

CHROM. 9528

CONTINUOUS ELEMENTAL ANALYSIS OF SULPHUR-CONTAINING SUBSTANCES BY GAS CHROMATOGRAPHY

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(Received March 17th, 1976)

SUMMARY

A method has been developed for the continuous determination of the carbon-to-sulphur ratio for the identification of components separated by gas chromatography. Components leaving the gas chromatograph are hydrogenated in a stream of hydrogen over a platinum gauze to produce methane, hydrogen sulphide, ammonia and water. The ammonia and water formed are absorbed before the gas mixture reaches the first detector, which thus records the amount of methane and hydrogen sulphide. A second absorber placed before the second detector removes the hydrogen sulphide, so that the second detector records the amount of methane formed. In this way, the C:S ratio can be determined for all of the components.

INTRODUCTION

In recent years gas chromatography (GC) has been used for the determination of the contents of carbon, hydrogen and also sulphur in organic substances. However, the methods which have been described are useful only for pure materials; *i.e.*, the procedure is similar to that used in classical elemental analysis and only the final step of such a determination is replaced by GC, which separates the individual components formed during decomposition of the analyzed material.

There are only a few methods which employ GC in this way to determine substances whose molecules contain sulphur. For example, Chicherina *et al.*¹ combusted the material at 1000° and then used GC to separate sulphur dioxide from carbon dioxide formed from carbon and acetylene formed from water by reaction with calcium carbide. The water formed is a product of the reaction between the hydrogen and oxygen in the molecule. Beuerman and Meloan² combusted the material at 850°, solidified the gaseous products by use of liquid nitrogen and then carried out the chromatography. Chumachenko and Aleksayeva³ also combusted the organic substance, and the combustion products were then chromatographed. Schuessler⁴ combusted the material in pure oxygen and chromatographically separated sulphur dioxide from the remaining combustion products. Mesaric⁵ determined sulphur in the presence of oxygen by oxidation on silver permanganate, where carbon monoxide is oxidized to carbon dioxide and sulphur is converted into carbonyl sulphide and

carbon disulphide. Another sensitive method of determining substances present in chromatographic mixtures containing sulphur is the use of special GC detectors, which are sensitive to the presence of this element in the molecule. Such detectors are the flame photometric detectors⁶, which are also sensitive to the presence of phosphorus, and the electrolytic detector⁷.

So far, no method is known which would enable both the identification of the peaks on a chromatogram of a sulphur-containing substance and the simultaneous determination of the sulphur-to-carbon ratio. Recently we have developed two methods, one of which enables the determination of the carbon-to-hydrogen ratio for all of the substances separated by GC⁸ and the second of which determines the carbon-to-nitrogen ratio⁹ in a similar way, if nitrogen is present in the molecule. The methods are based on almost simultaneous recording of the signals from two detectors, through which passes a mixture resulting from the decomposition of the chromatographically separated components, while one⁸ of the gaseous components is absorbed in the space between the detectors using a suitable absorption agent.

The present study is concerned with a similar method for the determination of the carbon-to-sulphur ratio in components leaving a chromatographic column. The method is sufficiently similar to the previous methods that it can be carried out on the same instrument under different experimental conditions. The principle of the method depends on the fact that components leaving a chromatographic column in a stream of hydrogen carrier gas are catalytically decomposed on platinum gauze at an elevated temperature. Methane is produced from the carbon present in the molecule, ammonia is produced from nitrogen, hydrogen sulphide from sulphur and water from oxygen. The mixture of these gases is first fed into an absorber where the water and ammonia are removed, and then the mixture of methane and hydrogen sulphide is led to the first thermal conductivity detector where their total amount is determined. The gases are then led through an absorber where the hydrogen sulphide is removed, so that the second thermal conductivity sensor records only the amount of methane. The two signals from the chromatographic detectors are recorded and compared and the C:S ratio can then be determined for all of the components of the chromatographed mixture; the components which contain sulphur can also be distinguished.

