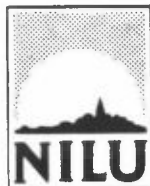


NILU TR : 8/83
REFERENCE : Q-303
DATE : OCTOBER 1983

TRACER GAS TECHNIQUES AT NILU

R. Heggen and B. Sivertsen



NORWEGIAN INSTITUTE FOR AIR RESEARCH

ROYAL NORWEGIAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

NILU TR : 8/83
REFERENCE : Q-303
DATE : OCTOBER 1983

TRACER GAS TECHNIQUES AT NILU

R. Heggen and B. Sivertsen

**NORWEGIAN INSTITUTE FOR AIR RESEARCH
P.O. BOX 130, N-2001 LILLESTRØM
NORWAY**

ISBN 82-7247-416-6

LIST OF CONTENTS

	Page
1 INTRODUCTION	5
2 SF ₆ AND CBrF ₃ AS ATMOSPHERIC TRACERS	5
3 EXPERIMENTAL PROCEDURES	6
3.1 Tracer release systems.....	6
3.2 Sampling systems	7
3.3 Tracer sample analysis	10
3.4 Calibration of the gas chromatographs	13
3.5 Uncertainties	15
4 APPLICATIONS AT NILU	16
5 REFERENCES	18
APPENDIX A: Columns for simultaneous gas chromatographic determination of SF ₆ and CBrF ₃	21

TRACER GAS TECHNIQUES AT NILU

1 INTRODUCTION

The tracer system; release equipment, samplers, calibration unit and portable gas chromatographs, was developed at NILU for extensive use in practical applications (1). The system was developed to meet the following requirements:

- easy to modify
- useful in different applications
- easy to handle (reload, prepare)
- light weight (portable) and sturdy
- preset timing for samplers
- rapid analysis in field.

These requirements have lead to less firm requirements on accuracy and low detection limits. For most practical purposes, however, the release rates can be adjusted to give concentrations within an optimum range ($\approx 10^{-6}$ p/p).

Two tracer gases have been applied in different experiments; sulphur hexafluoride (SF_6) and bromotrifluoromethane (CBrF_3). In most applications, when only one tracer is needed, SF_6 is always used. Only when there is a need for dual tracers (for identifying different sources) also CBrF_3 is applied.

2 SF_6 and CBrF_3 AS ATMOSPHERIC TRACERS

Sulphur hexafluoride and bromotrifluoromethane are both colorless, odorless, nontoxic, and inert gases, which can be detected at extremely low levels using electron capture gas chromatography. Pertinent physical data for SF_6 and CBrF_3 are given in Table 1.

Table 1: Physical constants of SF₆ and CBrF₃ *.

<u>Property</u>	<u>SF₆</u>	<u>CBrF₃</u>
Molecular weight	146.07	148.93
Vapor Pressure @ 70 ⁰ F	310 p.s.i.g.	190 p.s.i.g.
Specific Volume, 70 ⁰ F, 1 atm	2.5 ft ³ /lb	2.6 ft ³ /lb
Boiling Point @ 1 atm	-63.8 ⁰ C	-57.8 ⁰ C
Sublimation Temperature	-63.8 ⁰ C	-
Freezing Point @ 1 atm	-	-168 ⁰ C
Density Gas 70 ⁰ F, 1 atm	6.139 g/l	6.25 g/l
Density Gas @ b.p.	-	8.71 g/l
Critical Temperature	45.55 ⁰ C	67 ⁰ C
Critical Pressure	37.11 atm	39.1 atm
Critical Density	0.730 g/cm ³	0.745 g/cm ³
Solubility in Water, 25 ⁰ C 1 atm	0.004% (by weight)	0.03% (by weight)

* Matheson Gas Data Book, 1966.

Neither SF₆ nor CBrF₃ occur naturally in the atmosphere.

The principal use of SF₆ is as an electrical insulation medium in switching-gear and transformers. It is also used in industry to protect molten magnesium from oxidation. De Bortoli et al (1976) reported ambient SF₆ levels over Oslo to be approximately 4×10^{-13} p/p. This level is typical of most urban areas.

The principal use of CBrF₃ is as a fire extinguishing agent. Ambient CBrF₃ levels appear to be less than 1×10^{-11} p/p.

3 EXPERIMENTAL PROCEDURES

3.1 Tracer release systems

The tracer gases are usually released from 10 liters cylinders containing the liquefied gas. Through a reduction valve and a flow-meter the gas release is kept constant at the desired rate.

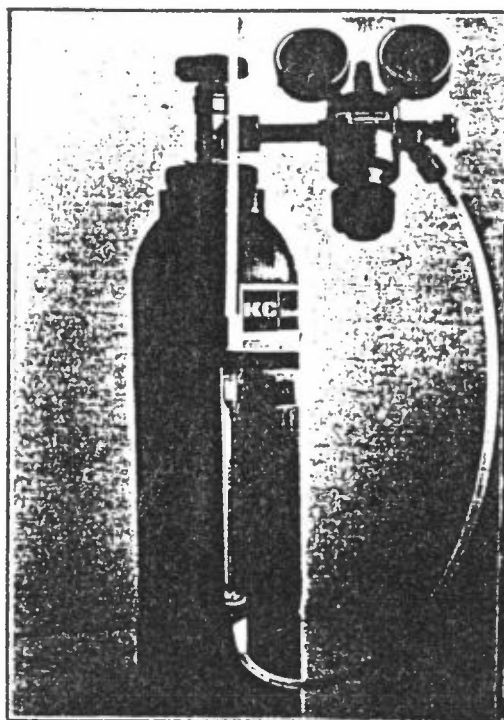


Figure 1: Tracer gas cylinder and gas flow meter.

At high release rates it is often necessary to supply heat to the cylinder to compensate for the heat loss due to evaporation. Syringe-pumps may be used for small gas releases ($0-10 \text{ cm}^3/\text{min}$).

