tight when the cap is screwed into place. The outlet tube also serves as the electron collector. Electrons are forced to this tube by 50 V negative pulses of 1.0 μsec duration at a frequency of 1.0 kHz applied to the body of the detector (fixed frequency pulse mode). Current flowing from the detector during these pulses is amplified by the electrometer. Since the leakage current between the detector body and the electron collector tube must be small compared to the conduction current through the gas ($\approx 10^{-9}$ A), high-quality ceramic capable of meeting this requirement at the elevated temperatures encountered must be used.

A fiberglass insulated nichrome heating element is wrapped around the spool, which contains wells for two thermocouples, one for controlling the temperature, and one for temperature readout. The entire unit is insulated with a blanket of fiberglass and placed in an aluminum box. Detector temperature is selected in 25°C increments from 150°C to 350°C by a front panel control with a stability of ± 1°C over 48 h.

Other components also located in the sealed chamber include a flowmeter for monitoring the carrier flow through the detector, a pressure transducer for measuring and controlling the internal pressure of the sealed compartment, and a temperature stable reference junction for all thermocouples. The flowmeter is a Tylan, 0–200 std. cm^3/min
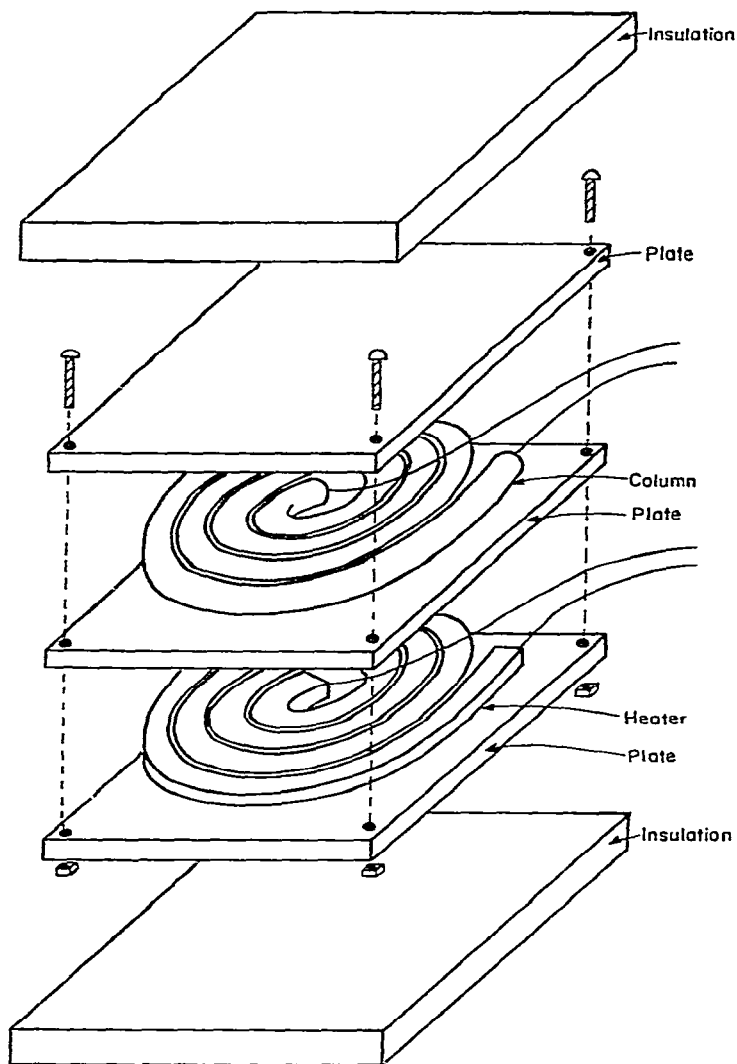
Fig. 2. Exploded view of chromatographic column and heater assembly.

