DETERMINATION OF SULPHUR COMPOUNDS IN NATURAL GAS BY GAS CHROMATOGRAPHY WITH A FLAME PHOTOMETRIC DETECTOR

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SUMMARY

The quantitative and qualitative gas chromatographic analysis of sulphur components in natural gas was performed by using a flame photometric detector. The optimal conditions were established and the identification of sulphur compounds was achieved by means of a model standard mixture. The permeation technique using standard mixtures was employed for calibration. The experimental data made it possible to determine the exponents n of the individual compounds and the mean exponent for thiol, sulphide, disulphide and hydrogen sulphide groups. The experimental values were compared with those obtained with an ITT Barton operational analyser. The analysis was performed by using two columns packed with Triton X-305 and polyphenyl ether–orthophosphoric acid. Whereas Triton X-305 proved to be excellent for separation of sulphides and disulphides, polyphenyl ether was useful for the separation of low-molecular-weight components. The described method has been employed to check operational analysers.

INTRODUCTION

The determination of sulphur components in gaseous fuels under operating conditions is difficult and places high requirements on the instrumentation. The ITT Barton Sulphur Titrator[1,2] is used in natural gas networks for continuous recording determinations of hydrogen sulphide, thiols (RSH), sulphides (RSR), disulphides (RSSR) and total sulphur (S_{total}). It is based on the coulometric titration principle and is suitable for measurements under operating conditions. However, there are certain imprecisions when using this instrument and it is unsuitable for checking or arbitrating determinations. Gas chromatography with selective detection can be used for precise or test determinations. Flame photometric detection (FPD) of compounds

containing sulphur and phosphorus are the most frequently used detection methods.

An electrochemical detector operating on the basis of the reduction of Cr^{6+} to Cr^{3+} was used when following odorants in gas[3] and its use is standardized in an ISO Standard[4].

An electrolytic conductimetric detector (Hall detector) is selective for sulphur-containing components and possibly for chlorinated and nitrogen-containing substances. Its response is linear, with no interferences from hydrocarbons[5,6].

Most laboratories analysing gases by gas chromatography use FPD in the determination of sulphur compounds. Poor reproducibility of determination results rather from the properties and character of sulphur compounds, their reactivity and absorption characteristics with respect to certain materials, than from the detection of these components themselves.

The calibration procedure presents the main problem in the determination of sulphur-containing components with FPD. The permeation technique[7] and the use of gaseous mixtures in pressure cylinders made of an aluminium alloys or with adjustment of the inner surface[8] are the commonly used calibration methods.

During FPD, it is first necessary to find the maximal response and, with respect to the non-linear response of the detector, also the exponents n for the components to be detected. As shown in several studies[9-13], in most FPD there is a maximal response for an oxygen to hydrogen ratio between 0.2 and 0.3, which has been reviewed by Burnett et al.[14]. Usually it is necessary to check experimentally the optimal adjustment of the detector. The non-linear response is one of drawbacks of FPD. The detector has an about quadratic dependence, which may be expressed as follows:

$$R = kS^n \tag{1}$$

$$S = kR^{1/n} \tag{2}$$

where R is the detector response, k constant, S the sulphur concentration and n the exponent. The following linear form is usually used:

$$\log S = \log k + \frac{1}{n} \log R \tag{3}$$

The sulphur concentration is dependent on the detector response obtained. The exponent n is different for different sulphur compounds and ranges between 1.2 and 2.2. Exponents for several sulphur-containing components obtained from the literature are given in Table I.

When using a constant exponent, a large error may be encountered, which may even exceed 100%[15]. To reduce the error resulting from the assumption of a quadratic response, Maruyama and Kakemoto[10] used the expression $H^{1/2}w$ ($H =$ peak height, $w =$ peak width at half peak height) when comparing different sulphur compounds and concluded that the FPD response is dependent on the number of sulphur atoms in the molecules and not on their structure.

This paper describes the determination of sulphur compounds occurring in natural gas with the use of the permeation technique for primary calibration and a mixture of sulphur compounds in a pressure cylinder as a secondary standard. Ex-

ponents for functional groups H_2S, RSH, RSR and RSSR were established. The measured values were compared with results obtained on the ITT Barton Sulphur Titrator. A computing integrator was employed for processing the chromatographic data.