3.2 Sampling systems

Air samples are collected in inexpensive plastic syringes on either instantaneous or time-averaged basis. Time averages are usually taken over 15 minutes with automatic battery powered samplers.

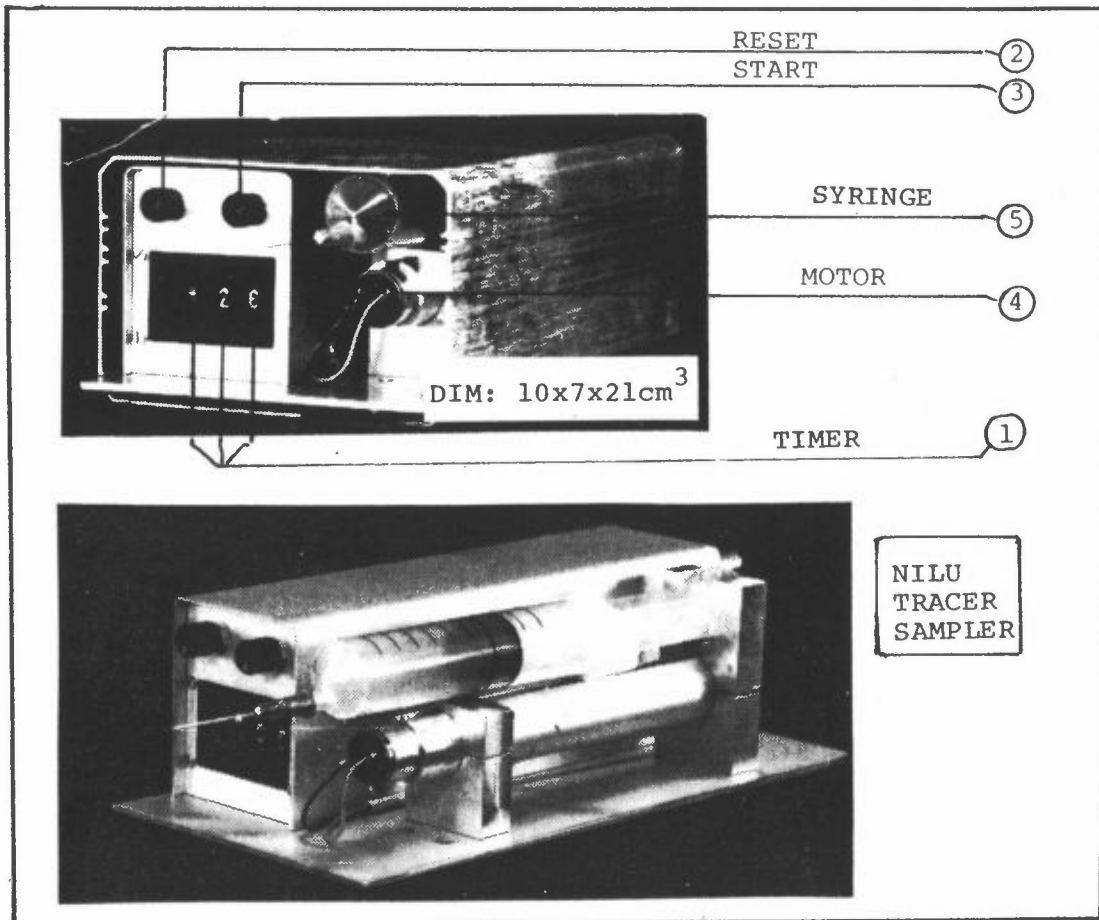


Figure 2: NILU automatic battery powered tracer sampler with electronic timer.

The desired number of automatic samplers are loaded with one syringe each. The air is pulled through a small bore hypodermic needle at the end of each syringe intake to prevent back-diffusion of the sample air. The samplers are programmed to start at a given time, before being put out at the desired location in the test area.

Another automatic sampler has been designed for collecting several instantaneous air samples. Up to 90 samples can be taken at a predetermined interval. The shortest interval is 2 seconds and the sampling time is about 0.5 sec.

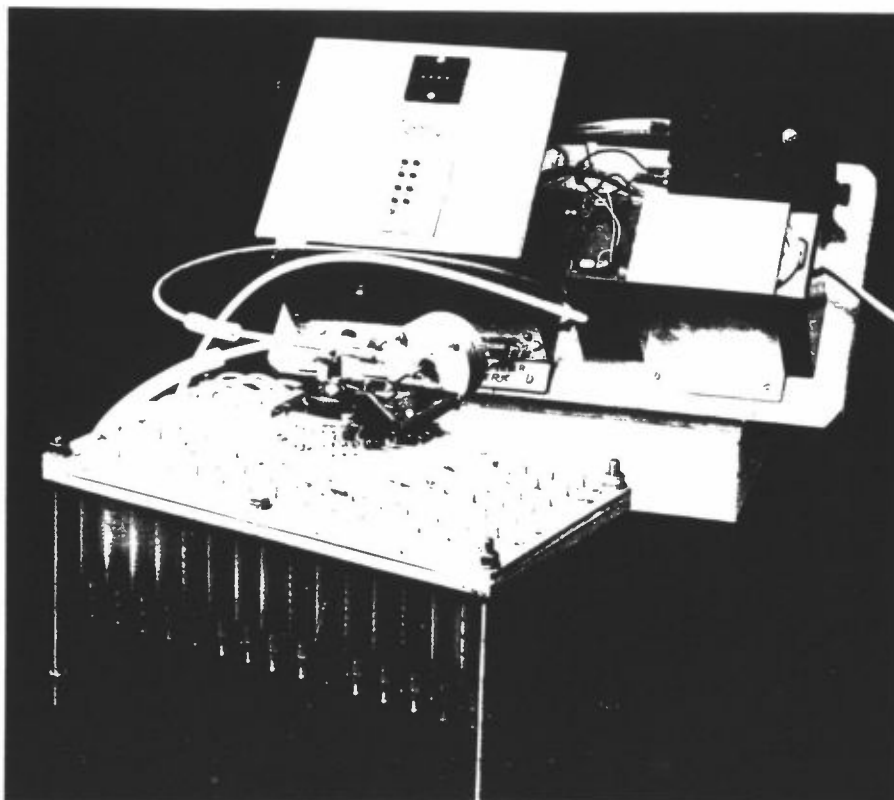


Figure 3: Automatic sequential sampler (0.5 sec averages at preset intervals).

