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ELECTRON CAPTURE DETECTION OF SULPHUR GASES IN CARBON DIOXIDE AT THE PARTS-PER-BILLION LEVEL

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SUMMARY

A gas chromatograph with an electron capture detector has been used to determine sulphur gases in CO₂ at the parts-per-billion* level, with particular application to the analysis of coolant from CO₂ cooled nuclear reactors. For COS, CS₂, CH₃SH, H₂S and (CH₃)₂S₂ the detector has a sensitivity comparable with the more commonly used flame photometric detector, but it is much less sensitive towards (CH₃)₂S and thiophene. In addition, the paper describes a simple method for trapping sulphur gases which might enable detection of sub parts-per-billion levels of sulphur compounds.

INTRODUCTION

Sulphur compounds are generally measured in gas chromatography with the sulphur specific flame photometric detector developed by Brody and Chaney¹, which can measure down to 2 ppb* levels². As a result, there is little information available in the open literature on the performance and application of the electron capture detector (ECD) in the analysis of sulphur compounds. Indeed, results quoted by Kilaraska³ suggest that the ECD is not very sensitive towards common sulphur gases. For instance, minimum detection levels of 500 ppm and 100 ppm were quoted for H₂S and COS, respectively. More favourable detection limits may be inferred from the work of Oaks *et al.*⁴, who compared the responses of ECDs and flame ionisation detectors towards organic sulphur compounds, but no detection limits were quoted. The relationship of molecular structure to electron capture sensitivity has been reviewed by Pellizari⁵, who defines an electron capture coefficient based on collision cross-sections, electron affinities, activation energies and bond stabilities, in order to predict relative sensitivities in electron capture detection. However, the existence of several instrumental variables makes application of the detector difficult. For instance, papers by Wentworth and Chen⁶, Devaux and Guiochon⁷, Chen and Wentworth⁸ and Aue and Kapila⁹ stress the importance for the optimisation of operating

* Throughout this article the American (10⁹) billion is meant.

conditions, of parameters such as detector cell temperature, applied voltage, pulse width and elimination of contamination.

This paper is intended to demonstrate the suitability and limitations of the detector for the gas chromatographic determination of parts-per-billion levels of sulphur gases in CO_2 . The application for which the work was required was the determination of the sulphur compounds in CO_2 coolant from CEGB Magnox and Advanced Gas Cooled Reactors and, in particular, the determination of the chemical form of ^{35}S in the coolant. A pre-concentration technique, which was developed in order to facilitate the latter determination, but which could be used to lower detection limits for certain sulphur compounds, is also described.

EXPERIMENTAL

The gas chromatograph used in this work was a Pye-Unicam Model 104 fitted with an ECD. The detector cell consists of a cylindrical 10-mCi ^{63}Ni radioactive source, held at earth potential which surrounds an inner probe held at a positive potential. The detector can be heated up to 350° , the optimum temperature varying for different compounds, depending upon the nature of the reactions involved. However, as a general rule, the detector must be operated at a temperature appreciably higher than column temperatures in order to prevent condensation in the detector of materials eluted from the columns, with resultant loss of sensitivity. The detector is generally operated in a pulsed mode, rather than at a constant d.c. potential, since this has been found to produce improved sensitivity¹⁰.

In the present application, high purity nitrogen was used as carrier gas. This passed from the cylinder via a molecular sieve trap to a mass flow controller and 3-way gas sampling valve. This valve could be fitted with stainless-steel or glass sampling loops of 0.5 cm^3 up to 25.0 cm^3 capacity. The column oven could be operated at temperatures from 35° up to 500° and was fitted with a single channel temperature controller; this provided linear temperature programming facilities for the oven. A flow splitting valve could be incorporated between the column exit and the detector, thereby allowing a small fraction (1/10, 1/25 or 1/100) of the carrier gas to go to the detector, whilst the majority of the flow was diverted to a cold trap loop or other trapping device in order that the separated compounds could be collected for other analyses. The detector was fitted with a second gas inlet, in addition to that from the column effluent, in order that the gas flow through the detector could be made up to the required volume when the splitter valve was in use. The minimum gas flow-rate specified for the detector was $40\text{ cm}^3\text{ min}^{-1}$; in all experiments described here a flow-rate of $50 \pm 5\text{ cm}^3\text{ min}^{-1}$ was used.

Many column packing materials for the separation of sulphur compounds are recommended in the literature. However, several of these materials, particularly those incorporating a liquid phase, are not suitable for use with an ECD, because its high sensitivity renders it very susceptible to contamination from column "bleed". For this reason, exclusively solid phase packing materials are recommended for use with an electron capture detector and the best materials for good separation of sulphur compounds appeared to be silica gel and Porapak.