EXPERIMENTAL AND RESULTS

Instrumentation

The measurements were performed on a Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy) with a single-flame photometric detector: the electrometer was equipped with a linearizing element. The photomultiplier of the detector operated at a voltage of 700 V. The attenuation of the electrometer was left at a value of 4 for the whole measurement time. The manual application of the sample into the column was performed with the help of a six-port valve (Carlo Erba) with a 6.3-ml Teflon loop.

An SP 4100 computing integrator (Spectra-Physics, Santa Clara, CA, U.S.A.) served for recording and treating the chromatographic peaks. A Dynacalibrator Metronic, Model 340-31-XS (Metronic, Santa Clara, CA, U.S.A.) was used to obtain precise concentrations of sulphur compounds from permeation tubes.

Comparative measurements were performed with an ITT Barton Sulphur Titrator, Model 286, with a preliminarily included analytical filter, Model 327 (ITT Barton, Monterey Park, CA, U.S.A.). This filter contains absorbers with solutions for obtaining the composition of sulphur compounds in gas passing continuously through. The absorbers contain (a) a molecular sieve and charcoal for obtaining a clear background (blank), (b) 1% cadmium sulphate + 2% orthoboric acid in water to remove hydrogen sulphide, (c) 10% sodium hydroxide solution to remove hydrogen sulphide and RSH and (d) 0.5% silver nitrate solution to remove hydrogen sulphide, RSH and RSR.

The resulting titration curves are evaluated manually.

Analytical conditions

Two chromatographic columns were used for the separation of the samples. Column I was 36 ft. × 1/8 in. I.D., Teflon, packed with 12% (w/w) of polyphenyl ether (five rings) + 0.5% orthophosphoric acid on Chromosorb T (40–60 mesh) (Supelco, Bellefonte, PA, U.S.A.). The initial temperature was 60°C for 6 min, then programmed at 10°C/min up to 140°C. The detector temperature was 125°C. Column II was 4 m × 3 mm I.D., glass, packed with 10% Triton X-305 on Supelcoport (80–100 mesh) (Supelco). The initial temperature was 60°C for 6 min, then programmed at 8°C/min up to 180°C. The detector temperature was 125°C. The flow-rates were as follows: carrier gas (nitrogen), 40 ml/min; hydrogen, 110 ml/min; air, 131 ml/min; and sample 20 ml/min. The paper chart speed was 0.5 cm/min.

Reagents

Standard gas mixtures in Spectra Seal pressure cylinders (hydrogen sulphide + methanethiol in nitrogen) (BOC Special Gases, London, U.K.) were used. A multi-component standard mixture in a pressure cylinder was also obtained from BOC Special Gases; for its composition, see Table II. All the cylinders were fitted with stainless-steel reducing valves with a metallic membrane (BOC Special Gases and

Matheson, Oevel, Belgium). Further gas samples (hydrogen sulphide, methanethiol, ethanethiol and dimethyl sulphide) were obtained from Dynacal Permeation Tubes (Metronic Assoc., Palo Alto, CA, U.S.A.). For identification, a set of Supelco 71 standards (Supelco) was used. The samples to be analysed were kept in stainless-steel pressure vessels of volumes 3 and 1 l (Hoke Inter., Cresskill, NJ, U.S.A.).

For the gas chromatography, technical gases of common quality (Technoplyn, Prague, Czechoslovakia) were used. Pressurized air was supplied with the help of an air pump. Drying and purification of these gases were effected with the use of filters consisting of a molecular sieve and silica gel (Applied Science, Labs., State College, PA, U.S.A.) and by pressure filters on the valves of the cylinders (Messer-Griesheim, Düsseldorf, F.R.G.).