The samples are usually analyzed immediately after each experiment using the portable electron capture gas chromatographs. If the analysis are not carried out within the first few hours, the hypodermic needles on all syringes are exchanged with caps. The simple sampling and analysis methods permit the collection of a large number of samples during a tracer experiment. In a tracer field study, these techniques allow the results of one experiment to be used in the design of succeeding experiments.

3.3 Tracer sample analysis

Air samples are analyzed using electron capture gas chromatography. The analysis and calibration system is shown in Figure 4.

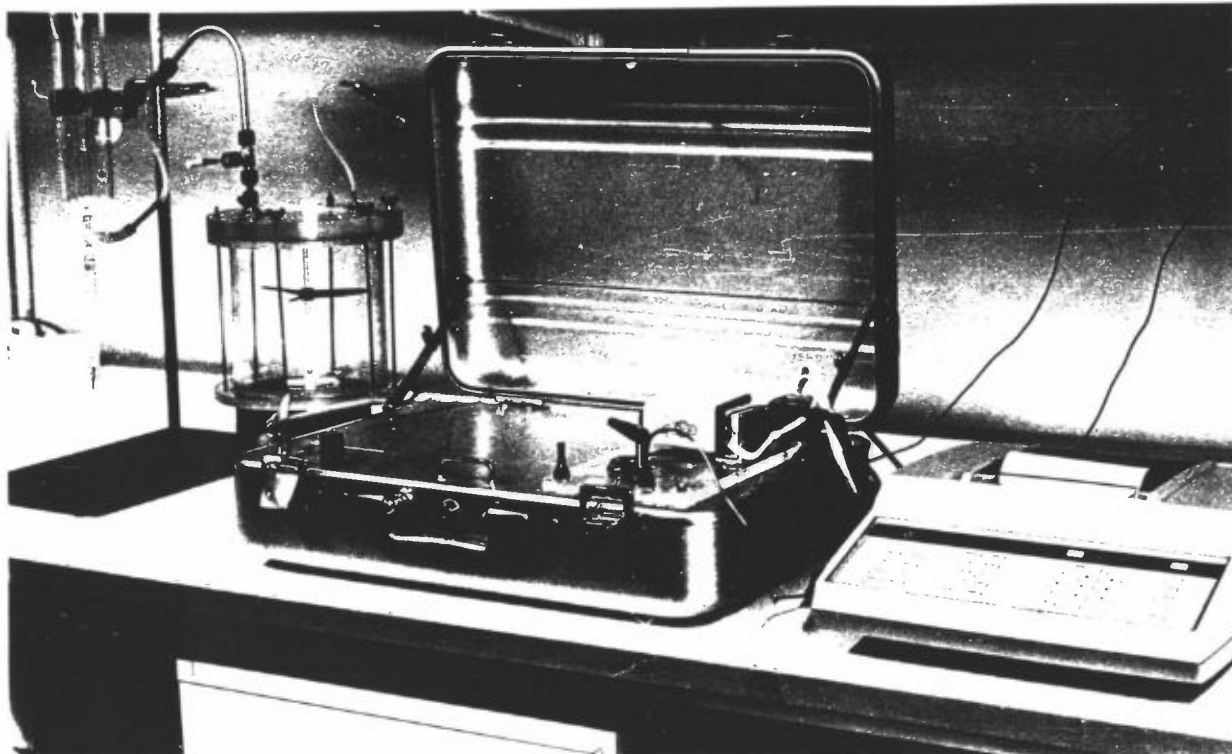


Figure 4: Tracer analysis and calibration system: portable electron capture gas chromatograph, integrator and exponential dilution chamber.

A stainless steel coaxial electron capture detector, electrically insulated with teflon and nylon plugs, is pulsed every 200 μsec with a 1 μsec wide pulse. The radio-active source used is a 200 mCi H^3 source bonded to a titanium substrate (U.S. Radium Corp., Bloomsberg, Pennsylvania). Analysis for

SF_6 is achieved using a stainless steel column (106 cm x 0.6 cm OD, 0.5 cm ID) packed with 5 A 80-100 mesh Alumina F-1 (Supelco Inc., Crans, Switzerland). Columns are filled with alumina and lightly vibrated before being coiled. The columns are conditioned at 300°C overnight with N_2 flowing continuously. Using prepurified N_2 at $100\text{ cm}^3/\text{min}$ as a carrier gas, O_2 elutes in 4 seconds and SF_6 in about 14 seconds. A typical chromatogram for SF_6 is shown in Figure 5 (see also Appendix A).