mass flowmeter calibrated for nitrogen. The pressure transducer (National Semi-conductor Model LX-1603) is part of the environmental control system for the sealed chamber. The flow of purge gas into the chamber is controlled by a needle valve, and the internal pressure is controlled by a servo system incorporating the pressure transducer, which operates an electric vent valve to maintain any desired pressure. To protect the system from overpressure in the event of a power failure or electronic malfunction, a spring-operated pressure release valve was installed which will vent the chamber if the internal pressure exceeds approximately 20 p.s.i. above ambient. Typically, the system has been operated at 650 torr ($\approx$ 25 torr above ambient pressure in Boulder, CO) but successful operation has been observed from $\approx$200 torr to $\approx$ 1500
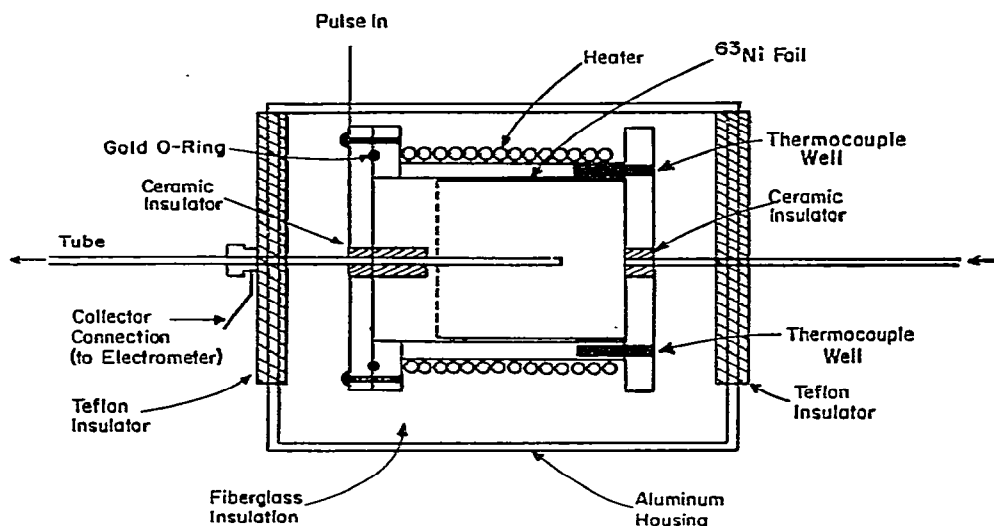
Fig. 3. Schematic diagram of electron-capture detector assembly.

torr absolute internal pressure. To ensure stable column and detector temperatures, a reference junction for the thermocouples is maintained slightly above the highest internal temperature encountered during various conditions of operation. This junction heater is driven by a thermistor controlled servo, which maintains $\pm 0.5°C$ stability. Thermistors are not used for direct control of the column and detector heaters because of the incompatibility of thermistors with the high temperatures and large temperature spans encountered with these heaters.

The electronic controls are all mounted outside the sealed compartment on the opposite side of the chassis plate. This allows circuit adjustments to be made with the chamber sealed. Circuits not previously mentioned include an electrometer and a meter on the front panel for monitoring various internal parameters. The electrometer is an integrated circuit low noise operational amplifier operated with $5 \cdot 10^8 \, \Omega$ feedback resistance providing a response of 0.5 mV output/1 ϱA input. Regulated power is supplied to the electronics at $\pm 15.0 \pm 0.1$ V d.c. with an input voltage in the range of 11–14 V d.c. When all heaters are controlling at nominal temperatures, the instrument draws ≈ 4 A at 12 V. A fully charged 110 A hour deep cycle storage battery can operate the instrument continuously for longer than 24 h, if the instrument is switched to battery power with all heaters at temperature. This power requirement could be supplied by ≈ 13 lb. of silver cell batteries for ≈ 10 h.

