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# GAS CHROMATOGRAPHIC SEPARATION OF SOME SULPHUR COMPOUNDS ON GLASS CAPILLARY COLUMNS USING FLAME PHOTOMETRIC DETECTION

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## SUMMARY

Due to the adsorptive properties of some sulphur compounds, gas chromatographic analysis of samples containing sulphur compounds requires columns proven to be inactive towards small amounts of certain test substances. Moreover, for reliable sulphur analyses using flame photometric detectors the columns should possess high resolution properties, since large amounts of hydrocarbons are known to quench the emission of small quantities of sulphur compounds when eluted simultaneously.

The purpose of this investigation is to exemplify the above statements with selective sulphur detection, and using glass capillary columns deactivated by a thin layer of non-extractable Carbowax 20M coated with SF-96. As a practical application, the gas phase of fresh tobacco smoke has been analyzed.

## INTRODUCTION

The flame photometric detector (FPD), presented in 1962 by Dräger and Dräger[1] and further developed for use in gas chromatography (GC) by Brody and Chaney[2], has been extensively used for the selective detection of volatile sulphur and phosphorus compounds. Several applications have been reported, such as the analysis of atmospheric sulphur compounds[3–8], of sulphur- and phosphorus-containing pesticides[9–11], of urinary volatile sulphur compounds[12] and of sulphur gases in soil atmospheres[13,14]. The GC separation has in most cases been performed on packed columns; the use of capillary columns seems to be rather uncommon. This might be due in part to the difficulty in preparing a capillary column which is sufficiently deactivated for the proper separation of sulphur compounds. Many sulphur compounds are extremely sensitive to adsorption and catalysis, and this is especially noticeable when they occur in low concentrations[15]. For example, if the "adsorption capacity" of the system is 20 pg for a given substance, adsorption will be very serious if the sample amount is 50 pg but hardly noticeable in the chromatogram if the amount of sample is 50 ng. Thus, an inert column system is a requisite for reliable analysis when utilizing the low limit of detection which is possible for sulphur with the FPD.

The low hydrocarbon response of the FPD is sometimes considered to be an advantage in the respect that separation would become less important[16]. However, large amounts of organic compounds are known to have a quenching effect on the sulphur response when eluted simultaneously[11,17–20]. For reliable quantitation, the sulphur compounds must therefore be separated from the major hydrocarbon peaks; in several cases, high-resolution capillary columns are required for such separations.

The use of deactivated Pyrex capillary columns for the separation of sulphur compounds is demonstrated in this paper. The detector employed was constructed at this laboratory.

## EXPERIMENTAL

Pyrex glass capillaries were drawn on a vertically operating Schimadzu glass-drawing machine, and etched with HF produced by the thermal decomposition of chlorotrifluoroethyl methyl ether[21]. They were then deactivated with a thin non-extractable layer of Carbowax 20M as described earlier[22] and coated dynamically[23] at a rate of 20 mm/sec with a solution of 10% (v/v) SF-96 methylsilicone in freshly distilled toluene.

The analyses were carried out on a home-made all-glass GC system; thus the only metal surface in contact with the sample was the needle of the injection syringe. The flame emission due to sulphur passed an interference filter (AGA Sweden) having a transparency maximum at 395 nm and a band width of 5 nm at half maximum, before being measured on a photomultiplier tube (EMI 9524B) operated at 1150 V The photomultiplier tube was enclosed in a glass cooler in which circulated acetone cooled by ice to 4°. The temperature in the flame section of the detector was 110°, and the temperature of the injection block was 120°.

Research cigarettes (University of Kentucky) were equilibrated at 65% relative humidity at 25° and smoked through a Cambridge filter by means of a 50-ml Hamilton glass syringe[24]. Puffs of 35 ml were drawn during 2 sec and at 1-min intervals. From the third puff, 5 ml of smoke was withdrawn by means of a gas-tight 10-ml syringe and injected in the gas chromatograph, the oven of which was cooled to −70° by spraying with liquid nitrogen. The oven temperature was then programmed to 190°.