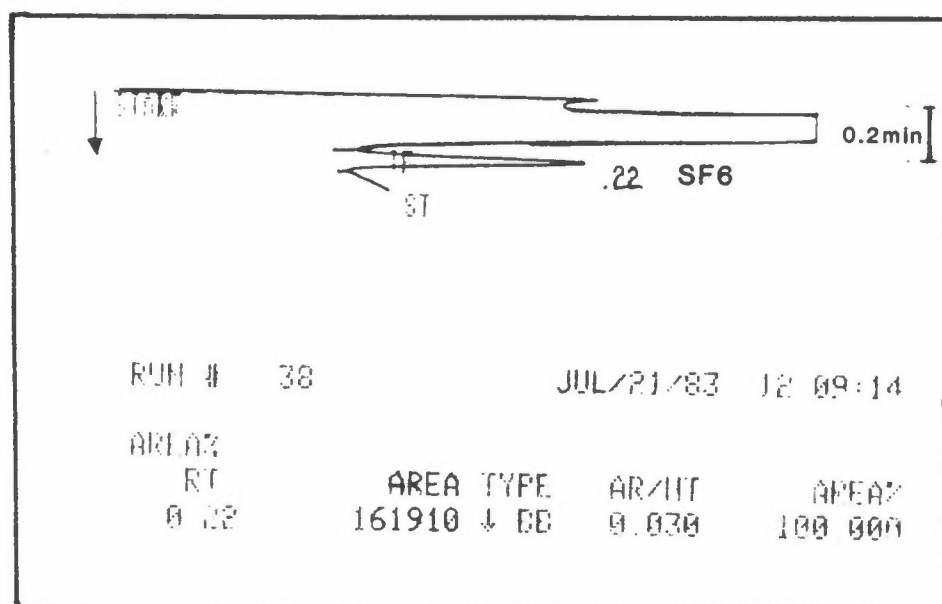


Figure 5: Typical SF_6 chromatogram.

$$[\text{SF}_6] = 200 \text{ ppt } (\approx 1.3 \mu\text{g}/\text{m}^3).$$

Columns for the separation of SF_6 and CBrF_3 are prepared by filling a 205 cm x 2.3 mm OD stainless steel tube with molecular sieve 5A, 80/100 mesh, washed, from Alltech Associates. Nitrogen gas at 2 bar is used for proper compaction of the fillings. After 12 hours conditioning at 280°C the columns are ready for use.

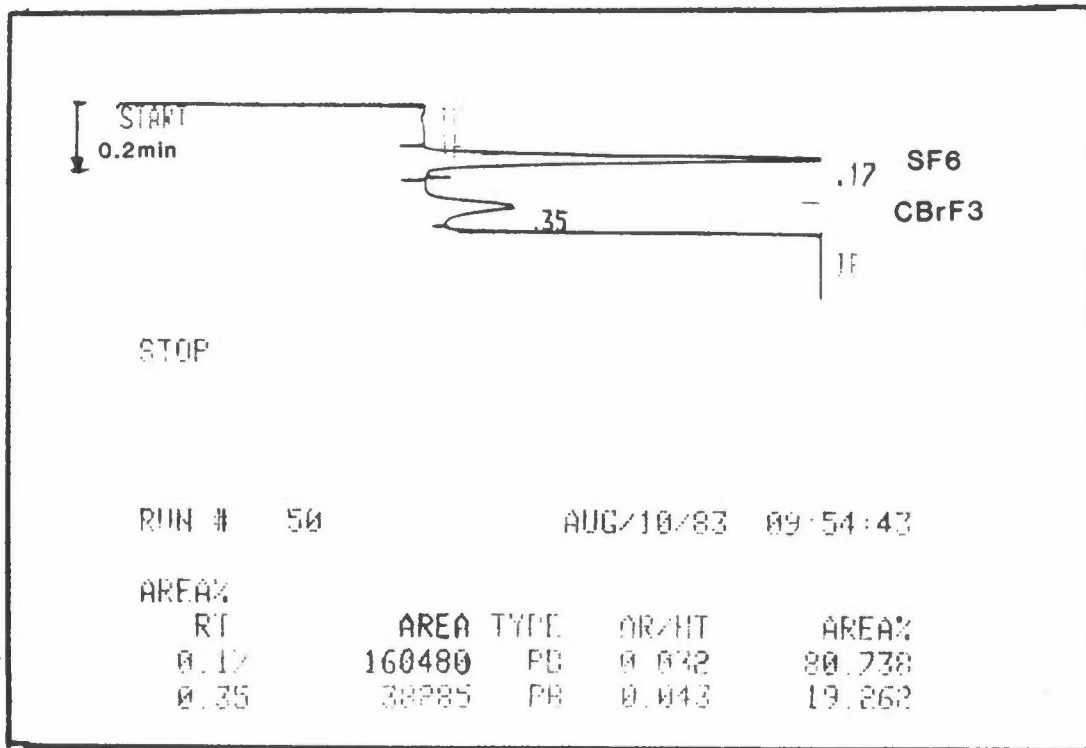


Figure 6: Typical SF₆ and CBrF₃ chromatogram.
 [SF₆] ≈ 200 ppt, [CBrF₃] ≈ 1000 ppt.

Figure 6 shows a chromatogram using a molecular sieve column at 45⁰ C and a nitrogen pressure of 5.0 bar. SF₆ elutes at about 0.2 minutes and CBrF₃ elutes at about 0.4 minutes.

The detection limit is about 10 ppt for SF₆, and about 50 ppt for CBrF₃. Analysis of SF₆ can be carried out with a sensitivity which is about 20 times better than that for CBrF₃.

The gas chromatographs are equipped with 6-port gas sampling valves (Valco, Inc., Houston, Texas) and 1.0 cm³ sampling loops. The columns and detectors are kept at a temperature of about 45⁰ C. As many as 100 samples can be analyzed per hour. Concentrations are determined from the area output on a HP reporting integrator (see Fig. 5 and 6).

