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GAS CHROMATOGRAPHIC DETERMINATION OF SULPHUR COMPOUNDS IN GASES USING A SINGLE-FLAME THERMIONIC DETECTOR

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SUMMARY

For both qualitative and quantitative determinations of individual sulphur compounds in technical gases from coal treatment, gas chromatography can be used. In order to separate these compounds, a column packed with Porapak Q, operating at 120° and using nitrogen as carrier gas, was employed. Under these conditions nearly a 100% separation of hydrogen sulphide and carbonyl sulphide was attained, which is essential in analysing gases from coal gasification.

To detect sulphur compounds in technical gases, a selective thermionic detector with a pressed caesium chloride tip was used with regard to a high content of further components in gases (carbon monoxide, carbon dioxide and hydrocarbons) and trace amounts of sulphur substances, except hydrogen sulphide.

The analysis of technical gases from pressure gasification of brown coals revealed that, in addition to a known amount of hydrogen sulphide, they contain mainly methyl mercaptan, carbonyl sulphide and trace amounts of carbon disulphide. Contrary to expectation, neither higher concentrations of carbonyl sulphide and carbon disulphide nor trace amounts of higher organic sulphur compounds [C_2H_5SH , $(CH_3)_2S_2$, etc.] were found.

INTRODUCTION

In view of the general problem of atmospheric pollution, a better knowledge of the contents of sulphur compounds in technical gases obtained from the pressure gasification of brown coals in the production of town gas is desirable. During this process, the sulphur contained in coal is transferred to the pressure gas, from which it is subsequently removed.

Sulphur in raw pressure gas occurs mainly as hydrogen sulphide (*ca.* 92–95%), the remainder being organic sulphur compounds, including CS_2 , COS , CH_3SH , $(CH_3)_2S$, C_2H_5SH , $(C_2H_5)_2S$, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$. In pressure gas plants, these substances are removed from the gas by washing with methanol at low temperatures and under pressure. During this process (Rectisol process), gases rich in carbon dioxide, hydrogen sulphide and the above sulphur compounds are formed.

For the final treatment of these gases, either by combustion or by their conversion into other sulphur compounds (H_2SO_4), the formation and reactions of sulphur compounds during the production and purification of pressure gas should be known.

The considerable volatility of most of these compounds permits us to use gas chromatography for their determination. Contrary to the methods used up to now, based on oxidation or reduction of organic sulphur compounds, gas chromatographic determinations can be carried out without their separation from a considerable excess of hydrogen sulphide. Moreover, they can be separated into individual components.

For separating organic sulphur compounds several types of polar liquid phases have been recommended¹⁻⁷. According to our experience, most of these phases are not suitable for such a purpose even if capillary columns are used, owing to the low separating capacity of these columns for hydrogen sulphide and carbonyl sulphide. As Hachenberg^{8,9} claims, Porapak Q is suitable for the separation of these two compounds. In applying the gas chromatographic analysis of sulphur compounds to the analysis of technical gases, a high efficiency of separation of mixtures of these two compounds in the presence of a considerable excess of hydrogen sulphide is necessary.

In addition to sulphur components, some other compounds in gases are also eluted, mainly carbon monoxide, carbon dioxide, hydrogen, methane and hydrocarbons. Currently used detectors, such as thermal conductivity (TCD) and flame-ionization detectors (FID), are also very sensitive to these substances. Hence the most important consideration in the analysis of sulphur compounds in the presence of these other substances is the use of highly sensitive and selective detectors such as the flame photometric detector (FPD) and the thermionic detector (TID).

We carried out a number of tests using the TID. In comparison with the sophisticated construction of the FPD, the advantage of the TID is that any FID can be converted into a TID according to Dressler and Janák¹⁰.

EXPERIMENTAL

Apparatus

A Chrom 4 chromatograph with a 2.5 m × 3.0 mm I.D. column packed with Porapak Q (60-80 mesh) was employed. Other chromatographic conditions are given in Table I.

TABLE I

CONDITIONS FOR SEPARATION OF HYDROGEN SULPHIDE, CARBONYL SULPHIDE AND ORGANIC SULPHUR COMPOUNDS

<i>Condition</i>	<i>Value</i>
Column temperature	116-120°
Overpressure of carrier gas (nitrogen)	0.133 MPa
Hydrogen flow-rate	26-31 ml/min
Air flow-rate	500 ml/min
Sensitivity	1:5000
Chart speed	10 mm/min
Background current	$3.8 \cdot 10^{-8}$ A
Alkali metal salt	CsCl (pressed)