EXPERIMENTAL

Chromatographic separations were carried out on a chromatograph equipped with a combustion detector¹⁰, which was adapted by the addition of a thermal conductivity detector. The apparatus is depicted in Fig. 1. The carrier gas (hydrogen) was led from gas cylinder (1) through gas purifier (2), manostat (3) and manometer (4) into the reference cells of the thermal conductivity detectors (7) and (8) and then through the chromatographic column (6) which was fitted with an injection block (5), combustion oven (9) and flow-meter (13). The first absorber (10) was connected between the oven (9) and detector (7), and the second absorber (11) was placed between the detectors (7 and 8). Both of the detectors (7 and 8) were connected to a recorder (12). The combustion oven (9) contained a quartz-glass tube (*ca.* 15 cm × 5 mm I.D.), in which was placed the platinum gauze. The oven was heated by means of a resistance coil. The temperature of the zone containing the platinum gauze was 800°. The gas purifier (2) comprises a set of glass tubes; the first of these tubes contained CHZ

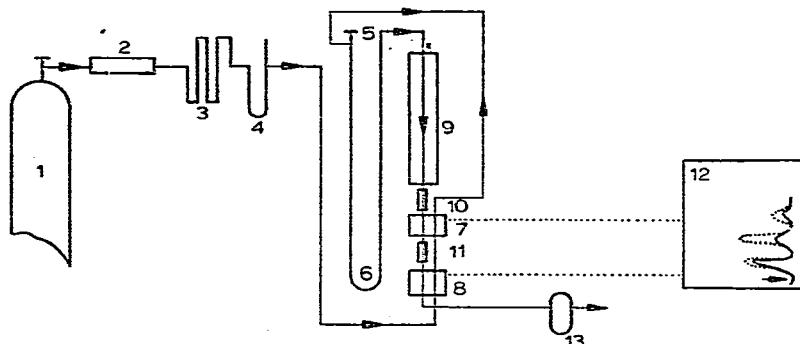


Fig. 1. A diagram of the apparatus for continuous elemental analysis of sulphur-containing components separated by gas chromatography.

ČSSP 9025 catalyst to remove oxygen, the second contained a molecular sieve and magnesium perchlorate to remove water, and the third contained phosphorus pentoxide deposited on cotton wool to remove the remaining traces of water. The size of the tubes chosen was dependent on the amount and purity of the hydrogen employed. The first absorber (10), employed to remove water and ammonia, comprised a glass tube (10 cm × 0.4 cm I.D.) which was half-filled with magnesium perchlorate and half with phosphorus pentoxide. The second absorber (11) comprised a glass tube (10 cm × 0.4 cm I.D.) containing caustic soda. This absorber was used to remove hydrogen sulphide. As previously^{8,9}, either a two-pen or a single-pen recorder can be used, equipped with a switch, changing the signal from one detector to the other every 5 sec. The sensitivity range of the detector was 0–1 mV. The thermal conductivity sensors were powered by a 6-V stabilizer. The baselines for recording the signals from the two detectors were made to coincide.

The sample size was the same as that used for normal chromatography. The chromatographic column had a convenient length; the packing and temperature were chosen according to the mixture to be separated. Here, a 150-cm glass column was used and was packed with Chromosorb G impregnated with 10% Dexsil 300 GC. According to the requirements of the system to be analyzed, the temperature of the column was varied between 110 and 295°. A suitable hydrogen carrier-gas flow-rate was 1.0–2 l/h. For calibration, known substances containing sulphur were used; the ratio of the area of the CH₄ + H₂S peak to that corresponding to CH₄ alone was determined. The areas of these two peaks were determined for all of the substances separated by GC.

RESULTS AND DISCUSSION

As in the determination of the C:H and C:N ratios, it is necessary that in the determination of the C:S ratio the method used should enable both the identification of sulphur-containing substances on the chromatogram and at least an approximate determination of the carbon to sulphur ratio. The results given in Table I should be evaluated on this basis. It is obvious that the precision of the determination of the C:S ratio is somewhat worse than that obtained by classical elemental analysis; however, it is sufficient to enable identification to be carried out.