3.4 Calibration of the gas chromatographs

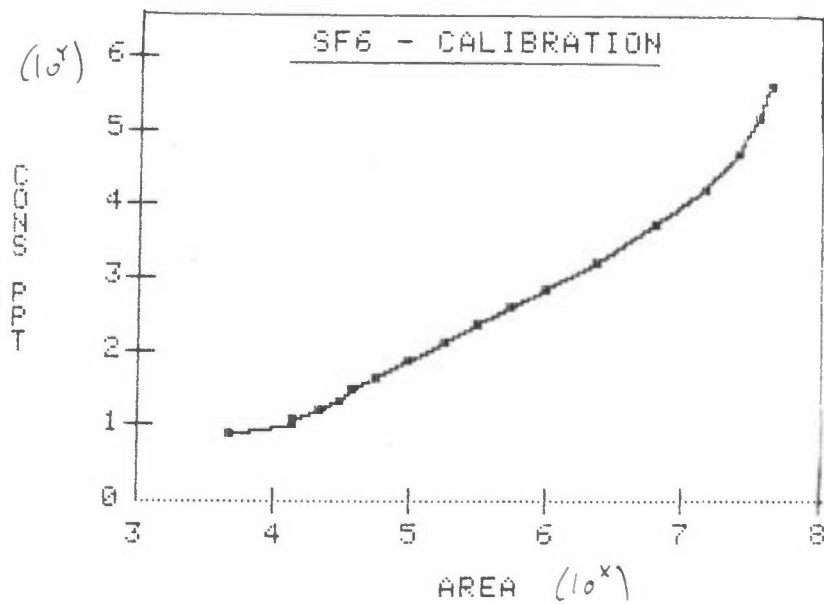
The proportionality constant between area and concentration, termed the calibration factor (KF), is determined using an exponential dilution calibration method. For a well-mixed vessel, the concentration, C, decreases according to:

$$C = C_0 \cdot \exp(-qt/V) \quad (1)$$

where C_0 is the initial concentration, q is the constant flow rate, V is the vessel volume, and t is the time since flow began. At any given time, the number of air changes, N , in the chamber since $t = 0$, is qt/V . If the chamber is perfectly mixed and flow is steady, a plot of $\ln C$ versus N will yield a slope of -1 . Using a lucite cylinder ($V = 2393 \text{ cm}^3$) equipped with a magnetically driven fan and flowing clean, dry air through the cube at $270 \text{ cm}^3/\text{min}$ typically yielded slopes within ± 0.01 of the prescribed value. The calibration system is shown in Figure 5. A microliter syringe, accurate to approximately $\pm 1\%$, was used to inject $3.0 \text{ }\mu\text{l}$ of SF_6 into the cube. This method produced calibration samples ranging from approximately 10^{-6} parts SF_6 /part air to 10^{-11} parts SF_6 /part air (10^6 to 10 parts per trillion, ppt). Samples are drawn from the cylinder exhaust line through a septum and into a 20 cm^3 syringe. The content is then injected into the sampling loop of the GC. A typical result of the calibration obtained with the dilution method is shown in Table 2 and in Figure 7.

Table 2: Calibration of chromatographic system for SF₆ - determination. Exponential dilution chamber 2393 cm³ air flow 272 cm³/minute.

Calculated concentrations ppt	Area measured by integrator	Calculated concentrations ppt	Area measured by integrator
384472	42526000	130.7	175790
141675	34715000	75.0	97128
46725	24688000	43.1	56486
15410	14119000	30.9	38058
5082	6010200	22.2	30741
1576	2188500	15.9	21607
690	927160	12.7	13637
396	530410	10.2	13574
228	304800	8.2	4802



Figur 7: SF₆ calibration curve.

This procedure allows calibration of a gas chromatograph over five orders of magnitude of the concentration. The curves become nonlinear at high concentrations because the detector becomes saturated with sample at those levels. In some cases the curves also become nonlinear near the detection limit. This results from the desorption of tracer from the walls of the cube.

A potentially serious problem associated with prolonged use of the gas chromatographs is contamination of the radioactive foil by deposition of eluted contaminants. As the foil becomes contaminated, the detector operating characteristics change. The concentrations of samples analyzed under these conditions can be in error as much as 15% to 25%. One way of monitoring changes in the detector response is to crosscheck samples between the gas chromatographs. Calibration cross-check data for these tests indicate that concentrations are accurate to within 15%.

3.5 Uncertainties

According to a standard error analysis, errors associated with the calculated calibration concentrations ranged from less than 3% at high concentrations to less than 7% near the detection limit. Calibrations repeated on consecutive days generally agree within less than 5%. The exponential dilution calibration system was used by Lamb and Shair (2) to determine the solubility at SF_6 in water. Since their results were within +6% of results obtained by very accurate volumetric-manometric methods, the absolute accuracy of the calibration appears to be approximately +6%.

The reproducibility in SF₆ analysis was examined from several samples taken in lab-conditions. A standard deviation of about 1% was found when analyzing 10 samples taken from a given gas mixture. Also when analysing alternating concentration levels the reproducibility at each level was about 1 to 2%.

The total uncertainty in the determination of individual SF₆ concentrations, including calibration, reproducibility, reading and sample handling, has been estimated to about 8-10%.

4 APPLICATIONS AT NILU

Several tracer studies have been conducted by NILU since 1978. Experiments have been carried out on different scales; indoor and outdoor and for a variety of purposes. A very brief description of a selection of these studies is presented below, to show the applicability of the technique.

A laboratory ventilation system study was performed in the NILU laboratory-office building to investigate the efficiency of the building ventilation system (3). The time for a complete air exchange ranged from 15 minutes in a small office to more than 4 hours in a large workhall.

Dilution in a wind tunnel was studied with SF₆ as supplement to an investigation of the deposition and effects of acid gases and aerosols upon the growth of young seedlings (4).

The fluoride emissions from aluminium smelters have been studied at several locations. Both the gas collection efficiency and the total release rates have been studied (5).

The wake downwind of an aluminium smelter hall was determined to examine the extent to which exhaust gases could be entrained back into the hall. As much as 11% of the tracer released above the roof during a certain wind direction was found to infiltrate into the hall (6).

Ventilation in automobile tunnels has been studied in several locations to investigate the recirculation into adjoining, parallel tunnels during near calm conditions, and to study total ventilation rates (7). Transport and dispersion in the surroundings of a tunnel mouth has also been studied (8).