In this work, two separating columns were used, a $100\text{ mm} \times 3.0\text{ mm}$ I.D. glass column filled with silica gel (Davison Grade, 100–200 mesh) and a $900\text{ mm} \times 4.0\text{ mm}$

I.D. glass column filled with Porapak R (80–100 mesh). Various column lengths were tested, but the above appeared to be the most satisfactory. The use of two different columns was necessary because complete separation of all the sulphur compounds and other electron capturing components likely to be present in CO₂ reactor coolant was not possible on a single column. Other compounds which could interfere with the analysis of sulphur were water and traces of halogenated organics. Where other strongly electron capturing molecules are present, it is necessary to ensure that they are all eluted from the column after an injection of sample; for instance, by heating the column to a high temperature. Otherwise they tend to build up on the column and bleed off slowly, leading to an eventual reduction in detector sensitivity.

The sulphur compounds which were analysed for were carbonyl sulphide (COS), hydrogen sulphide (H₂S), sulphur dioxide (SO₂) and methylmercaptan (CH₃SH), obtained from Cambrian Chemicals (Croyden, Great Britain), and carbon disulphide (CS₂), dimethyl sulphide ((CH₃)₂S), dimethyl disulphide ((CH₃)₂S₂) and thiophene (C₄H₄S) obtained from Hopkin & Williams (Chadwick Heath, Great Britain). In order to prepare standard mixtures of the sulphur compounds in CO₂ at ppb levels, the exponential dilution apparatus shown in Fig. 1 was employed. This comprised a 1.2-dm³ glass flask with a large PTFE-coated magnetic stirrer bar which was rotated at maximum speed. This flask was connected, as shown, via an injection head to a cylinder of CO₂ and to the chromatograph gas sampling valve, which was connected to a flow meter calibrated from 0 to 100 cm³ min⁻¹ in order to measure the flow through the exponential dilution flask. Initial dilutions of the sulphur compounds were made up in glass vessels fitted with injection septa and magnetic stirrers in order to give concentrations in the range 250–1000 ppm (v/v). Diluted samples were then injected into the CO₂ stream flowing into the exponential dilution flask to give concentrations between 50 and 1000 ppb (v/v) in the flask and the time and CO₂ flow-rate (generally 75 cm³ min⁻¹) were noted. By using various initial concentrations the efficiency of the mixing process was checked and found to be satisfactory. However, the CO₂ flow-rate could not be measured to an accuracy greater than ± 1 cm³ min⁻¹; therefore, in order to keep the error arising from flow measurements to *ca.* $\pm 3\%$ the

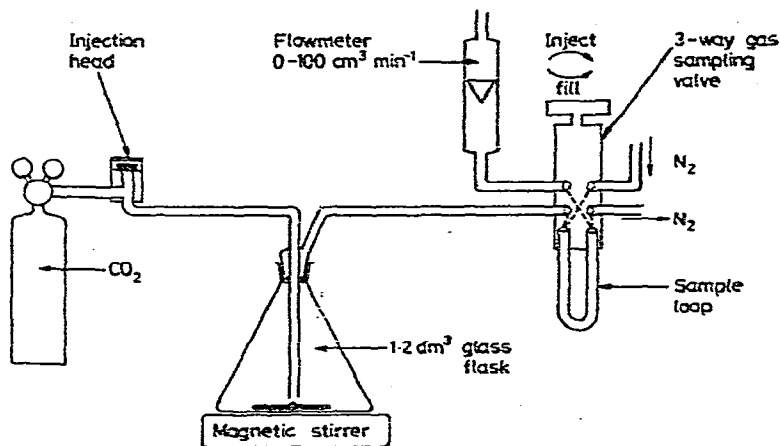


Fig. 1. Schematic arrangement of exponential dilution apparatus.

contents of the exponential dilution flask were never diluted by more than a factor of 20. In order to obtain pressurised gas samples at fixed concentrations for use with the pre-column concentration technique, gas mixtures were prepared in large glass flasks at pressures of *ca.* 2 atm, which was sufficient to provide a reasonably steady flow of gas through the pre-column.

The response of the detector is a function of concentration rather than mass. It is important, therefore, to use the same sample volumes and similar concentrations for standards and samples; also, since the detector response is linear only at low concentrations, samples must be suitably diluted to ensure that, if possible, the signal is linearly proportional to concentration. The response of the detector to each compound was examined over a range of detector temperatures and pulse spacings.

