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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 Lillestrom (Norway)
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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 SF_6 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 SF_6 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 columns[4–6], from which SF_6 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 SF_6. However, there are some difficulties in the GC detection procedure. The response factor of the electron-capture detector for $CBrF_3$ is about two orders of magnitude lower than that for SF_6, 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 (10^9) and trillion (10^{12}) are meant.

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stable molecular sieve columns for trace analysis of SF_6 and $CBrF_3$ in ambient air samples. The simultaneous detection of about 5 ppt SF_6 and 100 ppt $CBrF_3$ 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 SF_6 and $CBrF_3$ (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 water[8]. 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 AI 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 SF_6 from the oxygen signal. It was prepared as described above. Aluminium oxide (Alumina F-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, SF_6, $CBrF_3$ 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 SF_6 were eluted within 1 min at an inlet pressure of 1.1 bar.

RESULTS AND DISCUSSION

First measurements of SF_6 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 SF_6 from the oxygen signal and had to be activated after a short time. Dietz and Cote[5] proposed a nitric oxide-treated molecular sieve column to improve both peak shapes and long-term stability. However, separation of both SF_6 and $CBrF_3$ could not be achieved.

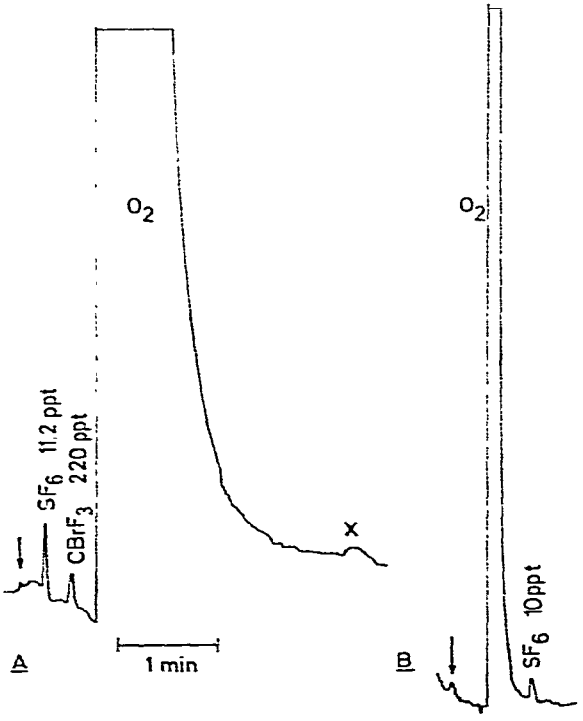

Fig. 1. Gas chromatograms of tracer gases on molecular sieve and aluminium oxide. A, Chromatogram of an ambient air sample separated on molecular sieve. The column was operated at room temperature; X = halogenated compound. B, Standard mixture containing 10 ppt SF_6 separated on aluminium oxide at room 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 industry[9] 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.

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