Pollutant dispersion in urban street canyons was studied in different streets during various meteorological conditions. SF₆ was released continuously from moving vehicles. The street canyon ventilation rate was determined (9), and experiments were also conducted to yield the emission rate of CO in typical driving and weather conditions of Oslo (10).

Pollutant dispersion downwind from a highway was studied during different meteorological conditions (10) to verify different models. The vertical spread was discussed in particular.

Dispersion parameters have been determined from SF₆-tracer experiments at different sites with variable surface roughness. SF₆ concentration profiles were compared with estimates based upon wind direction fluctuation measurements (11).

Dispersion experiments in complex terrain were conducted to determine the concentration patterns resulting from specified fluoride and SO₂ emissions from a planned aluminium smelter (12).

To design a measurement program of PAH in the surrounding of an aluminium smelter complex. SF₆ was released from the different possible release points in the smelter area (13). Similar studies were also performed at a cokeplant.

The diffuse leakages of hydrocarbons from petrochemical factories were studied using simple proportionality models on specified amounts of SF₆ and CBrF₃ released within the factory area (14).

In preparation of the many experiments a variety of release and sampling systems were developed. The tracers were also applied in a forest canopy experiment, in studies of dispersion above sea surfaces, ventilation rate of tankers and in verification of dispersion models for complex urban areas.

Further research and development and future use of the tracers in atmospheric investigations is expected at NILU. This technical report therefore should be considered a "state of the art 1983".

5 REFERENCES

- (1) Lamb, B.K. Atmospheric dispersion experiments using the NILU automatic weather station and SF₆ tracer techniques.
Sivertsen, B. Lillestrøm 1978. (NILU TN 12/78.)
- (2) Lamb, B.K. Determination of concentrations of halogenated compounds dissolved in various liquids by electron capture gas chromatography.
Shair, F.H. Anal. Chem. 48, 473-475 (1976).
- (3) Lamb, B.K. A tracer investigation of a laboratory ventilation system.
Lillestrøm 1978. (NILU TN 8/78.)

- (4) Dollard, G.J.
Vitols, V. Wind tunnel studies of dry deposition of H_2^{35} og SO_2 aerosols. Oslo-Ås 1980. (SNSF-project IR 55/80.)
- (5) Lamb, B.K. A preliminary tracer investigation of a gas collection system over an aluminium smelting pot. Lillestrøm 1978. (NILU OR 64/78.)
- (6) Lamb, B.K.
Vitols, V.
Skogvold, O.F. Atmospheric tracer techniques and gas transport in the primary aluminium industry. J. APCA, 30, 558-566 (1980).
- (7) Lamb, B.K. A tracer investigation of ventilation in an automobile tunnel. Lillestrøm 1979. (NILU OR 66/78.)
- (8) Gotaas, Y. Tracer investigation of air pollution around the outlet of a road tunnel. (In Norwegian). Lillestrøm 1979. (NILU OR 46/79.)
- (9) Lamb, B.K. A tracer investigation of pollutant dispersion in an urban street canyon. Lillestrøm 1978. (NILU TN 2/78.)
- (10) Larssen, S.
Grønskei, K.E. Methods for prediction of air pollution levels near streets and roads (in Norwegian). Lillestrøm 1982. (NILU OR 5/81.)
- (11) Sivertsen, B. Dispersion parameters determined from measurements of wind fluctuations, temperature and wind profiles. In: Proceedings of the ninth international technical meeting on air pollution modelling and its application (NATO/CCMS no. 103). Toronto (1978).

- (12) Sivertsen, B.
Lamb, B.K.
Grønskei, K.E. A tracer study of pollutant transport in a deep fjord valley.
Atmos. Environ. 17 (1983).
- (13) Sivertsen, B.
Vitols, V. A tracer study of dispersion patterns from Gränges Aluminium smelter in Sundsvall.
Lillestrøm 1980. (NILU OR 36/80.)
- (14) Sivertsen, B. Estimation of diffuse hydrocarbon leakages from petrochemical factories.
J. APCA. 33, 323-327 (1983).

APPENDIX A

Columns for simultaneous gas chromatographic
determination of SF₆ and CBrF₃

CHROM. 14,894

Note

Columns for simultaneous gas chromatographic determination of ppt* levels of the atmospheric tracers sulphur hexafluoride and bromotrifluoromethane in ambient air samples

R. HEGGEN and M. OEHME*

Norwegian Institute for Air Research, P.O. Box 130, N-2001 Lilleström (Norway)

(Received January 25th, 1982)

Sulphur hexafluoride has been widely used in tracer experiments for the identification and simulation of air pollution from stacks and diffuse sources. It was selected for such investigations mainly because of its non-toxic character, chemical stability and easy detection at very low concentrations by gas chromatography (GC) using an electron-capture detector.

The separation of SF₆ from air components, such as oxygen, is a major analytical problem. In some earlier investigations a packed silica gel column, followed by an activated charcoal column and alumina oxide columns, were used^{1,2}. However, the SF₆ signal then appears after the oxygen signal, causing interference problems and a decreased detection limit. Some rather sophisticated methods have also been described using preconcentration and backflush of the sample to improve the detection limit to a few ppt^{1,3}. By introducing specially treated molecular sieve columns⁴⁻⁶, from which SF₆ is eluted before oxygen, some of the problems mentioned above have been overcome, enabling the direct determination of a few ppt. However, most of the columns described need a reactivation of the molecular sieve after a few days to maintain the separation efficiency. This makes them less suitable for long-term measurements and automatic devices.

The application of two tracer gases is of considerable advantage for the evaluation of more complicated emissions especially when several sources are involved. Bromotrifluoromethane has been used in dual-tracer experiments due to its comparable properties to SF₆. However, there are some difficulties in the GC detection procedure. The response factor of the electron-capture detector for CBrF₃ is about two orders of magnitude lower than that for SF₆, and the separation of both tracers from oxygen is difficult. Lamb^{6,7} suggested a rather complex procedure for the preparation of a molecular sieve column, which makes possible the separation of both tracers from oxygen. Unfortunately, his columns were difficult to reproduce, and the lifetime was rather short.