Pre-column technique

Several different pre-columns were tested, particularly varieties of silica gel, since work in the literature by Adams *et al.*¹¹ indicated that silica gel would trap out COS and other sulphur compounds from a CO₂-rich gas flow. However, in the present work, the silica gels examined were found to function poorly as a trapping medium for COS and H₂S in 100% CO₂. It was found, however, that a Porapak Q glass column (900 mm × 4.0 mm I.D.) used under the following conditions was very suitable for the collection of sulphur compounds.

The column was cooled in an ice-water bath at 0°, and mixtures of the sulphur compounds in CO₂ with concentrations ranging from a few ppb up to 500 ppb (v/v) were passed at a flow-rate of 50 cm³ min⁻¹ on to the pre-column. At these concentrations the volume of gas which could be loaded on to the pre-column before breakthrough occurred was independent of the concentration of the sulphur compounds. It was found that 1.5 dm³ of COS in CO₂ and 1.0 dm³ of H₂S in CO₂ could be loaded on to the pre-column before breakthrough of COS and H₂S, respectively, occurred; for the other sulphur compounds the maximum loading was much greater. The maximum capacity of the pre-column was, therefore, fixed on the breakthrough level for H₂S, *i.e.* 1.0 dm³ of CO₂.

The loaded pre-column was then transferred from the ice-water bath, positioned in the gas chromatograph oven and connected to a 25 cm³ glass loop which was attached to the gas sampling valve. The loop was held in a thermos containing liquid nitrogen and it contained some glass wool to provide an efficient trap for the compounds which would be eluted from the pre-column. Helium was then passed through the pre-column at a flow-rate of 150 cm³ min⁻¹ for 20 min in the opposite direction to the previous CO₂ flow through the pre-column, and the oven temperature was raised to 100°. This procedure was sufficient to elute all the sulphur compounds from the pre-column. After turning off the helium flow, the contents of the glass loop were injected on to the Porapak R column at room temperature. As soon as the glass loop contents were injected, the liquid nitrogen was withdrawn and the loop was immediately immersed in a hot water bath at 80°. The initial portion of the chromatographic trace consisted of merged signals arising from the high concentrations of helium and CO₂. The CO₂ peak arose because, in addition to the sulphur compounds and other compounds which were trapped on the pre-column, *ca.* 50 cm³ of CO₂ were also adsorbed. Therefore, the total volume of CO₂ which was passed on to the pre-column was 1050 cm³, rather than the 1000 cm³ measured at the pre-column exit. When the

pre-column was back-flushed with helium into the cooled glass loop the CO₂ solidified and, in the above procedure, it was important to immerse the glass loop in the hot water bath at the moment of injection in order to vaporize the CO₂ quickly, otherwise its peak tailed badly on the gas chromatograph column and could interfere with analysis of H₂S.

The H₂S peak appeared after *ca.* 5 min and was eluted within *ca.* 2 min, COS appeared after *ca.* 8 min. After 12 min at room temperature the column was programmed at 10° min⁻¹ up to 105°, H₂O was eluted during this temperature rise and also any SO₂ or CH₃SH were eluted. The column was held at 105° for 15 min and after *ca.* 10 min (CH₃)₂S and CS₂ were eluted. The temperature was then raised to 150° and (CH₃)₂S₂ was eluted after *ca.* 10 min at this temperature. This stepwise raising of temperature was preferred to a continuous temperature rise from room temperature, because it provided time for the system to settle down at the higher temperatures in order to provide a steady baseline before the compounds were eluted. It was found that above *ca.* 100° baselines tended to drift whilst the column temperature was increasing, probably because of column "bleed", which appeared to persist in spite of the initial column purges which were performed at 230°.

The pre-column acted to concentrate the sulphur compounds from a 1.0-dm³ sample of gas into a 25-cm³ volume for injection on to the gas chromatograph. Hence, in order to check recovery of sulphur compounds from the pre-column, the detector responses from the gas samples concentrated by the pre-column were compared with the responses from 25-cm³ samples of gas which were *ca.* 40 times more concentrated.