Standard preparation

Permeation tubes containing known concentrations were used at a constant temperature to check the standards in the pressure cylinders. This precise concentration was obtained with the help of a Metronic Model 340-31.XS calibrator, where the concentration was varied as necessary by changing the calculated temperature and the flow-rate of the diluting gas. In the instrument, the internal pump was disconnected and the instrument was joined to an external nitrogen supply from a pressure cylinder. Nitrogen was used as the diluting gas to adjust the thiol content in the sample. In the calibrator, a calculated flow-rate of diluting gas was mixed with the flow through the permeation chamber at a constant temperature, adjusted by the manufacturer. The concentration calculation included a correction for atmospheric conditions. In this way, precise concentrations of the above compounds were obtained and, on the basis of these values, the standard mixtures in the pressure cylinders were recalibrated, which further served as a secondary standard.

Determination of optimal chromatographic conditions

The FPD response is strongly dependent on the mass flow-rate of a component through the detector. For each detector, it is necessary to find optimal gas flow-rates and detector temperature. The oxygen to hydrogen ratio is of a particular importance. A further dependence is given by the detector geometry in the sense that two identical detectors need not have the same conditions for their operation. The producer's manual recommends a very wide range of gas flow-rates, covering a range of oxygen to hydrogen ratios from 0.2 to 0.3. Hence it is necessary to find experimentally the maximal detector response for various oxygen to hydrogen ratios. In the course of our measurements, oxygen was first added at a rate of 8 ml/min. Later it was shown that the detector response was not altered when air was used instead of oxygen and subsequent measurements were therefore performed without addition of oxygen to the detector.

Maximal detector response was achieved for an at an oxygen to hydrogen ratio of 0.250, which represents flow-rates of 110 ml/min of hydrogen and 131 ml/min of air. The optimal detector temperature was 125°C.

Determination of the exponent $\bar{n}$

Owing to the non-linear response of the detector, it is necessary to know the exponent n in eqn. 1. For use in practice, the logarithmic relationship in eqn. 3 is

more suitable. For the experimental determination of the exponents, a linear regression method was employed, the exponent being calculated as the slope of the straight line obtained on log–log coordinates. The exponent was calculated for pure hydrogen sulphide, methanethiol, ethanethiol, dimethyl sulphide and dimethyl disulphide by measuring the response for five or six concentrations. A minicomputer (HP 9830) was used for the calculations. The exponent values found are given in Table I.

TABLE I

EXPONENT n VALUES

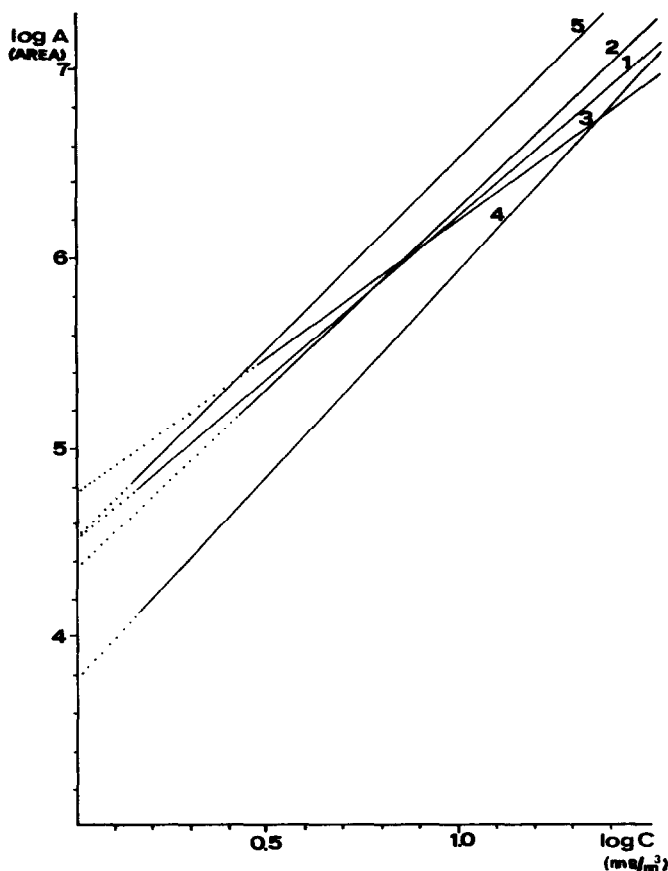| Compound	Ref. 14	Ref. 16	Ref. 17	Ref. 18	Ref. 19	This work
H_2S	1.81	—	1.91	1.76	1.91	1.81
CH_3SH	2.0	—	1.82	1.87	1.82	2.13
$(CH_3)_2S$	1.70	1.18	—	—	—	1.78
$(CH_3)S_2$	1.78	2.09	—	—	—	1.48

Fig. 1. Response (area) vs. concentration for five sulphur compounds. 1, Hydrogen sulphide; 2, dimethyl sulphide; 3, dimethyl disulphide; 4, methanethiol; 5, ethanethiol.