RESULTS

Laboratory testing of the instrument was carried out under various conditions on a number of chromatographic columns. Of the columns tested, the one best suited for analysis of several chlorinated species of interest was 10 % OV-101 (on Chromosorb W HP) (Fig. 4). On this column, the detection limit for 1,1,1-trichloroethane was established at $2.8 \cdot 10^8$ molecules, corresponding to (10.6 ppt for a 1.0 std. cm^3 sample), $1.5 \cdot 10^8$ molecules (5.4 ppt/std. cm^3) for carbon tetrachloride, and $6.4 \cdot 10^7$ molecules
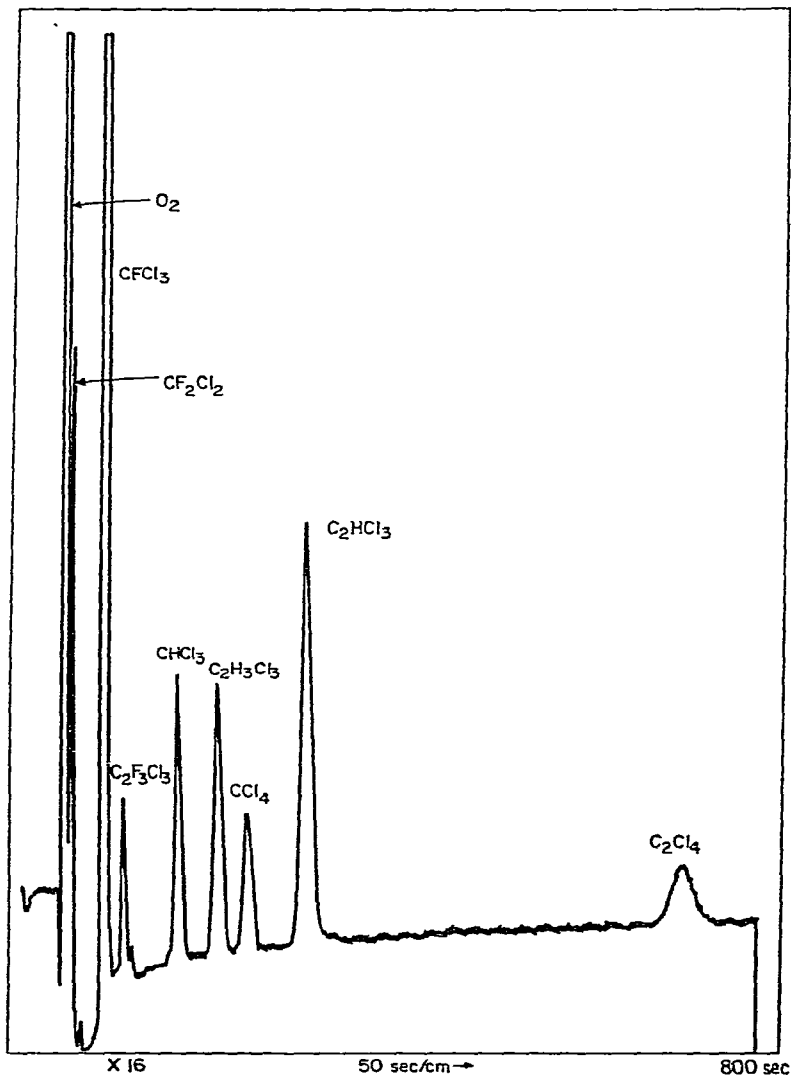
Fig. 4. Chromatogram of 1.64 std. ml sample of ambient laboratory air on a 10-ft. OV-101 column at 50°C.

for trichlorofluoromethane. These values were determined by extrapolation to a signal-to-noise ratio of 1 of the response of ≈ 500 ppt standards. These standards were provided by dynamic dilution of statically prepared ≈ 100 ppm standards in nitrogen, on a dilution system which has been previously described[3]. The output of the dynamic dilution machine was introduced directly into the gas chromatograph sample loop by a standard flush-and-fill technique. During these measurements, the environmental chamber was maintained at a pressure of 650 torr with nitrogen serving as the carrier and purge gas (same source). (A faulty heater circuit, which has been replaced, was responsible for the periodic baseline noise in Fig. 4.)