The aim of this work was to simplify the activation procedure, to improve the reproducibility of the separation efficiency and to increase the column lifetime. A detailed description of a method is given, which allows the preparation of highly

* Throughout this article, the American billion (10⁹) and trillion (10¹²) are meant.

stable molecular sieve columns for trace analysis of SF₆ and CBrF₃ in ambient air samples. The simultaneous detection of about 5 ppt SF₆ and 100 ppt CBrF₃ in a 1-ml air sample is possible.

EXPERIMENTAL

Instruments

A simple home-made gas chromatograph was used for all experiments. The whole system, including the electron-capture detector, was operated isothermally either at room temperature or at 40–60°C. The electron-capture detector was of the pin-cup type equipped with a tritium copper foil of 400 mCi. The detector was operated at a pulse width of 2 μsec, a pulse rate of 250 μsec and a pulse amplitude of –30 V. A two-channel recorder (Model 585; Linear Instrument, Irvine, CA, U.S.A.) was used for the registration of the chromatograms. For quantitative analysis a Model 3390 integrator system (Hewlett-Packard, Palo Alto, CA, U.S.A.) was employed. A manual valve (Valco six-port HP valve; Valco Instruments, Houston, TX, U.S.A.) with a loop of 1 or 5 ml was used for sample introduction. Ambient air samples were collected in 50-ml polyethylene disposable syringes using a home-made automatic sampling device.

Nitrogen of 99.995% purity was used as the carrier gas. A metal bellow pressure reduction valve (Type HBS300; L'Air Liquide, Paris, France) and a stainless-steel molecular sieve trap were used to prevent contamination of the GC system. Calibrations were done by means of an exponential dilution vessel with standard gas mixtures prepared from 99.9% pure SF₆ and CBrF₃ (Kali Chemie, Hannover, G.F.R.)

Column preparation

Dual tracer column. A stainless-steel column (2.5 m × 2 mm I.D.) was connected to a 25-ml glass pipette filled with about 12 ml of 5A molecular sieve (80–100 mesh). It is very important to remove any dust from the column material by washing it with 0.1 M hydrochloric acid and deionized ultrapure water⁸. After washing, the molecular sieve was dried for 12 h at 300°C. A commercially available, prepurified and acid-washed Type 5A molecular sieve (80–100 mesh) (No. 5605; Alltech, Deerfield, IL, U.S.A.) is also suitable and can be used without pretreatment. The other end of the column was connected to a diaphragm vacuum pump (Type Al 17, Neuberger Inc.) with an empty impinger in between. Nitrogen, at a pressure of 1.3 bar, was applied to the inlet of the glass molecular sieve pipette and the column filled slowly, with slight tapping. The pressure should be increased step by step to about 2 bar at the end of the filling procedure. The packing has to be done with extreme care to prevent the formation of dust from the molecular sieve. After filling, the column was activated at 300°C for 12 h under a nitrogen flow of about 10 ml/min.

Single-tracer column. This column allows only the separation of SF₆ from the oxygen signal. It was prepared as described above. Aluminium oxide (Alumina Γ-1, 80–100 mesh, No. 2-0284; Supelco, Bellefonte, PA, U.S.A.) was used for packing and the column was activated at 400°C for 12 h.

Measuring procedure

The gas chromatograph, operated at ambient temperature and an inlet pressure of 3 bar, was calibrated with standard gas mixtures from an exponential dilution vessel. Ambient air samples were taken with automatic samplers in 50-ml syringes. After the injection of 1 ml air, SF₆, CBrF₃ and oxygen were eluted within 3 min. Because of the presence of other halogenated trace compounds in the samples, one has to wait about 5 min before the next injection. This conditioning time is reduced to about 3 min when the column is operated at 40°C. From the single-tracer column, oxygen and SF₆ were eluted within 1 min at an inlet pressure of 1.1 bar.

RESULTS AND DISCUSSION

First measurements of SF₆ were made with the alumina columns, which were easy to prepare and gave a reasonably low detection limit of about 5 ppt (see Fig. 1). Based on the work of Simmonds *et al.*⁴, columns packed with standard molecular sieve were used for some investigations. These were only able to separate SF₆ from the oxygen signal and had to be activated after a short time. Dietz and Cote⁵ proposed a nitric oxide-treated molecular sieve column to improve both peak shapes and long-term stability. However, separation of both SF₆ and CBrF₃ could not be achieved.

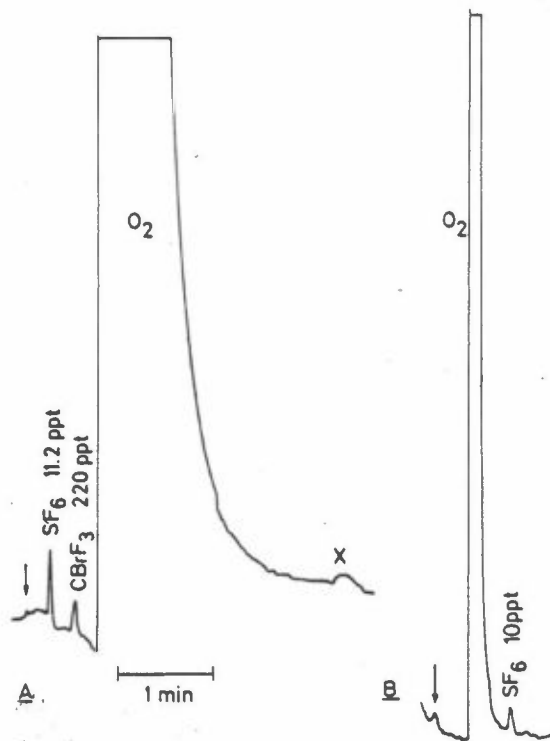


Fig. 1. Gas chromatograms of tracer gases on molecular sieve and aluminium oxide. A, Chromatogram of an ambient air sample separated on molecular sieve. The column was operated at room temperature; X = halogenated compound. B, Standard mixture containing 10 ppt SF₆ separated on aluminium oxide at room temperature.