## RESULTS AND DISCUSSION

In the detector modification used, the column effluent was mixed with hydrogen and led into the burner jet. The flame was thus similar to that of a conventional flame ionization detector (FID), Fig. 1. Such an arrangement was found to give the highest signal to noise ratio[25] and no solvent flame-out effects were experienced[25]. For 1-butanethiol, the optimum response was achieved with a hydrogen gas flow-rate of 190 ml/min and an air flow-rate of 120 ml/min. However, the response was found to vary somewhat between sulphur compounds, probably due to the different efficiency of the formation of $S_2$ species[26,27]. The flame was also supplied with nitrogen from the column, at a flow-rate which was relatively small, 0.9 ml/min, when capillary columns were used for the separation. Nitrogen is considered to be of great importance, acting as a third body for the formation of $S_2$ species[28–30]. Consequently the flame might be deficient in nitrogen. However, the addition of up to 10 ml/min of purge nitrogen

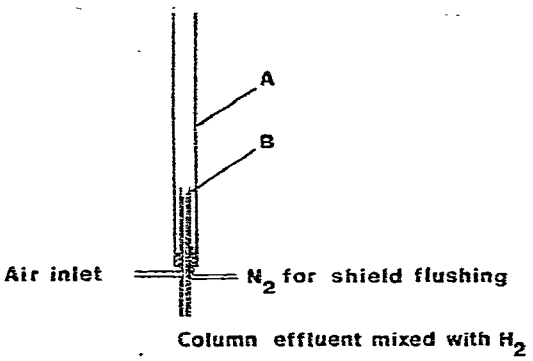


Fig. 1. Burner used in the flame photometric detector. A = Pyrex glass sheath and B = quartz tube jet (0.8 mm I.D.).

to the flame had no effect on the peak height for 1-butanethiol, and at higher purge rates the response was slightly lowered, probably due to cooling of the flame. It is assumed that nitrogen for the reaction is supplied by the air outside the flame. A further possibility is the action of the sheath wall as a third body in the formation of $S_2$ species[30,31].

The presence of organic compounds in the flame is found to decrease the sulphur response of the detector. This might be due to inactivation of excited $S_2$ species by collision with hydrocarbons and/or their decomposition products, as proposed by Sugiyama *et al.*[20]. The quenching effect of *n*-hexane on the response of 1-propanethiol was examined. The lowest amount of hydrocarbon that caused a detectable reduction of the sulphur response was 150 ng (Fig. 2). The reduction of sulphur response as a consequence of the presence of the hydrocarbon was essentially the same for 250 pg and 10 ng of 1-propanethiol. This was also observed by Sugiyama *et al.*[20] for benzo[*b*]-thiophene, but Perry and Carter[19] found an increased quenching effect of 2-methyl-1-propanol when the amount of 2-methyl-2-propanethiol was lowered. The importance of efficient separations for the detection of small amounts of thiophene in benzene is demonstrated in Fig. 3.

In some chromatographic systems, hydrocarbons cause a negative signal on the FPD. This is considered[32,33] to be due to a background of sulphur compounds being continuously eluted from the column, thus raising the baseline. However, the baseline

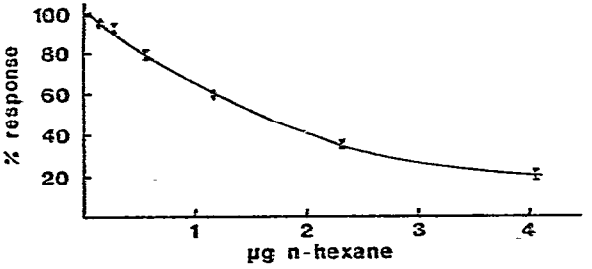


Fig. 2. Quenching effect of *n*-hexane on the response of 1-propanethiol. ▼ = 10 ng of 1-propanethiol; ▲ = 250 pg of 1-propanethiol. Pyrex glass capillary column (20 m × 0.25 mm I.D.), treated with Carbowax 20M and coated with SF-96.