Pressure stability of the instrument was tested by subjecting the chromatograph to simulated stratospheric pressures. Since the only point in the entire plumbing system which is in contact with ambient air is the outlet of the pressure servo valve, pumping on this panel-mounted orifice simulates reduced ambient pressures. No visible effects were noted at the electrometer output as the "ambient" pressure was cycled from room pressure ($\approx$625 torr) to <1 torr. Throughout this test, the internal pressure was maintained at 650 torr with a short-term stability of $\approx$0.5 torr. Long-term stability (>20 days) was $\pm$10 torr which appeared to be the limit of the transducer stability. In another test, the carrier flow was maintained at a constant level while the internal pressure was varied from $\approx$200 torr to $\approx$1500 torr, allowing the
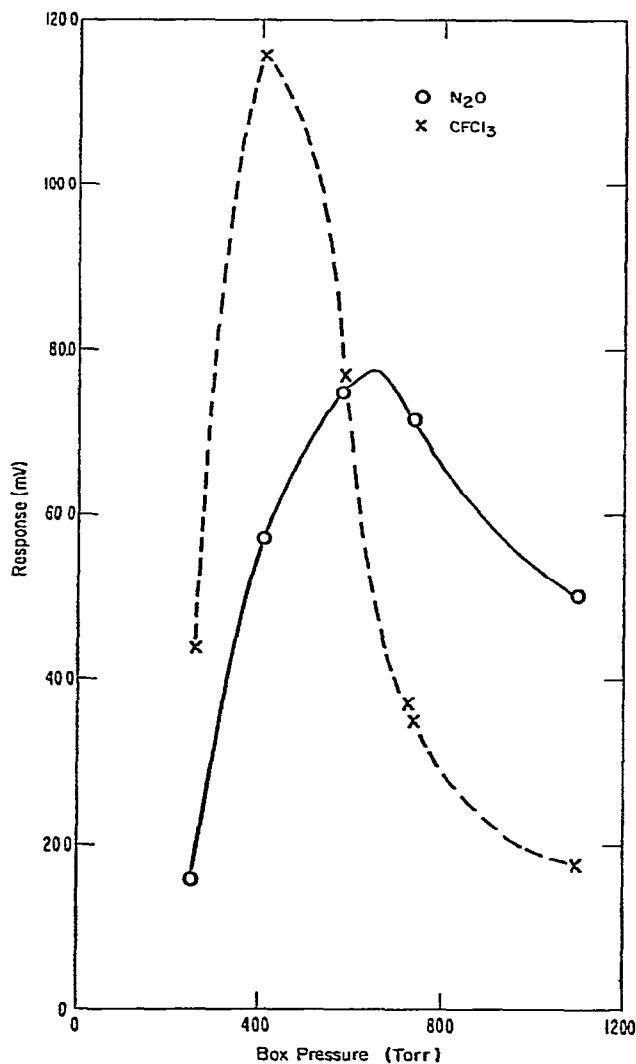

Fig. 5. ECD response to N_2O and $CFCl_3$ vs. box pressure.

system to servo at various pressures while chromatograms of identical samples were made. The standing current in the detector decreased exponentially with a decrease in pressure, while sensitivities for various materials showed maxima at different pressures (Fig. 5). Obviously, the detector is quite sensitive to changes in the operating pressure, and can be specifically optimized for certain species. The benefits of pressure optimization which are possible in an instrument such as this may be substantial, and require further investigation.

Concurrent with the development of this instrument, our laboratory was investigating carrier gas doping techniques termed selective electron capture sensitization (SECS). The negative-ion chemistry involved in SECS chromatography requires a high degree of cleanliness in the system to realize the full potential of the technique, and, indeed, to attempt to understand the chemistry. The inherent leaks in the plumbing of our commercial instruments permitted "contamination" of the carrier gas stream, particularly by oxygen[5–8], due to its relative abundance, and carbon dioxide, both of which can significantly affect the ion chemistry within the ECD.