In further work, exponents of 2.13, 1.78 and 1.48 were used for the groups RSH, RSR and RSSR, respectively.

Fig. 1 shows logarithmic calibration graphs of response *versus* concentration. We checked that it is possible to define the calibration graph in log–log coordinates only when the hypothetical intercepts are known. This means that it is impossible to use published exponents, but it is necessary to plot a calibration graph for each sulphur compound. In practice, we use one exponent value for the whole homologous series, which leads to a faster determination but with a lower precision.

Quantitative determination

As a secondary standard, the multi-component mixture prepared by BOC Special Gases and checked with the help of primary permeation standards was used. For its composition and a chromatogram, obtained on both columns under the above-mentioned conditions, see Table II and Figs. 2 and 3.

TABLE II

IDENTIFICATION OF COMPONENTS AND CONTENTS OF SULPHUR IN CALIBRATION MIXTURE AND FOUR SAMPLES

Peak No.	Compound	n	S in calibration mixture (mg/m^3)	S in samples (mg/m^3)			
				1	2	3	4
1	H_2S	1.81	34.3	5.2	8.2	12.0	6.0
2	CH_3SH	2.13	25.8	5.2	—	7.2	—
3	C_2H_5SH	2.13	8.6	1.5	1.0	1.8	1.0
4	$(CH_3)_2S$	1.78	6.5	2.8	1.5	1.5	1.5
5	C_3H_7SH	2.13	13.1	2.4	2.3	2.0	0.4
6	$(C_4H_9)_2SH$	2.13	12.1	3.2	0.5	0.8	—
7	$(C_2H_5)_2S$	1.78	12.0	5.1	3.2	23.0	3.0
8	$(CH_3)_2S_2$	1.48	4.0	3.1	2.8	13.0	3.0
9	$(C_3H_7)_2S$	1.78	9.1	5.1	—	3.2	—
10	$(C_2H_5)_2S_2$	1.48	3.0	1.8	—	—	—
11	$(C_4H_9)_2S$	1.78	2.0	1.9	—	—	—
12	Unidentified	1.48	2.0	1.0	—	—	—
13	Unidentified	1.48	1.0	0.5	—	—	—
14	$(C_4H_9)_2S_2$	1.48	1.0	0.9	—	—	—
—	Total	—	134.5	39.8	19.5	64.5	14.9

An SP 4100 computing integrator was used for the quantitative evaluation of the chromatographic peaks. An external standard method was used and the integrator DIALOG program was extended by introducing the exponent n. Certain methods programmed in the ROM were converted in a desired manner into the RAM and thus it was possible to work with relevantly corrected areas. The resulting report was obtained as actual concentrations.