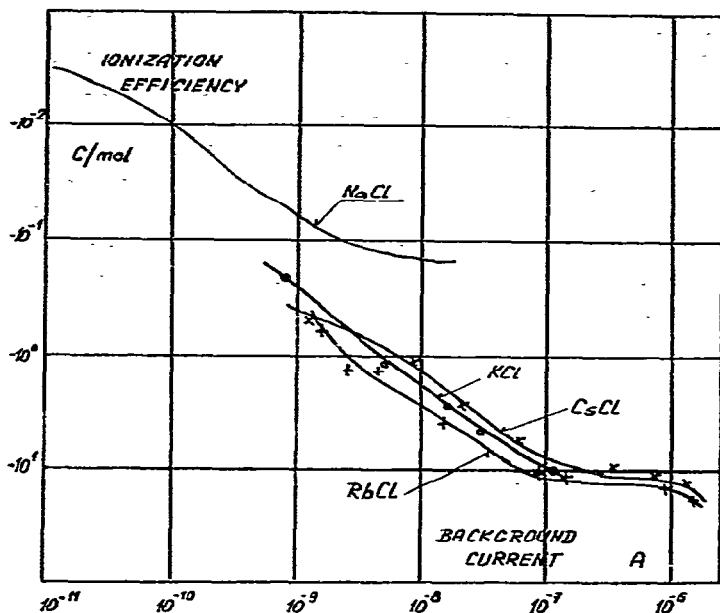


Fig. 1. Diagram of ionization efficiency of TID for hydrogen sulphide versus background current for various alkali metal chlorides.

Materials and methods

In order to obtain preliminary qualitative results, pure carbonyl sulphide, methyl mercaptan and nitrogen were used for the preparation of standard mixtures. The standard mixtures of gases were prepared in glass pipettes under a pressure of 0.356 MPa without using a sealing liquid, because it is always absorbing one of the components of the mixture and also sampling for chromatographic purposes by means of a syringe is easier.

The dependence of the ionization efficiency on the intensity of the background current according to Dressler and Janák¹¹ was determined, and indicated that with the mixture nitrogen-1% (v/v) hydrogen sulphide the intensity of the negative response

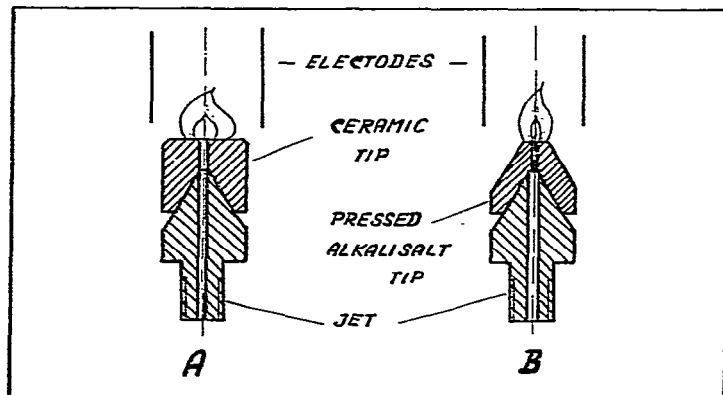


Fig. 2. Tips of TID: (A) ceramic tip; (B) pressed alkali metal salt tip.

increases according to the type of alkali metal chloride used in the order $\text{Na} < \text{K} < \text{Cs} < \text{Rb}$ (Fig. 1). Caesium chloride and rubidium chloride provided the highest negative response, while the former gave more reproducible results. Instead of a ceramic tip filled with saturated solution of an alkali metal salt, a tip pressed from an alkali metal salt with a hole drilled in it¹⁰ was used. The latter type of tip is durable and its response is only slightly dependent on the time when the detector is used. According to our experience, the response shape, especially with hydrogen sulphide, is dependent only on the shape of the upper surface of the tip. A flat, straight shape leads to tailing (Fig. 2A), whereas with a conical top on the tip (Fig. 2B) waves of hydrogen sulphide, carbonyl sulphide and methyl mercaptan are formed without tailing.

RESULTS AND DISCUSSION

Technical gases were sampled, using glass pipettes working under an overpressure of about 0.1 MPa, from operating streams in accordance with the recommended practice for manipulating such gases, and injected into the chromatograph with a syringe. The chromatograms obtained are shown in Figs. 3–6.