By the time all of the system tests on the new instrument were completed, it was apparent that due to its immunity from such leaks it would be a valuable new tool for pursuing SECS methods. In this laboratory, the response of the ECD to a variety of materials which have low electron capture cross-sections has been enhanced by the addition of N_2O to the carrier gas[9–11]. Hydrogen, carbon monoxide, carbon dioxide, methane, and vinyl chloride (C_2H_3Cl) are examples of substances which display significant enhancement when analyzed with an N_2O doped carrier gas.

The instrument described is currently being tested in the field at an alpine research station near the continental divide in Colorado. Ambient levels of $CFCl_3$, $C_2F_3Cl_3$, $CHCl_3$, CCl_4, $C_2H_3Cl_3$, C_2HCl_3, and C_2Cl_4 are being measured using a pure nitrogen carrier and purge. A similar instrument with N_2O doped nitrogen carrier is being used for the detection of hydrogen, methane, and carbon monoxide. Both instruments have been operated from a standard "deep cycle" 12 V marine battery for up to 24 h without measurable changes in sensitivity or system noise demonstrating their adaptability for use in remote sites without electrical power and in mobile platforms such as motor vehicles and aircraft.

To summarize, a gas chromatograph equipped with an ECD has been constructed for portable operation. The detector and all other parts of the plumbing system are enclosed in a sealed compartment which is temperature and pressure controlled, which makes the unit ideal for field operation where the outside ambient pressure is subject to wide variations such as encountered in operation from balloons or aircraft, and in the evaluation of doped carier gas techniques. The chromatograph itself weighs about 37 lb., and the total weight of the field measuring system, including chromatograph, carrier gas supply, sufficient for one week of continuous operation calibration gas supply and battery for ≈20 h of operation is 130 lb. For shorter operating periods this weight can obviously be reduced by using smaller gas supply bottles and a smaller battery*.

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* The commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure or apparatus. In no case does such identification imply recommendation, endorsement, or that the item is the best available for the purpose.

REFERENCES

1 R. D. Hudson and E. I. Reed (Editors), *The Stratosphere: Present and Future*, NASA Ref. Pub. 1049, 1979, p. 309.
2 A. L. Schmeltekopf, P. D. Goldan, W. J. Harrop, T. L. Thompson, D. L. Albritton, M. McFarland, A. E. Sapp and W. R. Henderson, *Rev. Sci. Instrum.*, 47 (1976) 1479.
3 P. D. Goldan, Y. A. Bush, F. C. Fehsenfeld, D. L. Albritton, P. J. Crutzen, A. L. Schmeltekopf and E. E. Ferguson, *J. Geophys. Res.*, 83 (1978) 935.
4 New England Nuclear Corp., 575 Albany, Boston, MA, *Foil NER-002*, or Hamersham Corp., 2636 S. Clearbrook Dr., Arlington Heights, IL, *Foil NBC-7020*.
5 H. J. van de Wiel and P. Tommassen, *J. Chromatogr.*, 71 (1972) 1.
6 E. P. Grimsrud and D. A. Miller, *Anal. Chem.*, 50 (1978) 1141.
7 E. P. Grimsrud and R. G. Stebbins, *J. Chromatogr.*, 155 (1978) 19.
8 P. G. Simmonds, *J. Chromatogr.*, 166 (1975) 593.
9 M. P. Phillips, R. E. Sievers, P. D. Goldan, W. C. Kuster and F. C. Fehsenfeld, *Anal. Chem.*, 51 (1979) 1819.
10 R. E. Sievers, M. P. Phillips, R. M. Barkley, M. A. Wizner, M. J. Bollinger, R. S. Hutte and F. C. Fehsenfeld, *J. Chromatogr.*, 186 (1979) 3.
11 P. D. Goldan, F. C. Fehsenfeld, W. C. Kuster, M. P. Phillips and R. E. Sievers, *Anal. Chem.*, 52 (1980) 1751.