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THE COUPLING OF THE FLAME PHOTOMETRIC DETECTOR AND THE FREE FATTY ACID PHASE (FFAP) CAPILLARY COLUMN IN THE TRACE ANALYSIS OF SULPHUR COMPOUNDS

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SUMMARY

Trace amounts of sulphur compounds in gaseous mixtures, in organic liquids and in particulate matter were detected by means of a photometric detector coupled with a FFAP capillary column.

This system permitted the detection of some sulphur compounds in citrus oils and confirmed that the odour of diesel exhausts is not due to the presence of sulphur compounds.

INTRODUCTION

The trace determination of sulphur compounds in gaseous and liquid mixtures can be successfully carried out by gas chromatography by coupling a high-efficiency glass capillary column, coated with FFAP, with a flame photometric detector (FPD). It was previously pointed out that FFAP columns exhibit a much higher efficiency than any other stationary phase for the analysis of complex mixtures, such as the exhaust gases of diesel engines[1] and essential oils[2]. The flame photometric detector, designed by BRODY AND CHANEY[3], has a specific response for sulphur compounds; it is arranged with a photomultiplier tube viewing a region above the flame through a narrow-band optical filter.

When sulphur compounds are introduced into the hydrogen-rich flame, they produce a strong luminescence between 300 and 423 nm. By using a filter that permits transmission at 394 ± 5 nm, a selectivity ratio of sulphur to non-sulphur compounds between 10,000:1 and 30,000:1 is achieved.

Such a gas chromatographic system was used to detect sulphur compounds in a gaseous mixture (an odoriferous additive mixture in town gas), in organic liquids (citrus oils) and in a sample of particulate matter (emissions from diesel engines).

EXPERIMENTAL

A flame photometric detector with a 750 V power supply and electrometer

(Tracor Inc., Austin, Tex., U.S.A.), assembled on a gas chromatograph (Carlo Erba, Milan, Model G.I. 450), was used.

The column consisted of an 80-m glass capillary of 0.28 mm I.D. coated with FFAP: a 15% solution of FFAP in methylene chloride solvent was made to flow very slowly (6.5 cm/min) through the capillary and the solvent was then volatilized in a stream of nitrogen.

This column yields a HETP value of 0.40 mm for *n*-hexadecane (capacity ratio, $k' = 3.31$). The flow-rate through the column was about 0.5 ml/min at room temperature with a carrier gas (nitrogen) inlet pressure of 0.5 kg cm^2.

The detector temperature was maintained at 115°. The detector gases, of research grade, were previously purified by means of 4A molecular sieve traps. The optimum flow-rates were found to be 150 ml/min for hydrogen, 10 ml/min for oxygen and 30 ml/min for air.

RESULTS AND DISCUSSION

Fig. 1 shows the gas chromatogram obtained under isothermal conditions (50°) by injecting the vapour of a prepared mixture containing mercaptans, sulphides and disulphides; it can be seen that the FPD is particularly useful for the evaluation

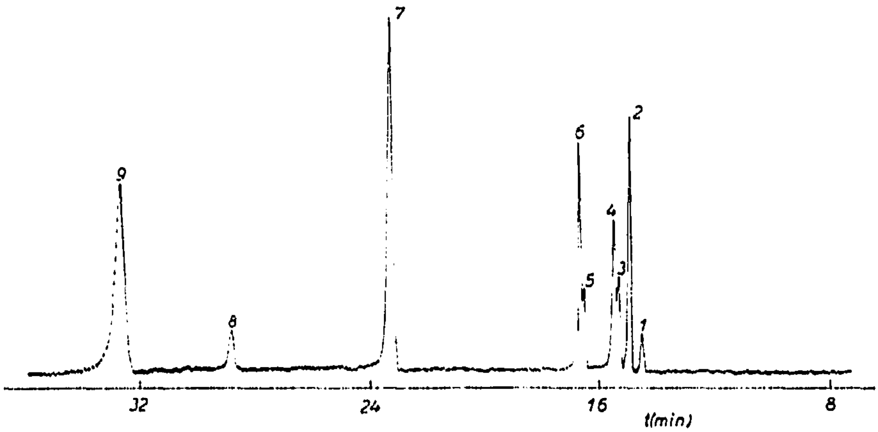

Fig. 1. Gas chromatogram of a mixture of sulphur compounds. Conditions: 80-m glass capillary column coated with FFAP; temperature, 50°; carrier gas, N_2, 0.5 ml/min; flame photometric detector. 1 = Hydrogen sulphide; 2 = sulphur dioxide; 3 = methyl mercaptan; 4 = carbon disulphide; 5 = dimethyl sulphide; 6 = ethyl mercaptan; 7 = thiophene; 8 = dimethyl disulphide; 9 = tetramethylene sulphide.

of sulphur compounds with different chemical structures, owing to the fact that the radiation detected by the FPD is due exclusively to the S_2 group. A similar chromatogram obtained on a gaseous mixture used as an odoriferous additive to town gas is shown in Fig. 2.