RESULTS AND DISCUSSION

The practical quantitative detection limits, *i.e.* for 10 cm³ samples of CO₂ injected on to the column, are listed in Table I in terms of ppb (v/v). For comparison, de-

TABLE I

DETECTION LIMITS OF SULPHUR COMPOUNDS WITH ELECTRON CAPTURE DETECTOR

Typical detection limits for the flame photometric detector towards sulphur compounds are *ca.* 2 ppb.

| Compound | Detector temperature (°C) | Detection limit in 10 cm ³ CO ₂ (ppb, v/v) | Pulse space (μsec) |
|--|---------------------------|--|--------------------|
| H ₂ S | 225 | 9 | 150 |
| | 250 | 12 | 150 |
| COS | 250 | 0.5 | 500 |
| | 250 | 1 | 150 |
| CH ₃ SH | 250 | 5 | 150 |
| (CH ₃) ₂ S | 250 | 50 | 150 |
| CS ₂ | 250 | 1 | 150 |
| | 350 | 0.2 | 150 |
| (CH ₃) ₂ S ₂ | 250 | 12 | 150 |
| | 350 | 3 | 150 |
| C ₄ H ₄ S (thiophene) | 250 | 500 | 150 |

tection limits obtained for some organochlorine compounds are given in Table II. The detection limit was defined in terms of a measurable and reproducible peak area on the chart recorder and this, in general, corresponded to a signal *ca.* 3–4 times the background noise level. Detection limits are given at the most sensitive detector temperature and pulse width and at a detector temperature of 250° and pulse width of 150 μ sec, since these conditions were subsequently chosen as representing the best compromise during a general analysis. Accurate data for SO₂ were not obtained because of severe sample losses on the column and injection parts. It has been stated by Koppe and Adams¹² that H₂S is also easily lost by absorption on metal and glass surfaces; however, in the present work with H₂S in dry CO₂ mixtures, this was not found to be a problem, but with mixtures which contained any water vapour, losses of H₂S were experienced.

TABLE II
DETECTION LIMITS OF CHLORINATED HYDROCARBONS WITH ELECTRON CAPTURE DETECTOR

| Compound | Detector temperature (°C) | Detection limit in 10 cm ³ CO ₂ (ppb, v/v) | Pulse space (μ sec) |
|---|---------------------------|--|--------------------------|
| C ₂ HCl ₃ (trichloroethylene) | 250 | 0.6 | 150 |
| C ₂ H ₃ Cl (ethyl chloride) | 250 | 8 | 150 |
| C ₂ Cl ₄ (tetrachloroethylene) | 250 | 0.1 | 150 |
| CH ₂ Cl ₂ (dichloromethane) | 250 | 2 | 150 |

It can be seen from Table I that with the exception of COS, a pulse space of 150 μ sec was the optimum setting. COS was anomalous in another respect, because it was the only compound exhibiting a negative response which occurred at a detector temperature of 125–175°, *i.e.* there was an increase in the standing current in the detector. This behaviour can arise if compounds are absorbed on the detector electrodes giving rise to a contact potential¹³. Indeed, for prevention of contamination and reproducibility of response the detector is generally operated at a temperature above 200°. The detector response to (CH₃)₂S₂ and CS₂ was *ca.* 5 times greater at the highest detector temperature of 350° than at 250°. For the other compounds the most sensitive response occurred between 225 and 275°; at lower temperatures than 200° sensitivities were generally reduced, possibly due to detector contamination. Increased sensitivity at a higher temperature is indicative of a dissociative electron capture reaction, whilst a decrease in sensitivity at higher temperatures indicates a non-dissociative reaction⁶.

The retention volumes of the various sulphur compounds and also water are presented in Figs. 2 and 3 over a range of temperatures for the Porapak R and silica gel columns. These data show that the sulphur compounds were eluted in a reasonable analysis time (*i.e.* <15 min with accompanying good ratio of peak height to width) over a very wide range of column temperatures. For instance, COS and H₂S were eluted in a few minutes at room temperature on both columns, but temperatures

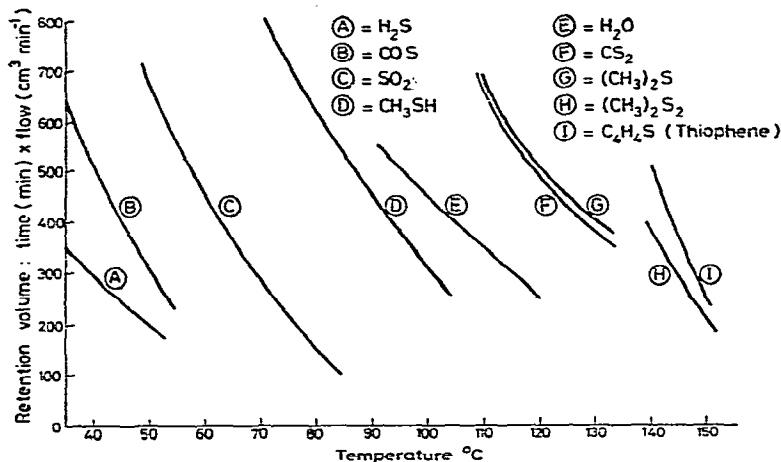


Fig. 2. Retention volumes of sulphur compounds and water on a 900 mm \times 4.0 mm I.D. glass column filled with Porapak R (80-100 mesh).