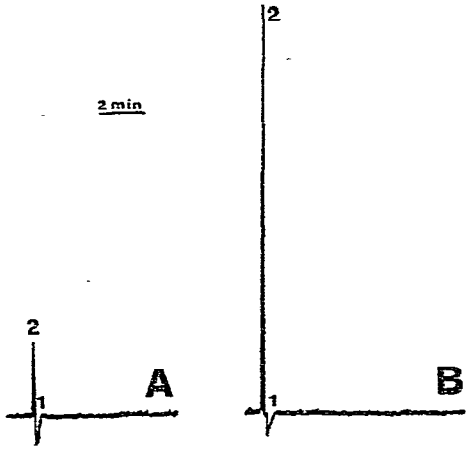


Fig. 3. Effect of separation power on the FPD response. Pyrex glass capillary column (90 m × 0.25 mm I.D.), treated with Carbowax 20M and coated with SF-96. 1 = Benzene; 2 = thiopene (100 pg). A = Poor separation at column temperature 110°; B = good separation at 28°.

is stable when programming the temperature up to 200°. This sulphur background response is quenched when a major hydrocarbon component is eluted, thus resulting in a negative peak. In the system used in this investigation a negative peak for *n*-hexane was first observed with a sample amount of 250 ng. Consequently slight quenching of sulphur compounds might take place at concentrations lower than those giving a response on the FPD. The detection limit for sulphur is *ca.* 40 pg, and this low detection limit might be explained by the enhancement in peak heights caused by the continuous background of sulphur eluting from the column[32,34]. The width and form of the negative hydrocarbon peaks depends to a considerable extent on the condition of the glass sheath of the detector. An adsorptive sheath leads to broad tailing hydrocarbon peaks. This peak-broadening effect was reduced when the sheath tube was continuously flushed with nitrogen at a flow-rate of 110 ml/min. In addition, the flushing should reduce the effect on the flame of sulphur and phosphorus compounds adsorbed on the sheath. However, silanization of the sheath caused a broadening of the hydrocarbon peaks, and this seems to be due to increased adsorption of hydrocarbons.

Using conventional flame photometry, Dagnall *et al.*[35] found that acetonitrile and pyridine produced intense CN emission at 389 nm. Moreover, the interference of CN bands has been reported[36] in the analysis of the pesticides Methidathion and Diazinon when measured at 383 nm. In my system, no positive response was observed for acetonitrile, pyridine or α-picoline, which otherwise would interfere in the analysis of the tobacco smoke.

Since the smallest detectable amount is limited by the noise level, it is essential to reduce the noise when attempting to obtain a low detection limit. The overall noise consists of several components: the flame, the interference filter, the photomultiplier and the electronics. The flame noise has been found to be dependent on the burner design[25,33] and the gas flow-rates. However, a great deal of the noise originates from the photomultiplier tube, and is reduced when the tube is cooled[5,37–39] (Fig. 4). In addition the dark current is lowered and stabilized[40]. The individual photomultiplier

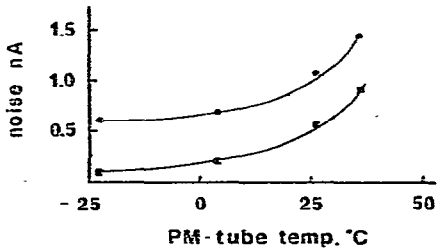


Fig. 4. The effect of photomultiplier (PM) temperature on the detector noise. ● = Flame on; ■ = flame extinguished.

tubes are found to differ somewhat. Thus it is important to optimize the tube voltage when attempting to achieve a high signal to noise ratio. The noise from a detector connected to a packed column might be reduced with the aid of an RC-filter[5,41], thus increasing the time constant of the detector. However, this method is quite unsuitable when capillary columns are used, since the narrow peaks eluted from these require a detection system showing a low time constant if a true peak representation is to be obtained. The highest frequency noise is suppressed due to the time constant of the amplifier and recorder.

Capillary columns have to some extent been used for the separation of sulphur compounds. Capillaries of materials such as stainless steel[42,43], nickel[12,39,44] and glass[45] have been used. These materials are considered to be active to sulphur compounds and some kind of deactivation is necessary. In most cases, this deactivation has been obtained by means of thick layers of polar stationary phases, and a final on-column deactivation was achieved by the injection of large amounts of a suitable sulphur compound. However, such deactivation does not seem to be sufficient, and in the results presented some of the sulphur compounds occurring in low concentrations formed broad and tailing peaks. It also appears that the polar phases have been chosen primarily for deactivation purposes, and that the chromatographic properties have been somewhat neglected. PTFE seems to be the most inert material[5–7]; however, its low critical surface tension does not allow coating of capillaries with the stationary phases used. It is possible to etch PTFE, *e.g.*, with sodium–naphthalene–tetrahydrofuran[46], thus improving its wettability. However, at this laboratory it was found that the inert properties were lost with such treatment.

