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Application of gas chromatography with electron-capture detection to trace analysis of halogenated compounds

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ABSTRACT

The construction, operation and examples of applications of the automatic AF-1 analyser for the trace analysis of halogenated compounds in air and other gases are described. The instrument is a gas chromatograph containing the electron-capture detector with a sensitivity of 10^{-6} ppm for strongly electronegative compounds, such as SF_6 and Freons. The analyser is useful for trace investigations when halogenated compounds are applied as tracers in the determination of ventilation rates and dispersion patterns within coal mines etc. and in the tightness investigations of industrial installations.

INTRODUCTION

A schematic diagram of a tracer experiment is shown in Fig. 1. The data obtained allow one to establish a relationship between the "input" and "output" of an investigated object and permit the calculation of a mathematical model or several physical parameters, such as the flow velocity of gaseous streams, air exchange rate in at low air flows, transit air time, recirculations, mean residence time of the tracer and dispersion rate, depending on the kind of objects investigated.

Numerous organic and inorganic materials have been used as tracers but most

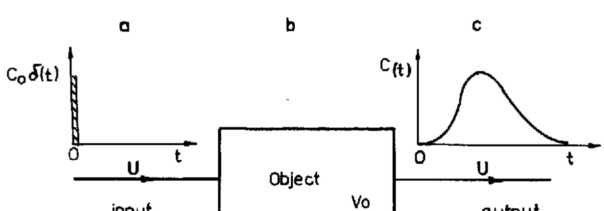

Fig. 1. Schematic diagram of tracer experiment. (a) Tracer δ-Dirac's injection form on the investigated object input; (b) investigated object, V_0 = volume, u = rate of air flow; (c) the tracer residence time distribution function at the investigated object output.

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have certain inherent drawbacks. At low concentrations chemical tracers are not detected as easily and they are often highly adsorbed on many surfaces. Radioactive substances can be detected at low concentrations, but they are difficult to handle and likely to be unacceptable to persons working near the objects being investigated.

A useful tracer gas must be detectable at low concentrations, must be safe, odourless, chemically and thermally stable, and should not occur naturally in the environment. Sulphur hexafluoride (SF_6) and some Freons, such us F12B1, F12B2 and F114B2, meet these essential requirements. Halogenated compounds, with electron-capture constants k_1 around 10^{-7} cm^3/s, can be detected at a very low concentrations ($< 10^{-6}$ ppm) by gas chromatography with electron-capture detection. Halogenated tracer techniques have been shown to be useful in air and gas migration studies in meteorology and aerology[1–4], and also in oceanography[5,6] and hydrology[7,8].

Some of the Freons, such as F12, F11, F113 and F10, now occur "naturally" in the environment[9]. The application of these Freons as tracers is possible at a concentration about 100 times higher than that of the other freons, to eliminate the influence of their background concentration.

EXPERIMENTAL

The AF-1 analyser is a portable gas chromatograph equipped with an electron-capture detector, operated at constant frequency, and a strip-chart recorder. Fig. 2 shows the instrument and a its circuit diagram is presented in Fig. 3. The mea-

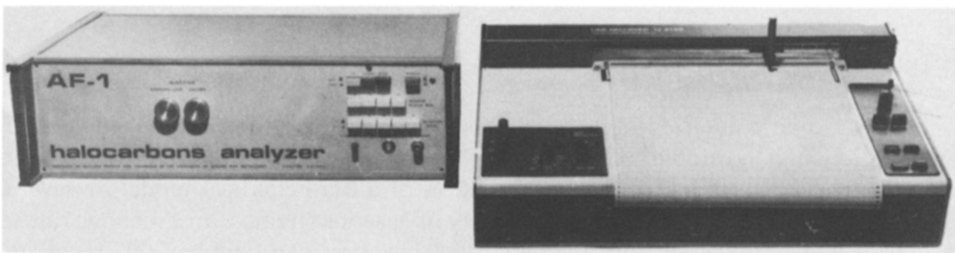

Fig. 2. Photograph of the AF-1 halocarbons analyser. Weight, 15 kg. Dimensions, 350 × 200 × 400 mm.