To check the above method, a sample containing the same components as the calibration mixture, but diluted with natural gas, was prepared. Samples of the natural gas transported from Czechoslovakia to West European countries contains very small amounts of sulphur on average, typically up to 10 mg/m^3. There are, of course,
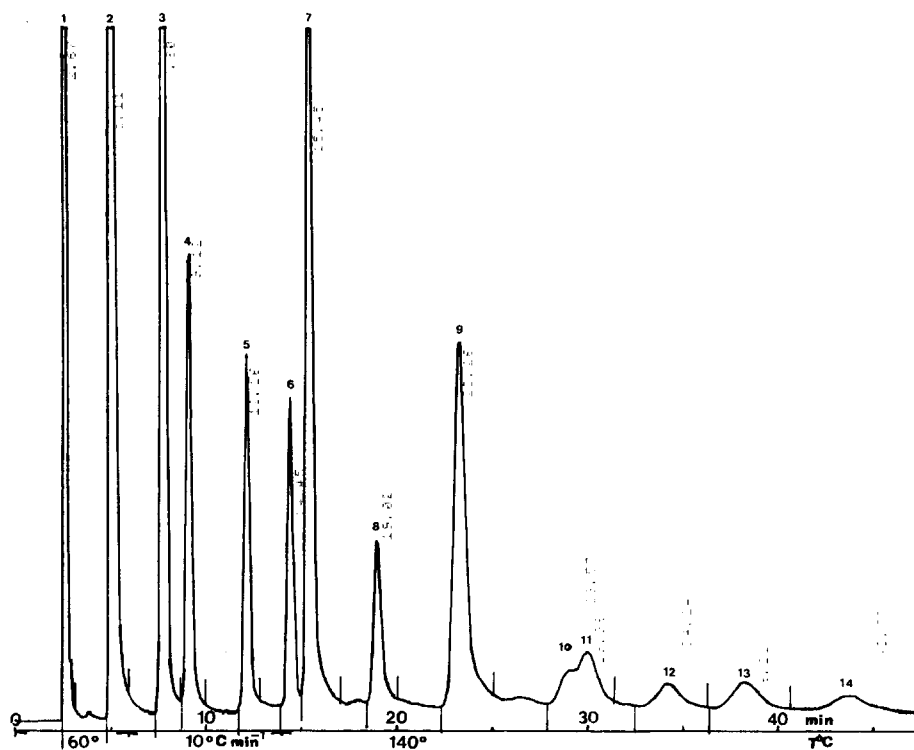
Fig. 2. Chromatogram of BOC calibration mixtures obtained using column I (see text).

individual variations and this situation is shown in Fig. 4. The separation is shown only for column I. For identification of the components, see Table II.

To establish a system that could provide reproducible measurements, it is necessary in the first stage to perform at least 20 injections (applications) of the sample before one gets reliable results, especially in case of hydrogen sulphide analysis. By using the above described procedure, the reproducibility of the method is about 1% relative.

DISCUSSION AND CONCLUSION

Two columns suitable for the determination of sulphur compounds in natural gas were tested. A Teflon column filled with polyphenyl ether–orthophosphoric acid is suitable for the separation of sulphur compounds with lower boiling points. It is also able to separate very well ethanethiol from dimethyl sulphide. Carbonyl sulphide, which is eluted immediately after hydrogen sulphide, was not present in our samples.