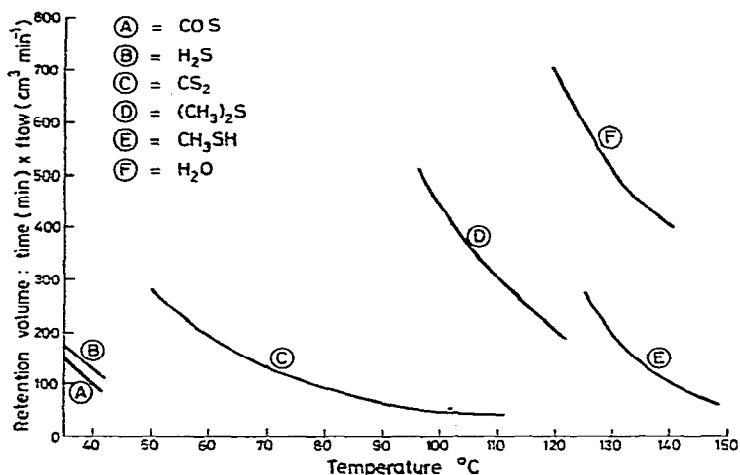


Fig. 3. Retention volumes of sulphur compounds and water on a 100 mm \times 3.0 mm I.D. glass column filled with silica gel (Davison Grade, 100-200 mesh).

above 100° were required to elute CS₂, (CH₃)₂S₂, (CH₃)₂S, and thiophene on Porapak R and (CH₃)₂S and CH₃SH on silica gel. Silica gel was a poor column for separating H₂S and COS but it was a better column than Porapak R for separating CS₂ and (CH₃)₂S.

Recovery of sulphur compounds using the pre-column technique was found to be >90% for COS, CH₃SH and (CH₃)₂S₂ from 1.0 dm³ of CO₂ containing concentrations of sulphur compounds down to 2-3 ppb (v/v). However, with concentrations of CS₂ below *ca.* 5 ppb and H₂S below *ca.* 20 ppb, there was some loss in the procedure and recoveries varied erratically. It was considered that >66% recovery of CS₂ and H₂S could not be guaranteed with concentrations below 3 ppb and 15 ppb, respectively.

The object of the technique was to concentrate the ^{35}S activity from 1.0 dm^3 of CO_2 reactor coolant in order to collect sufficient ^{35}S activity to determine the mass and activity of the sulphur compounds simultaneously. In conjunction with the pre-column technique the effluent from the gas chromatograph column was split and 1/11 of the column flow was directed to the detector, whilst 10/11 was collected for ^{35}S determination. Hence, the technique was not developed to attempt to improve the detection limits of the ECD, *i.e.* by collecting the sulphur compounds from 1.0 dm^3 of gas and then passing the whole amount through the detector. However, tests were performed in this mode of operation with low concentrations ($<1\text{ ppb}$) of COS in CO_2 and the technique was shown to be effective at trapping and recovering these very low concentrations of COS.

The detection limits obtained with the ECD are marginally better for COS than have been reported for the flame photometric detector and about an order of magnitude better for CS_2 . For CH_3SH , H_2S and $(\text{CH}_3)_2\text{S}_2$ they are slightly worse than for the flame photometric detector and for $(\text{CH}_3)_2\text{S}$ and thiophene they are about two orders of magnitude worse. The ECD response to other organic sulphur compounds may be qualitatively predicted from the above compounds, *i.e.* in comparison to the flame photometric detector it will be as sensitive towards disulphides, less sensitive towards mercaptans and much less sensitive towards thioethers.

The flame photometric detector requires three gas supplies (air, nitrogen and hydrogen) hence, in certain applications, *e.g.* for remote sampling or where weight is at a premium, the ECD, which requires only nitrogen, may have advantages. Major drawbacks, however, to the ECD in comparison with the sulphur specific flame photometric detector are its very good sensitivity towards halogenated compounds, which are often present in effluent gas streams, and its susceptibility towards contamination. Nevertheless, the response of the detector was reproducible from day to day, provided that high temperature purges were performed between series of sample runs.

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