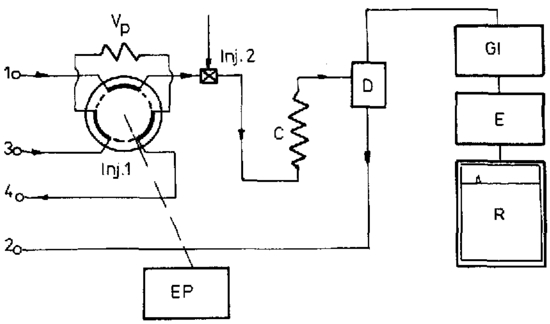

Fig. 3. Circuit diagram of the AF-1 analyser.

TABLE I

OPERATING CONDITIONS

Tracer	*Detector temperature (K)*	*Column temperature (K)*	*Column length (m)*	*Column packing*	*Carrier gas*
SF_6	300	300	1	Silica gel or molecular sieve 5 A	N_2 or Ar + 10% CH_4, 40 ml/min
Freons F12 or F12B1, F11 or F12B2, F113, F114B2, F10	573	300	3	10% DC 200 on chromosorb W	N_2 or Ar + 10% CH_4, 60 ml/min

surement unit contains two gas circulations: the carrier gas path (1 and 2) and the investigated gas path (3 and 4). The carries gas path includes the automatic gas sample injector Inj 1, the manual syringe injector Inj 2, the gas chromatographic column C and the electron-capture detector D. The investigated gas path includes the automatic gas sample injector Inj 1 and sample loop V_p. The measuring unit also contains all associated electronics, *i.e.*, the detector supply pulse generator GI, elec-

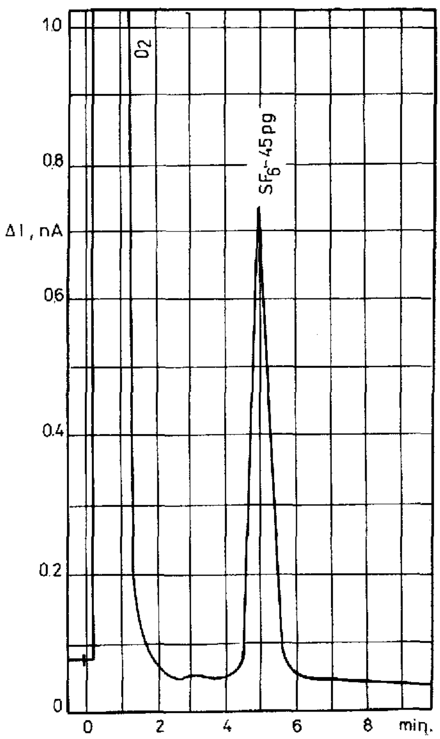

Fig. 4. Example of SF_6 analysis in a 5-ml air sample.

TABLE II

TECHNICAL PARAMETERS OF THE AFI ANALYSER WITH SF_6 AS TRACER

Parameter	*Value*
Gas sample injection volume	5 ml
Detection limit for SF_6	10^{-13} g/ml
Carrier gas and flow-rate	High-purity N_2 or Ar + 10% CH_4 (O_2 < 1 ppm), 40 ml/min
Detector β-source	^{63}Ni, 15 mCi
Linear range	100
Chromatographic column	1 m, silica gel
Detector and column temperature	300 K
Sampling and injection	Manually or automatically every 15 min

trometer E and time programmer EP that controls he automatic sampling operation system Inj 1. The strip-chart recorder R serves for monitoring the detector output. The operating conditions are given in Table I.

RESULTS

An example of the analysis of an air sample with SF_6 as the tracer is presented in Fig. 4. and technical parameters are given in Table II. The analysis of the back-

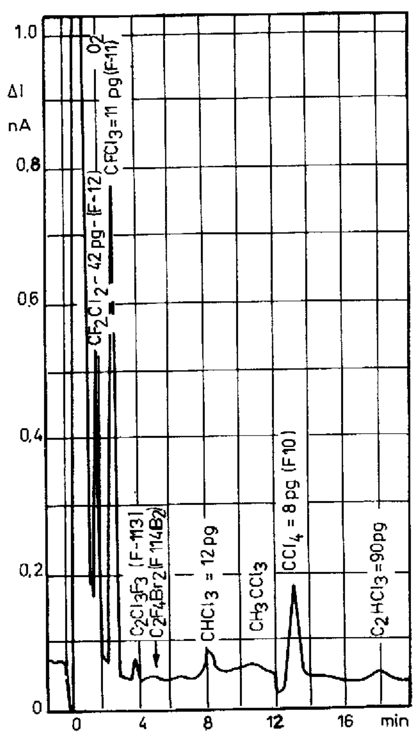

Fig. 5. Example of background analysis of halogenated compounds in a 5-ml air sample.