By comparing the peak areas of carbonyl sulphide and methyl mercaptan from the technical sample with those from the standard mixture by means of a calibration graph, the concentrations of these compounds in the technical gases were calculated (Table II). The following technical gases from a pressure gas plant were analysed:

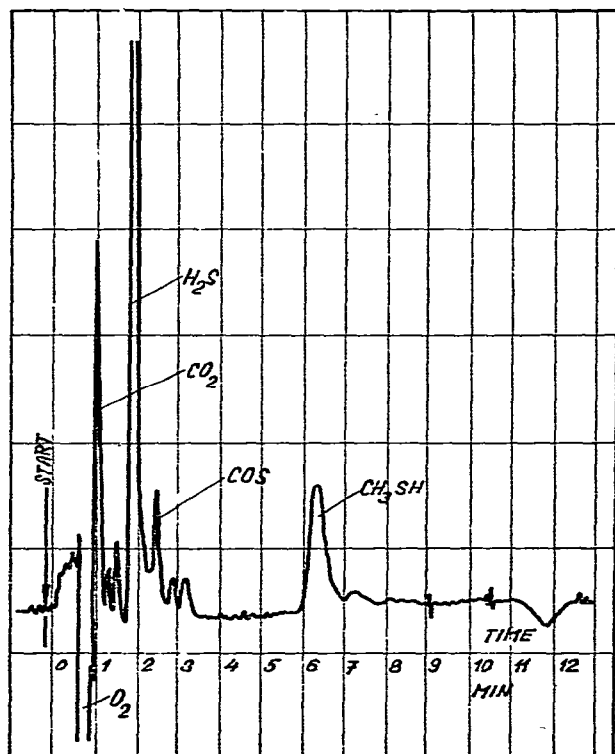


Fig. 3. Chromatogram of raw gas. Injection of 1 ml of gas (0.103 MPa; 20°). Conditions as in Table I.

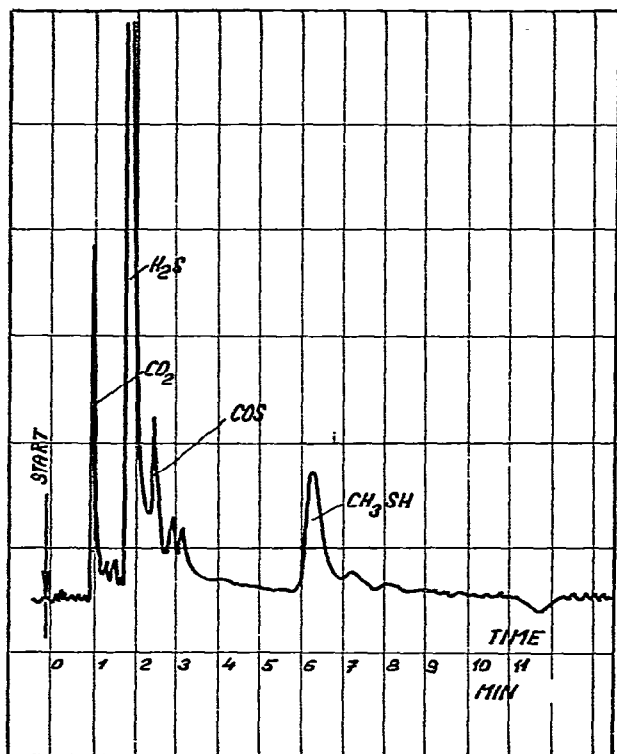


Fig. 4. Chromatogram of waste gas. Injection of 0.2 ml. Conditions as in Fig. 3 and Table I.

raw gas, after being cooled to 20–25°, entering the Rectisol, waste gas from the regeneration of methanol, hydrogen sulphide rich gas and clean gas leaving the Rectisol and supplied to the gas network.

The chromatograms in Figs. 3–6 and the results in Table II show that the content of methyl mercaptan in all of the technical gases was higher than that of carbonyl sulphide, which is contrary to the results obtained by other workers who analysed gases from coal treatment using other processes. For example, Koch and Paul¹² found that of the organic sulphur contained in gas from low-temperature carbonization of

TABLE II

CONTENTS OF ORGANIC SULPHUR COMPOUNDS AND HYDROGEN SULPHIDE IN TECHNICAL GASES FROM A PRESSURE GAS PLANT

Technical gas sample*	Gas (mg/Nm ³)		
	H_2S	COS	CH_3SH
Raw gas	5200	173	300
Waste gas	24,570	275	1523
Hydrogen sulphide rich gas	206,300	2460	14,532
Clean gas	59	10.5	—**

* See text for descriptions.