Essential oils

The determination of all the constituents of essential oils is of great interest for characterizing a flavour in terms of a chromatographic spectrum of the olfactory

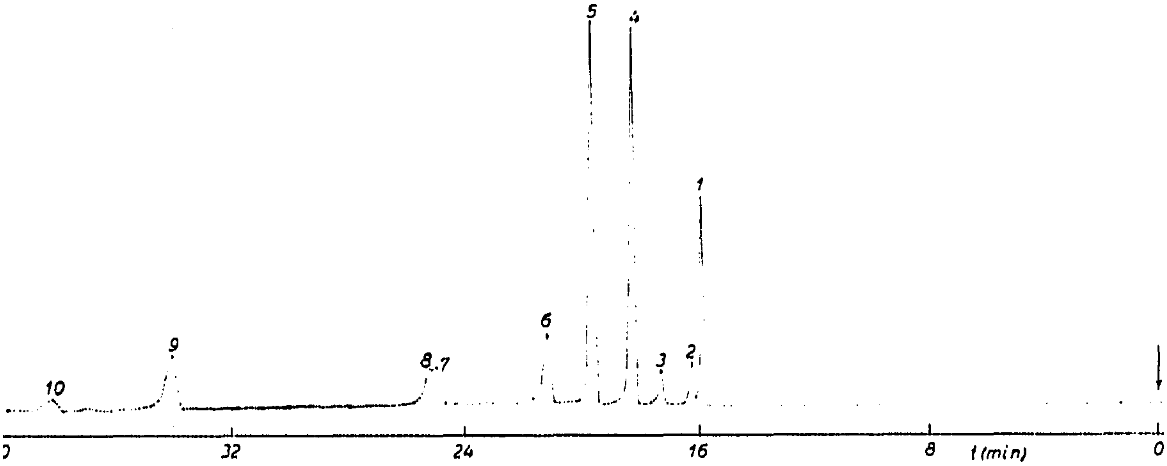

Fig. 2. Gas chromatogram of a mixture of sulphur compounds used as an odoriferous additive in town gas. Isothermal temperature, 40°; other conditions as in Fig. 1. 1 = Dimethyl sulphide; 2 = ethyl mercaptan; 3 = isopropyl mercaptan; 4 = *n*-propyl mercaptan; 5 = diethyl sulphide; 6 = *sec.*-butyl mercaptan; 7 = *n*-butyl mercaptan; 8 = thiophene. Peaks 9 and 10 were not identified.

properties. It has been recently shown[4] that about 340 peaks are present in a chromatogram of orange oil produced on the same column as we used and that almost the same number of compounds are contained in other citrus oils.

The replacement of the FID with the FPD permitted the detection of sulphur compounds in several citrus oils. The chromatograms in Fig. 3 were obtained on orange, lemon, tangerine and bergamot oils, originating from Murcia (Spain) and Sicily (Italy).

From a comparison of these chromatograms, we concluded that the number of sulphur compounds present in the oils changes only for oils from different fruits, and that there is no quantitative difference between oils from the same fruit obtained from different sources. The analyses were performed under the same operating conditions by eluting 2 µl (1:20 splitting ratio) of each oil under isothermal conditions (120°).

Although the substances detected are present only in trace amounts, it is possible that they make a significant contribution to the aroma. Attempts at extraction with $AgNO_3$ solution showed that such compounds are not characterized by the presence of the functional –SH group of mercaptans; in fact, there is no difference between the chromatograms obtained on residues from the extraction and those obtained on the original oils.