Aue *et al.*[47] discovered that when Chromosorb W coated with Carbowax 20M was heat-treated to 280° and then exhaustively extracted, a thin non-extractable layer of phase remained. The support was found to possess a high degree of deactivation after this treatment. A further advantage is that the deactivated support can be coated with different stationary phases, *e.g.*, Carbowax or less polar phases; thus it is possible to adapt the chromatographic properties to the actual separation problem. This deactivation method has been applied in our laboratory to the deactivation of glass capillary columns[22], and in this investigation such deactivated columns are used for the separation of sulphur compounds. As column material, Pyrex glass was chosen due to its slightly acidic properties which are favourable for the slightly acidic sulphur compounds. The silicone oil SF-96 was found to be a suitable stationary phase for these analyses, since it gives highly efficient columns when using my coating methods[23].

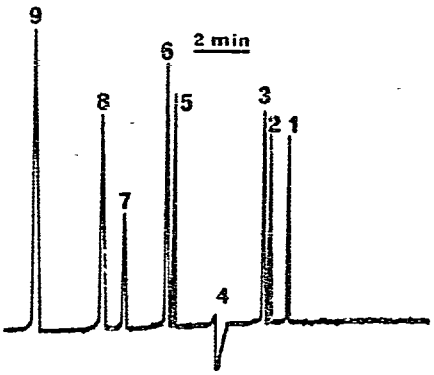


Fig. 5. Gas chromatogram (FPD) of a test mixture. Column as in Fig. 3. Column temperature, 28°. Sample amount, 75–300 pg. Peaks: 1 = methanethiol; 2 = dimethyl sulphide; 3 = carbondisulphide; 4 = *n*-hexane; 5 = 2-butanethiol; 6 = thiophene; 7 = diethyl sulphide; 8 = 1-butanethiol and 9 = dimethyl disulphide.

Moreover, the use of a non-polar phase minimizes the retention times and thus some of the possibilities for adsorption and catalysis. However, newly prepared columns showed a slight adsorption of sulphur compounds, and an additional deactivation was necessary. About ten injections of 50 ng of a sulphur compound, having a suitable boiling point, usually resulted in a deactivation that allowed reproducible peak heights. A chromatogram of a test mixture of methanethiol, dimethyl sulphide, carbon disulphide, 2-butanethiol, thiophene, diethyl sulphide, 1-butanethiol and dimethyl disulphide is shown in Fig. 5.

Using flame photometric detection, sulphur compounds in the gas phase of tobacco smoke have been analyzed on packed columns[48–51] and on nickel capillary

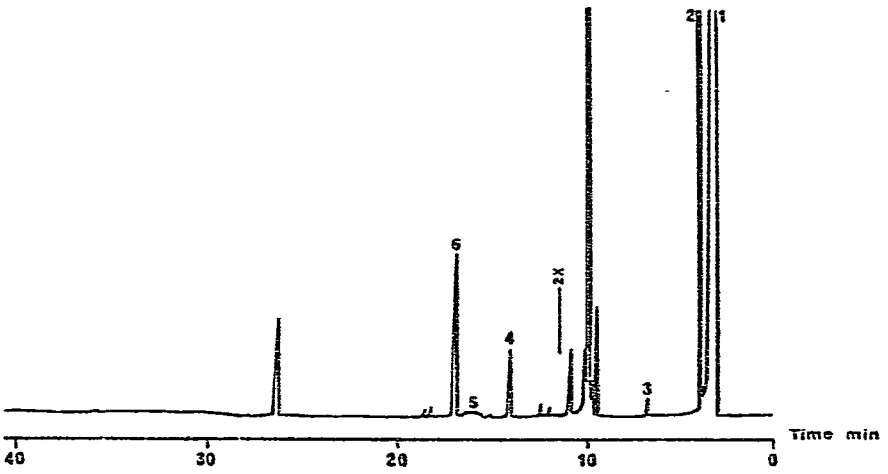


Fig. 6. Gas chromatogram (FPD) of the gas phase of tobacco smoke. Column as in Fig. 3. Splitting ratio, 1:145. Carrier gas, nitrogen. Initial temperature on injection, −70°; programmed to −5° at 25°/min and to 190° at 5°/min. Peaks: 1 = hydrogen sulphide; 2 = carbonyl sulphide; 3 = sulphur dioxide; 4 = thiophene; 5 = unknown and 6 = dimethyl disulphide.