A glass column containing Triton X-305 proved useful when using a temperature programme for the separation of sulphur compounds with higher boiling points. It is unable to separate ethanethiol from dimethyl sulphide. Carbonyl sulphide is eluted similarly to hydrogen sulphide, so that the separation is not successful when
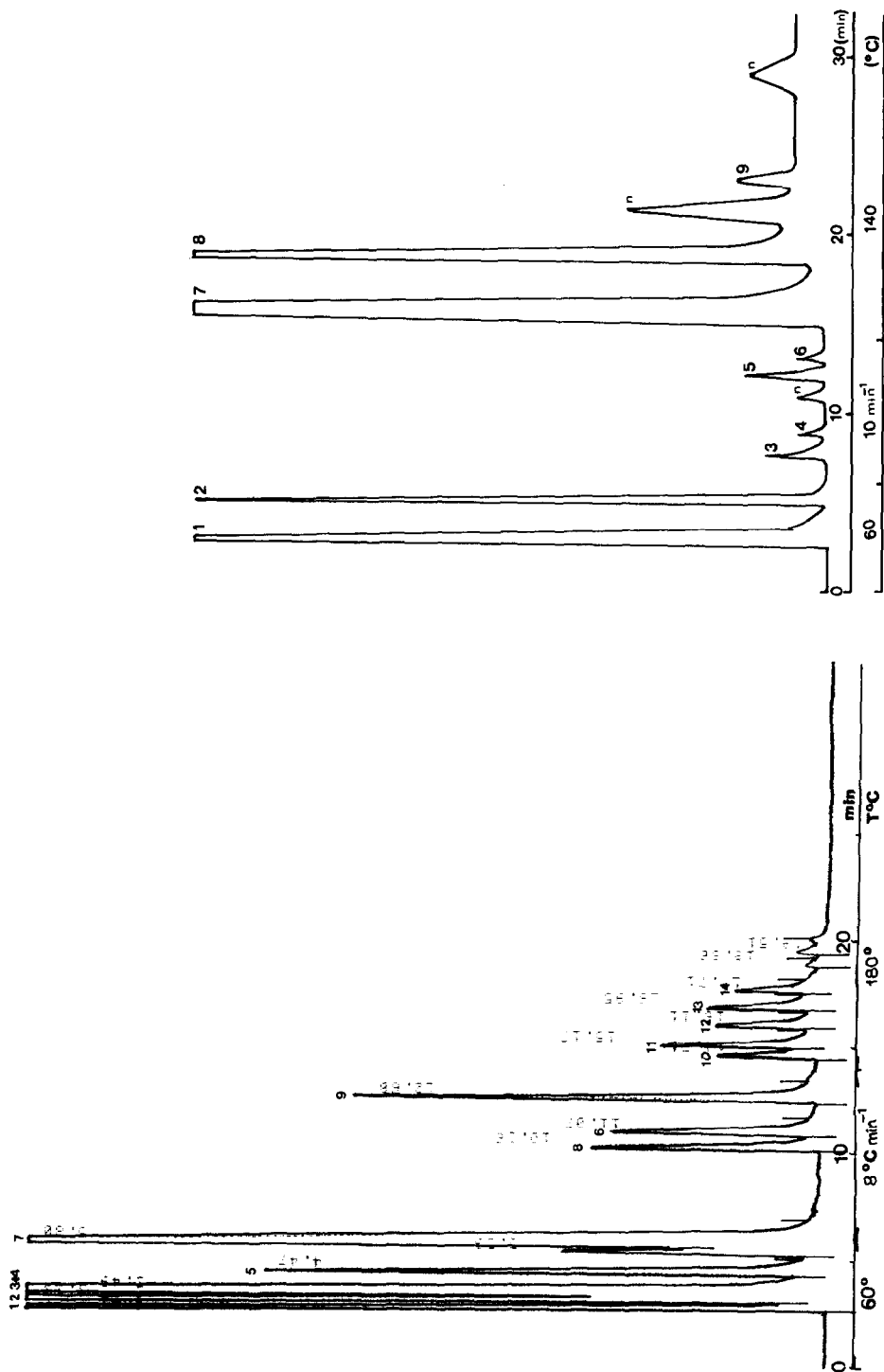
Fig. 3. Chromatogram of BOC calibration mixtures obtained using column II (see text).

Fig. 4. Chromatogram of a sample of natural gas (Velké Kapušany) ($\bar{S}_{total}$ = 64.5 mg/m^3) obtained using column I (see text).

there is an excess of either component. In both columns, the equilibration of the "saturation" of the system with sulphur is time consuming.

The interference of hydrogen sulphide with methane (92%) (quenching effect[21]) was negligible and essentially did not affect the measurements. It was shown to be very useful to use the special Spectra Seal pressure cylinders for keeping reactive sulphur compounds. The quantitative evaluation was carried out on the basis of determining the exponents of pure substances representing particular homologous series: H_2S, RSH, RSR and RSSR. On the basis of these exponents, logarithmic calibration graphs were plotted. However, the line does not pass through the origin. The hypothetical point of intersection of the calibration graph with the ordinate remains unknown and therefore it is necessary to perform the calibration for particular components. Exponents obtained from the literature may serve only as a check on the accuracy of the measurements.

TABLE III

CONTENTS OF SULPHUR IN FOUR SAMPLES OF NATURAL GAS OBTAINED WITH THE ITT BARTON SULPHUR TITRATOR

Name	S in samples (mg/m^3)			
	1	2	3	4
H_2S	3.0	5.0	12.0	5.0
RSH	15.0	2.0	10.0	2.0
RSR	18.0	5.0	45.0	9.0
Total	35.0	15.0	65.0	16.0

The agreement of the experimental results with data from the ITT analyser used for operational analyses is satisfactory, as can be seen from Table III. The described method is suitable for detailed analyses of sulphur compounds in natural gas using the permeation technique for the calibration.

The work presented here is intended to serve as a basis for the use of the method in practice for checking operational analysers on the Transit Pipeline.

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