TABLE I
DETERMINATION OF THE C:S RATIO

Compound	C:S Ratio		ΔS^*	No. of determinations
	Theoretical	Found		
Carbon disulphide	0.5:1.0	0.5:0.98	-0.02	16
Diethyl sulphide	4.0:1.0	4.0:1.00	0.00	12
Butyl propyl sulphide	7.0:1.0	7.0:1.00	0.00	4
Dibutyl sulphide	8.0:1.0	8.0:1.03	+0.03	8
Diisopentyl sulphide	10.0:1.0	10.0:0.98	-0.02	3
Ethyl phenyl sulphide	2.0:1.0	2.0:0.91	-0.09	6
Phenyl propyl sulphide	3.0:1.0	3.0:1.03	+0.03	14
Benzyl methyl sulphide	2.0:1.0	2.0:0.95	-0.05	6
Benzyl ethyl sulphide	3.0:1.0	3.0:0.98	-0.02	8
Benzyl propyl sulphide	4.0:1.0	4.0:1.02	+0.02	10
Cresyl methyl sulphide	2.0:1.0	2.0:0.93	-0.07	5
Cresyl ethyl sulphide	3.0:1.0	3.0:1.05	+0.05	5
Cresyl propyl sulphide	4.0:1.0	4.0:0.98	-0.02	4

* Difference between found and theoretical value for sulphur.

As mentioned, two signals were recorded, one corresponding to the sum of methane and hydrogen sulphide (provided that the substance contains sulphur), the other to methane alone. Consequently, when the substance did not contain sulphur, the areas of the peaks from the two detectors were identical. This is illustrated in Fig. 2, showing the recordings from the two detectors and where the peak corresponding to the signal from the second detector is slightly shifted. In order to obtain accurate results, it was necessary to first inject a standard substance into the chromatograph, *i.e.*, a substance with a known C:S ratio. The recorded peak areas were then used for further calculations in which the C:S ratio was determined from the difference in peak areas corresponding to the sum of methane and hydrogen sulphide and that due to methane alone.

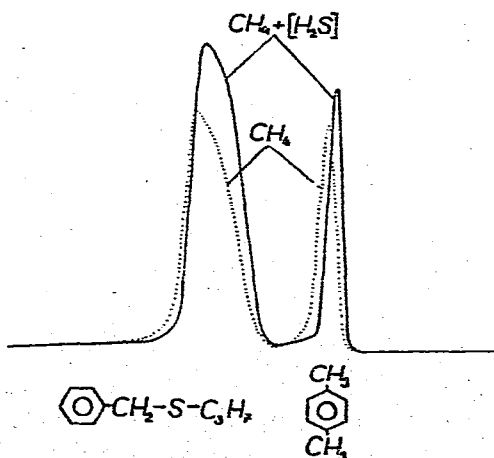


Fig. 2. Chromatogram of a mixture of xylene and benzyl propylsulphide. Column: Dexsil 300 GC on Chromosorb G; temperature, 275°; hydrogen carrier-gas flow-rate, 1 l/h.

It is important to note that substances containing an aromatic ring behave as if this aromatic centre were absent. Apparently, under the conditions chosen, a phenyl group dissociates in the same manner as benzene or other aromatic substances. Consequently, phenyl sulphides behave as if the phenyl group is replaced by hydrogen. A benzyl group, from which a phenyl group dissociates, loses its $-CH_2$ group as methane. The methyl group in cresyl sulphides also yields methane. This dissociation mechanism on the platinum gauze is probably caused by the fact that the temperature is not very high (800°), so that only partial molecular destruction occurs. Preliminary experiments showed that all of the aromatic substances behaved in this way, and this observation will be exploited in a study dealing with further problems in the identification of individual chromatographic peaks.

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