Further experiments to separate both CBrF_3 and SF_6 from oxygen were conducted with the molecular sieve column prepared according to the method of Lamb^{6,7}, which recommends an overnight activation procedure at 300°C , followed by a partial deactivation with water. Another suggestion was to activate the column at 175°C for 12.5 h. All of these columns, filled with standard quality molecular sieve, however, showed a relatively high pressure drop, and had to be operated at 3.6 bar inlet pressure. For the separation of both tracers from oxygen, the columns were useful only for a few days, and their performance decreased rapidly thereafter.

The use of other stationary phases, such as Carbosphere (80–100 mesh) (Alltech, No. 5682) and a carbonaceous molecular sieve (Carbosieve B, 60–80 mesh, Supelco, No. 1-0250), gave no improvements. Both column packings showed extreme tailing of the oxygen signal and insufficient separation of the SF_6 signal from both oxygen and CBrF_3 .

The standard quality molecular sieve, used in the first experiments, contained a lot of very fine particles, which made the preparation of low pressure drop columns very difficult. Furthermore, the molecular sieve material is rather brittle and does not tolerate vibration of the column under the filling procedure. The large pressure drop and high content of dust do not allow a reproducible activation of the column. The use of acid-washed, dust-free molecular sieve (see Experimental) and the development of a careful packing procedure eliminated the problems mentioned above. The activation was carried out at 300°C or more to get stable and highly active columns.

The purity of the carrier gas is decisive for the long-term stability. A pressure regulator with metal bellow seals and a stainless-steel filter cartridge (filled with molecular sieve) were used to maintain the purity of the nitrogen. Commercially available purification cartridges, made from acrylic glass, cannot be recommended since they may cause contamination, which disturbs the function of the detector.

The presence of late elution peaks of chlorinated hydrocarbons considerably increases the analysis time. The operation of the separation column at an elevated temperature (about 40 – 50°C) reduces the retention time for such compounds, without any influence on the separation efficiency for the tracer gases. A sample analysis cycle of 3 min is then possible (see Fig. 1).

The lower detection limit can be improved to 2 ppt and 50 ppt, respectively (signal-to-noise ratio 5:1) when a 5-ml loop is used. The separation efficiency deteriorates slightly, but is still sufficient for the low concentrations.

Applications of the tracer technique

The GC system described has been used for several thousands of samples without any serious problems. Applications of the tracer gas technique have been in the assessment of inert gas ventilation system efficiency in oil tankers, investigations of the transport of pollutants in the primary aluminium industry⁹ and the control of the air conditioning and ventilation system efficiency in buildings. Major organic compounds in air, such as aliphatic and aromatic hydrocarbons, did not influence the lifetime of the column. Even under field conditions, where heavily polluted air masses were analysed, no reactivation or bake-out of the column was necessary for at least 3 months.

For indoor measurements, interferences caused by Freons from very small leakages in refrigeration systems can be a severe problem. The presence of ppb

amounts of Freons, which elute just after the tracer compounds, precludes any determination.

REFERENCES

- 1 A. Turk, S. M. Edmonds and H. L. Mark, *Environ. Sci. Technol.*, 2 (1968) 44.
- 2 L. A. Niemeyer and R. A. McCormick, *J. Air. Pollut. Control Assoc.*, 18 (1968) 403.
- 3 C. A. Clemons, A. I. Coleman and B. E. Saltzman, *Environ. Sci. Technol.*, 2 (1968) 551.
- 4 P. G. Simmonds, G. R. Shoemaker, J. E. Lovelock and H. C. Lord, *Anal. Chem.*, 44 (1972) 860.
- 5 R. N. Dietz and R. A. Cote, *Environ. Sci. Technol.*, 7 (1973) 338.
- 6 B. K. Lamb, *Ph. D. Thesis*, California Institute of Technology, Pasadena, CA, 1978.
- 7 B. K. Lamb, personal communication.
- 8 M. Oehme and W. Lund, *Talanta*, 27 (1980) 223.
- 9 B. K. Lamb, V. Vitols and O. Skogvoid, *J. Air Pollut. Control Assoc.*, 30 (1980) 558.



NORSK INSTITUTT FOR LUFTFORSKNING

NILU

(NORGES TEKNISK-NATURVITENSKAPELIGE FORSKNINGSRÅD)
POSTBOKS 130, 2001 LILLESTRØM
ELVEGT. 52.

TLF. (02) 71 41 70

RAPPORTTYPE Teknisk rapport	RAPPORT NR. TR 8/83	ISBN--82-7247- 416-6
DATO AUGUST 1983	ANSV.SIGN. O.F. Skogvold	ANT. SIDER 29
TITTEL Tracer gas technique at NILU		PROSJEKTLEDER B. Sivertsen
FORFATTER(E) R. Heggen and B.Sivertsen		NILU PROSJEKT NR.
		TILGJENGELIGHET** A
OPPDRAGSGIVER		OPPDRAGSGIVERS REF.
3 STIKKORD (á maks. 20 anslag) Tracer gas Tracer equipment		Tracer experiments
REFERAT (maks. 300 anslag, 5-10 linjer)		
TITLE		
ABSTRACT (max. 300 characters, 5-10 lines. Tracer gas techniques have been applied at NILU since 1978. The report describes the tracer gas equipment frequently in use; release system, sampling equipment, portable gas chromatographs, calibration and analysis. The variety of applications are briefly presented.		

**Kategorier: Åpen - kan bestilles fra NILU A
Må bestilles gjennom oppdragsgiver B
Kan ikke utleveres C