Emission from diesel engines

One of the most important problems in air pollution control is the evaluation of the odour emission from diesel engines. In a recent paper, GORETTI AND LIBERTI[1] succeeded by means of a FFAP column in analyzing material condensed from the exhaust gases of diesel engines operating under controlled conditions. The analysis was carried out on the ethereal extracts from the particulate matter. The presence of about 200 components was demonstrated; the same substances are present in the

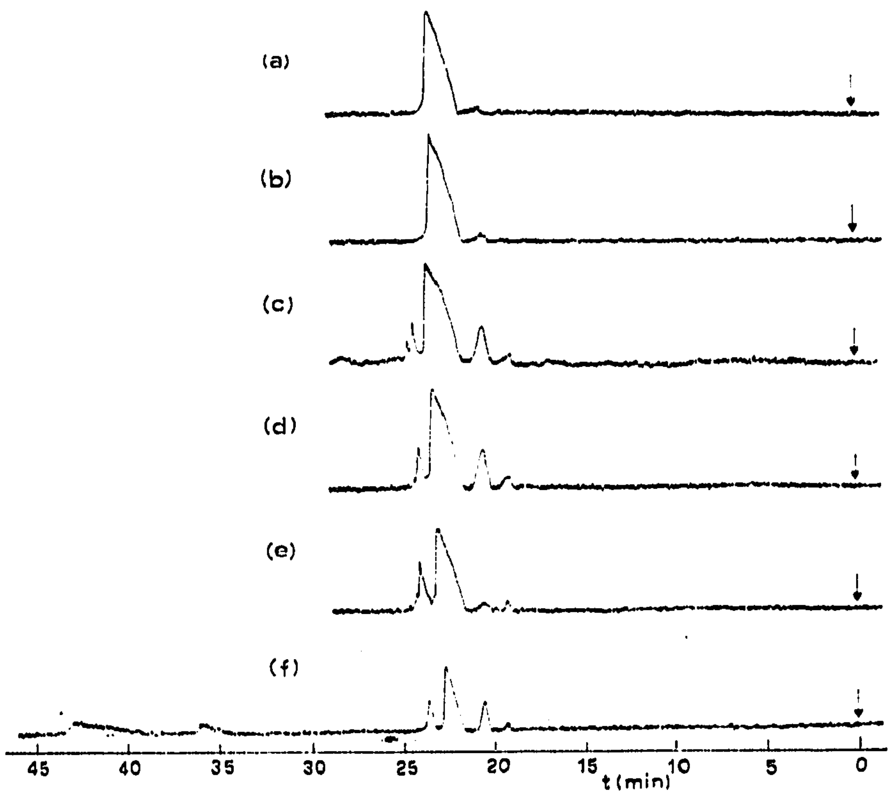

Fig. 3. Gas chromatograms of sulphur compounds contained in trace amounts in citrus oils. Isothermal temperature, 120°. (a) Orange (Murcia); (b) orange (Sicily); (c) lemon (Murcia); (d) lemon (Sicily); (e) tangerine (Sicily); (f) bergamot (Reggio Calabria).

ethereal extracts from aqueous condensates obtained by passing the exhaust gases through cold traps.

The FPD detects only trace amounts of three compounds, as shown in the chromatogram in Fig. 4. As the analyses of four samples taken during different power cycles of the engine (from 1200 to 2400 rev./min) resulted in identical chromatograms, it can be said that the generation rate and the number of sulphur compounds do not change with different operating conditions of the engine. Moreover, as these compounds are present in only trace amounts in comparison with oxygenated substances, it can be deduced that the odour of the exhaust gases from diesel engines cannot be ascribed to these compounds.

This result is in agreement with the results achieved by CIOFFI *et al.*[5], who dem-

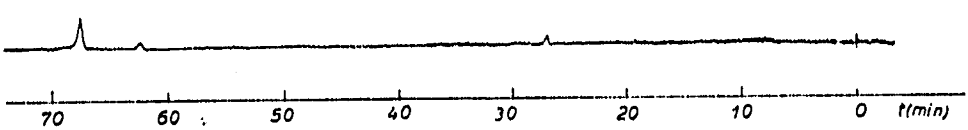

Fig. 4. Trace amounts of sulphur compounds detected in particulate matter from diesel engine exhausts. Programmed temperature: 80 to 205° at 1.25°/min.

onstrated the stoichiometric oxidation to sulphur dioxide of the sulphur present in diesel oil. This theory is also confirmed by the results of studies by AARONSON AND MATULA[6] and WESSLER[7], who, after fuelling engines with sulphur-free hexadecane and *n*-heptane still obtained evil-smelling exhaust gases.

CONCLUSION

From the results reported in this paper, we concluded that the coupling of the FFAP capillary column with the FPD could be satisfactorily used as a versatile technique for the analysis of complex mixtures of sulphur compounds. This system enabled, for the first time, the presence of sulphur compounds in citrus oils to be shown and confirmed that sulphur compounds cannot be involved in the odour of the extract of the particulate matter from diesel engine emissions.

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