columns[39,44]. A reduction in sulphur response due to the quenching effect of organic compounds is certainly a possibility when packed columns are used for the separation. Due to the large number of components in the tobacco smoke, the risk of artefact formation is unusually high. This has been demonstrated by Horton and Guerin[48] for the analysis of sulphur compounds in tobacco smoke. They found drastic losses of $H_2S$ when the smoke was in contact with stainless steel for 4 sec. When aging the smoke for 30 sec in a stainless-steel loop, a substantial increase in higher-molecular-weight sulphur components was observed, probably formed by the reaction of low-molecular-weight sulphur compounds, *e.g.*, $H_2S$ and other constituents of the smoke. These observations indicate the need for inert chromatographic systems as well as sampling methods. Trapping the smoke on an adsorbent such as Tenax GC[39,44] might introduce artefacts and losses: the use of an unsuitable transfer line from the smoking device to the chromatograph might have the same effect. The injection of fresh tobacco smoke by means of a glass syringe is assumed to minimize the formation of artefacts[24,52–55]. It is also likely that artefacts are formed in the injection part of the chromatograph. Thus it is essential to keep the injection temperature as low as possible and to minimize the sample residence time in the injection system.

A typical gas chromatogram (FPD) of a relatively low amount of fresh tobacco smoke is shown in Fig. 6 and that of a somewhat larger sample is shown in Fig. 7. In the case of compounds present in low concentrations, especially those disposed to adsorption, the peak form might be improved if the sample amount is increased, as can be seen when comparing peak 5 in Figs. 6 and 7; the large peaks, however, show slight tailing in Fig. 7, which is probably due to overloading of the column. The relation between the amounts of the reactive substances $H_2S$, COS and $SO_2$, respectively, agrees with the results achieved by Horton and Guerin[48] when special precautions are taken in order to avoid artefacts; our deactivation thus seems to be equivalent. Moreover, when using nickel capillary columns, Bertsch[39] found a large number of higher-molecular-weight sulphur compounds in high concentrations. Our results, however, show the presence of only a few high-intensity peaks and a considerable

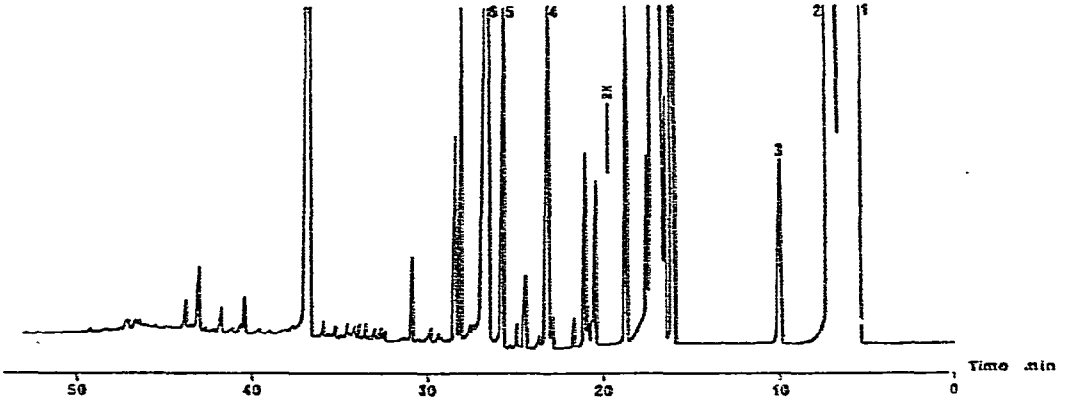


Fig. 7. Gas chromatogram (FPD) of the gas phase of tobacco smoke. Column as in Fig. 3. Splitting ratio, 1:7. Initial temperature on injection, −70°; programmed to 195° at 5°/min. Peaks: 1 = hydrogen sulphide; 2 = carbonyl sulphide; 3 = sulphur dioxide; 4 = thiophene; 5 = unknown and 6 = dimethyl disulphide.

number of sulphur compounds occurring in low concentrations; these findings also seem to agree with the results obtained by Horton and Guerin[48] for the analysis of sulphur compounds in the gas phase of tobacco smoke.

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