** Not detectable.

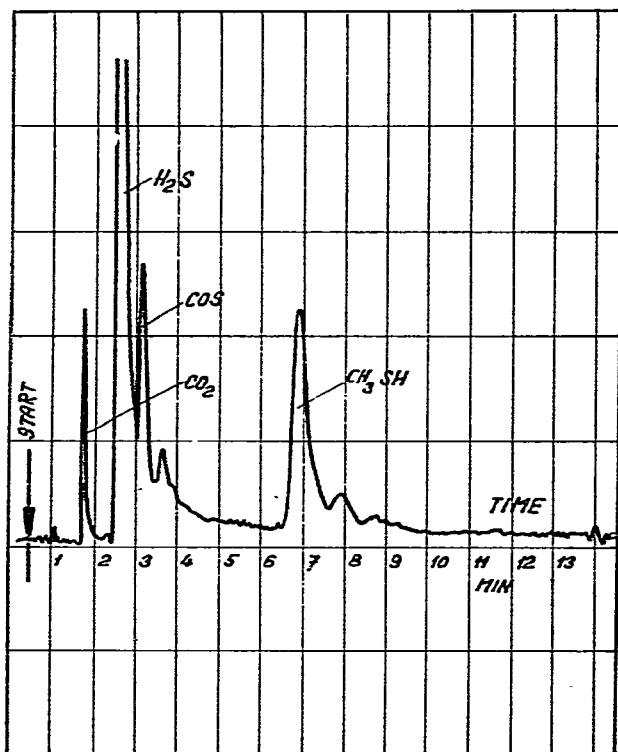


Fig. 5. Chromatogram of hydrogen sulphide rich gas. Injection of 0.05 ml. Conditions as in Fig. 3 and Table I.

brown coal, 34% (v/v) is in the form of carbonyl sulphide and 13% (v/v) in the form of methyl mercaptan.

A higher content of methyl mercaptan in raw gas is probably due to the process of coal gasification under pressure, which results in the greater formation of methane from carbon at the expense of carbon monoxide.

The waste gas and hydrogen sulphide rich gas displayed, in agreement with the gas purification process, high contents of carbonyl sulphide and methyl mercaptan (Figs. 4 and 5). As a result of the high efficiency of the purification process (Rectisol), the amount of carbonyl sulphide in clean gas, as shown in Fig. 6, was near to the detection limit and its content could not be determined by our method.

In all instances a satisfactory separation of hydrogen sulphide and carbonyl sulphide, which is particularly important in analysing waste gas and hydrogen sulphide rich gas, was attained.

Other sulphur organic compounds with higher boiling points, which would be eluted after methyl mercaptan, could not be detected in the raw gas. By increasing the sensitivity, but at the expense of reproducibility (strong noise), trace amounts of carbon disulphide (*ca.* 1 mg/m³) were found. The retention time of this compound, under the conditions given in Table I, was 18 min.

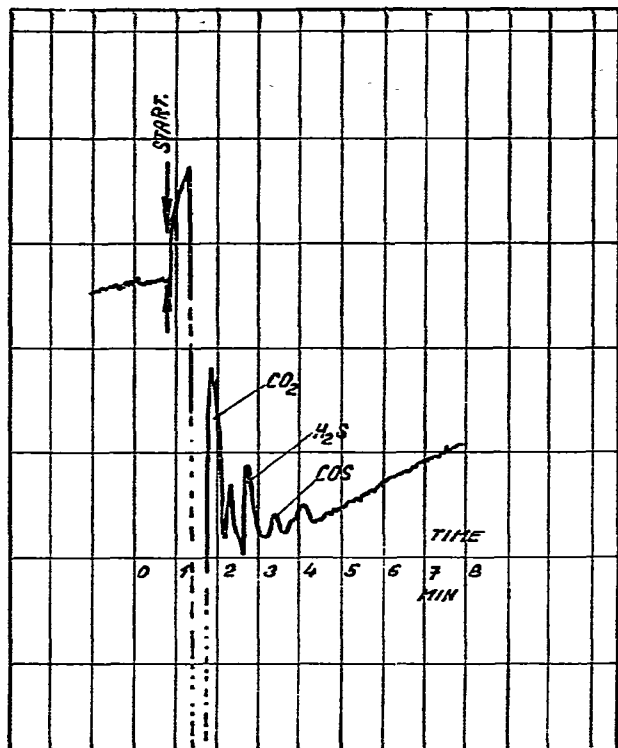


Fig. 6. Chromatogram of clean gas. Injection of 2.0 ml. Conditions as in Fig. 3 and Table I.

CONCLUSIONS

By using a TID, small amounts of organic sulphur compounds in the presence of a considerable excess of other gaseous components to which a TID shows low sensitivity can be determined with both high sensitivity and selectivity. The separation of hydrogen sulphide, also present in the excess, and to which the TID is sensitive, is made possible by using Porapak Q.

For converting an FID into a TID, caesium chloride pressed into a tip with a conical top was found to be suitable.

Contrary to previous measurements by other methods, the organic sulphur compounds in technical gases from pressure gas plants were found to be represented mainly by methyl mercaptan and by a minor amount of carbonyl sulphide.

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