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## Note

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### Rapid gas chromatographic determination of sulphur hexafluoride in air

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The use of sulphur hexafluoride as a tracer in diffusion studies<sup>1,2</sup> is widespread as the gas is inert, chemically and thermally stable and can be detected at very low concentration by means of an electron capture detector. Some difficulties in its determination by gas chromatography might be experienced, however, as various components in air interfere unless suitable fractionating devices are used.

Adsorption columns of silica gel and activated carbon in series at 120° have been used for this purpose<sup>3</sup>. Under these conditions, oxygen, carbon dioxide and sulphur hexafluoride are eluted in that order and the analysis time is about 4 min.

The determination of sulphur hexafluoride can also be carried out on a 5 Å molecular sieve column, where it is eluted before oxygen<sup>4</sup>. The analysis of an air sample requires about 8 min.

In both procedures, water vapour present in air samples does not yield a symmetrical peak. This can be a source of interference because when the column becomes saturated, water vapour reduces the sensitivity of the detector.

This paper reports a rapid gas chromatographic procedure for the trace determination of sulphur hexafluoride on a single column, where it is separated from oxygen, carbon dioxide and water vapour. The analytical procedure is suitable for routine use and no column re-conditioning for removal of water is necessary as moisture is not retained on the chromatographic support.

## EXPERIMENTAL

### *Gas chromatographic apparatus*

A Carlo Erba (Milan, Italy) Fractovap Model GI gas chromatograph with an electron capture detector was used; the detector was equipped with a heater and a 10-mCi nickel-63 source.

Pre-purified nitrogen (containing 10 ppm of water and 5 ppm of oxygen) was used as the carrier gas. Further removal of water was achieved by passing the carrier gas through a trap containing 5 Å molecular sieves that had previously been activated by heating in an oven for 36 h at 320°.

The separation of sulphur hexafluoride from other air components was obtained on Graphon and Porapak columns, and in both chromatograms water vapour yielded a symmetrical peak.

TABLE I  
COLUMN OPERATING CONDITIONS

Conditions	Graphon column	Porapak Q column
Length (m)	2	2
Internal diameter (cm)	0.4	0.4
Mesh size	40-60	80-100
Column temperature (°C)	25	80
Detector temperature (°C)	100	100
Carrier gas (nitrogen) flow-rate (ml/min)	20	45
Scavenger gas (nitrogen) flow-rate (ml/min)	75	50
Column inlet pressure (kg/cm <sup>2</sup> )	0.6	1.0
Excitation potential (V)	10	10

#### Graphon column

A 2 m × 4 mm I.D. stainless-steel tube was packed with 40-60 mesh Graphon, which is a graphitized carbon black with a surface area of about 90 m<sup>2</sup>/g. After preliminary experiments, peak tailing due to water was eliminated by coating the adsorbent with 0.3% (w/w) of 1:1 glycerol-orthophosphoric acid<sup>5</sup>. The number of theoretical plates referred to the water peak was 1600.

#### Porapak column

A 2 m × 4 mm I.D. stainless-steel tube was packed with 80-100 mesh Porapak Q. No further treatment was needed as oxygen, carbon dioxide, sulphur hexafluoride and water vapour yield symmetrical elution peaks.

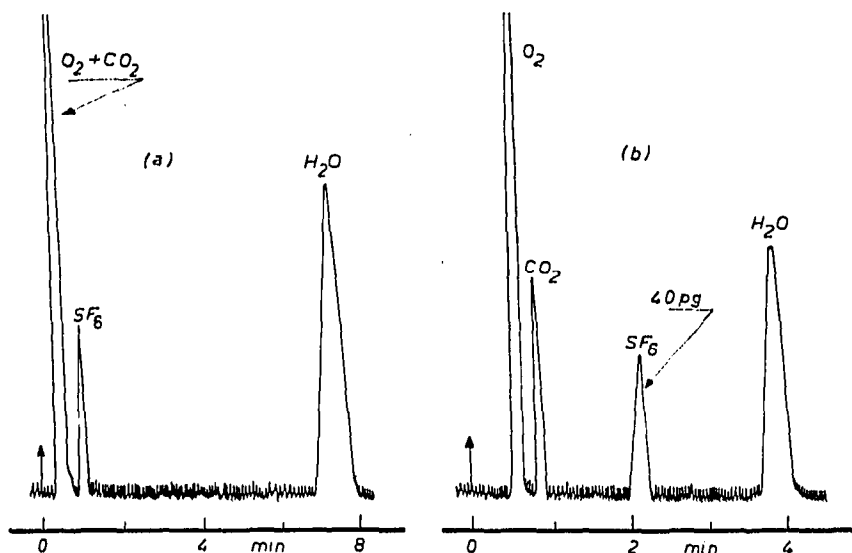


Fig. 1. Chromatograms of nitrogen samples containing oxygen, carbon dioxide, sulphur hexafluoride and water vapour. (a) 2 m × 4 mm I.D. Stainless-steel column packed with surface-modified Graphon carbon black; column temperature, 25°. (b) Same column as in (a), packed with Porapak Q; column temperature, 80°.

TABLE II  
GAS CHROMATOGRAPHIC RESULTS

Parameter	Graphon column	Porapak Q column
O <sub>2</sub> capacity ratio*	0.0	0.0
CO <sub>2</sub> capacity ratio*	0.0	0.5
SF <sub>6</sub> capacity ratio*	1.3	3.2
H <sub>2</sub> O capacity ratio*	22.5	6.6
H <sub>2</sub> O retention time (min)	8	4
Number of theoretical plates for water peak	1600	1800

\* The capacity ratios for O<sub>2</sub>, CO<sub>2</sub>, SF<sub>6</sub> and H<sub>2</sub>O are referred to retention time of the hydrogen peak.

Calibration was carried out with pure sulphur hexafluoride purchased in liquid form in small cylinders under pressure (Matheson, Coleman and Bell, East Rutherford, N.J., U.S.A.) and by dilution with plastic syringes in 2-l glass flasks fitted with a stopcock and a rubber septum. Flasks were first partially evacuated with a vacuum pump, sulphur hexafluoride was injected through the rubber septum and air was then introduced through the stopcock so as to bring the pressure in the flask to atmospheric. Concentrations of sulphur hexafluoride from 100–1 ppb were obtained in two or three steps.

## RESULTS

The gas chromatographic behaviour of both columns was determined with a gas mixture containing oxygen, carbon dioxide, water vapour and sulphur hexafluoride. The columns and operating conditions are specified in Table I. Typical chromatograms are shown in Fig. 1; they were obtained by injecting 1 ml of a standard gas mixture in which the sulphur hexafluoride concentration was 7 ppb (about 40 pg of pure tracer).

According to Table II, both columns yield satisfactory results but the Porapak Q column seems to offer some advantages in comparison with the Graphon column. The Porapak Q column gave a better resolution of sulphur hexafluoride; the operating conditions were not critical and could be varied considerably. It is worth noting that on a Porapak Q column, water has a lower capacity ratio (6.6 compared with 22.5 on the Graphon column); this means that the analysis time for an air sample on this column is lower in comparison with that on the Graphon column. This feature is interesting in diffusion studies, where usually a large number of samples have to be analyzed and a shorter analysis time is desirable. It has been found that the use of a shorter column (1 m) at the same temperature for an air sample still gives complete resolution with an analysis time of only 2 min.

## REFERENCES

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