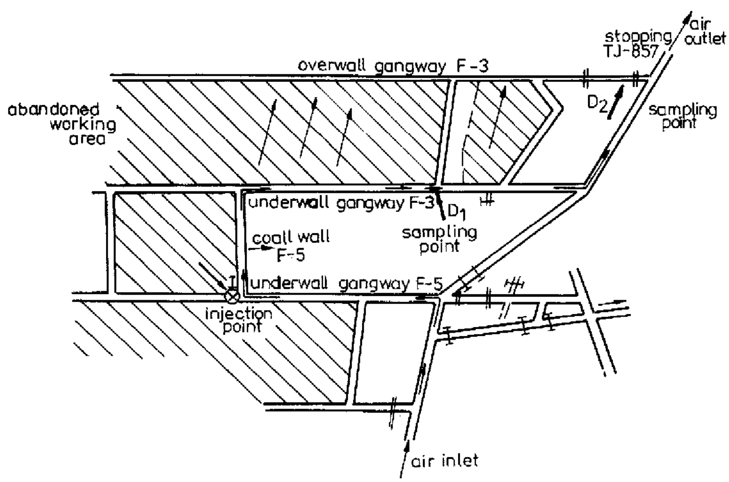

Fig. 6. Map of excavation mine: I = tracer injection point; D_1, D_2 = sampling points.

ground concentration of some freons in air is shown in Fig. 5. A very low detectability range at the level 10^{-12} g/ml for strongly electronegative compound makes possible the direct analysis of gaseous samples without enrichment.

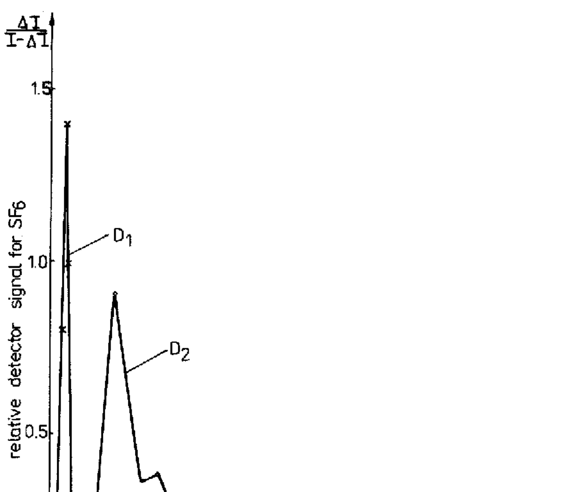

Fig. 7. Tracer concentrations at points D_1 and D_2 (Fig. 6) as a function of time from the moment of injection.

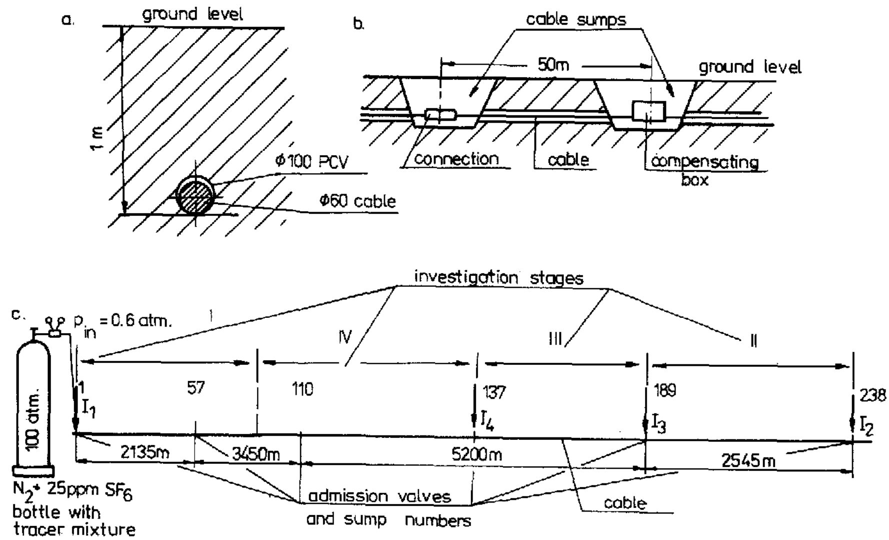

Fig. 8. Tightness investigations of telecommunication cable coating (a), (b) location of investigated cable; (c) the thightness investigation stages.

Application to the investigation of the migration of air in mines (ref. 10)

The results of air and gas flow investigations in a coal mine are shown in Figs. 6 and 7. The tracer method was used to demonstrate that there is air migration through abandoned workings wall F-3 in the direction of isolation stopping TJ-857. In each injection, 1 l of SF_6 was introduced into the flowing air at point I. The air at points D_1 and D_2 was sampled using glass syringes and analysed with the AF-1 analyser. Fig. 7 illustrates the changes in the tracer concentration at points D_1 and D_2 as a function of time, starting from the moment of injection. The following results were obtained.

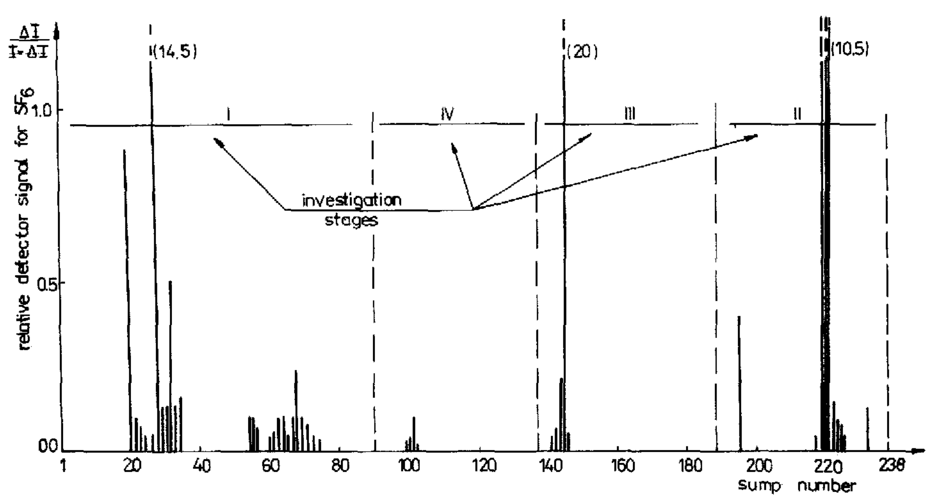

Fig. 9. Tracer concentrations in each cable sump as the result of tightness investigations.

The transit time for the tracer from the injection point I to point D_1 is 20 min, hence the average air flow velocity for this distance of 920 m is 0.75 m/s. In the abandoned workings wall F-3 there are two main gas migration passages, which is evident from two maxima excluding the main maximum. The abandoned workings wall F-3 is leaky, *i.e.*, in addition to two passages there are other connections, as shown by the "tail" of tracer residence time distribution curve.

Application to tightness localization of telecommunication cable coating

The set-up is shown in Fig. 8a and b. The cable of length about 14 km I.D. 60 mm is located 1 m underground in a PVC pipe of I.D. 100 mm and passes through 238 cable sumps. The cable contains 86 connections and eight compensation boxes which balance its wave resistance. Because of the length of the cable, its tightness investigations were divided into four stages (see Fig. 8c). In each stage a tracer mixture of nitrogen containing 25 ppm of SF_6 was injected continuously into the cable from a high-pressure bottle via admission valves I. The air from each cable sump was then sampled with 50-ml glass syringes and analysed using the AF1 analyser.

The results of these qualitative investigations, *i.e.*, the dependence of the relative detector signal, $\Delta I/(I-\Delta I)$ (where I is the detector standing current) on the cable sump number for each investigation stage are illustrated in Fig. 9. Three large leaks were found from the compensation boxes (sumps 27, 144 and 220) and several smaller leaks from the cable connections.

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