Journal of Chromatography, 349 (1985) 465–468
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 693

ON-LINE ANALYSIS OF SULPHUR COMPOUNDS IN NATURAL GAS WITH FLAME PHOTOMETRIC DETECTION

LUDWIG HUBER* and HANS OBBENS
Hewlett-Packard GmbH, D-7517 Waldbronn (F.R.G.)

SUMMARY

A gas chromatographic system is described which gives information on hydrogen sulphide, carbonyl sulphide, and tetrahydrothiophene in natural gas every 6 min. The separation is achieved with a novel combination of packed and capillary columns. Fully automated hardware adapts the system for on-line monitoring.

INTRODUCTION

Traces of sulphur compounds in natural gas have to be analysed for different reasons. Hydrogen sulphide, even when present in low amounts, causes corrosion problems. Carbonyl sulphide must also be monitored, because it might be converted into hydrogen sulphide in gas depots. Organic sulphur compounds may be present in natural gas as mercaptans or sulphides. In some countries sulphur odorants *e.g.* tetrahydrothiophene (THT) or mercaptans are added to natural gas for safety reasons.

The use of the highly sensitive and selective technique of flame photometric detection (FPD) for analysis of trace sulphur compounds in natural gas has been described[1,2]. Because of the wide boiling range of sulphur compounds present in natural gas, two different columns and two separate injections have been necessary to perform a complete analysis. This paper describes a method that allows the analysis of hydrogen sulphide, carbonyl sulphide, and tetrahydrothiophene every 6 min. The method can be adapted to the analysis of additional organic sulphur compounds.

EXPERIMENTAL

Apparatus

The gas chromatographic (GC) system consisted of a Hewlett-Packard (HP) 5880A gas chromatograph, equipped with a flame photometric detector, two automated sampling valves and two columns (Fig. 1). The gas-sampling valves and sample loops were installed in a thermostatically controlled, heated compartment.

Separation of hydrogen sulphide and carbonyl sulphide was performed on a Porapak QS column. The Porapak material was acetone-washed and loaded with 0.5% phosphoric acid to increase inertness and to prevent tailing of hydrogen sul-

0021-9673/85/$03.30

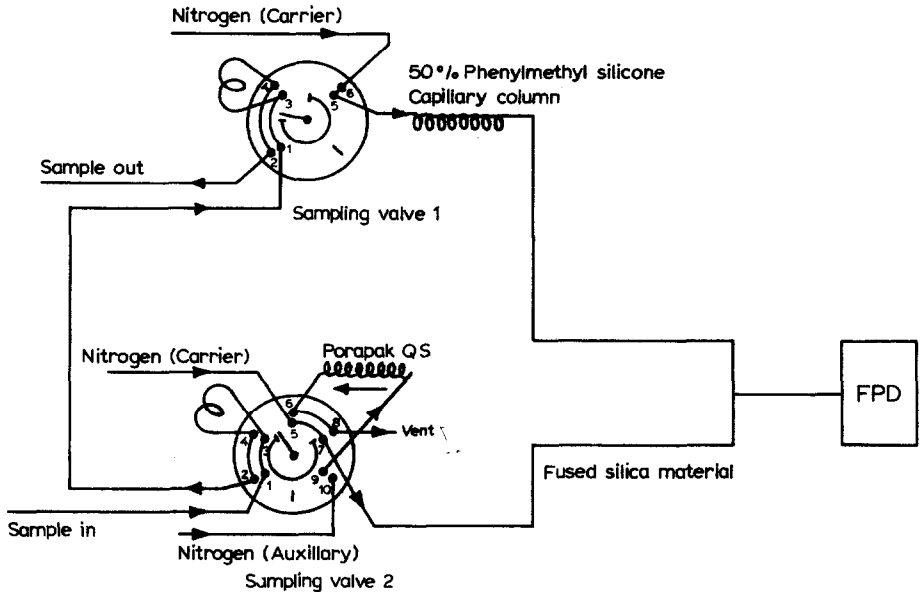

Fig. 1. Schematic diagram of the chromatographic system; FPD = flame photometric detector.

phide. The separation of tetrahydrothiophene is performed on a very-thick-film 50% phenyl methyl silicone phase. The tube material for this column was fused silica. Fused-silica tubing was also used to connect valve 2 and the detector. This tubing and the silicone column were inserted into the detector block via an HP capillary column nut (P/N 18740-20870) and a graphite ferrule (1 mm I.D.; P/N 5080-8773).

A BASIC program controlled the entire analytical sequence and carried out post-run calculations. Alternatively, a data communication interface can be used to transmit analysis reports to an external computer, which could be separate from the gas chromatograph. The report also can be transmitted via a modem to a central control station.

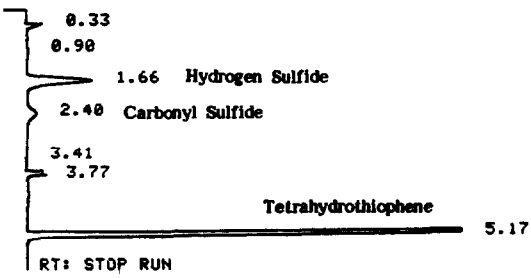

Fig. 2. Typical chromatogram. Oven temperature, 65°C isothermal; column 1, 600 × 0.2 mm I.D. PTFE, Porapak QS 60–80 mesh, acetone-washed, 0.5% phosphoric acid; column 2, 10 m × 0.53 mm I.D. fused-silica, 2.2-μm film of 50% phenyl methyl silicone; carrier gas, nitrogen; flow-rate in column 1, 17 ml/min; flow-rate in column 2, 13 ml/min.

TABLE I

SINGLE LINE REPORTS

No.	*Time*	*Date*	*H_2S (ppm)*	*COS (ppm)*	*THT (ppm)*	*Total (ppm)*
1	14:21	OCT 29	8.04	4.21	12.12	24.37
2	14:27	OCT 29	8.01	4.24	12.08	24.33
3	14:34	OCT 29	8.02	4.20	12.09	24.31
4	14:40	OCT 29	7.93	4.18	12.07	24.18
5	14:46	OCT 29	7.85	4.15	12.06	24.06
6	14:52	OCT 29	7.96	4.13	12.09	24.18
7	14;58	OCT 29	7.88	4.16	12.11	24.15
8	15:04	OCT 29	7.88	4.10	12.13	24.11
9	15:11	OCT 29	7.92	4.06	12.09	24.07
10	15:17	OCT 29	7.81	4.16	12.13	24.10
11	15:23	OCT 29	7.85	4.18	12.15	24.18
12	15:29	OCT 29	7.88	4.25	12.11	24.24

RESULTS

The chromatographic process was controlled by a run table. At the start of the analysis valve 2 was actuated. The sample was partly introduced into the Porapak column. A typical chromatogram and the chromatographic conditions are shown in Fig. 2. Hydrogen sulphide and carbonyl sulphide were eluted from the Porapak column within 3 min; at 3.5 min, the Porapak column was back-flushed, and valve 1 was actuated. After 5 min, tetrahydrothiophene was eluted, without any tailing.

The entire analysis sequence was controlled by a BASIC program. The program assumes a calibration table in the memory of the gas chromatograph. After the program has been started, five calibration runs are performed automatically, and the S.D. of the response factors is calculated. Only if the S.D. is within specified limits, the program continues with sample analyses. If the S.D. exceeds a specified limit,

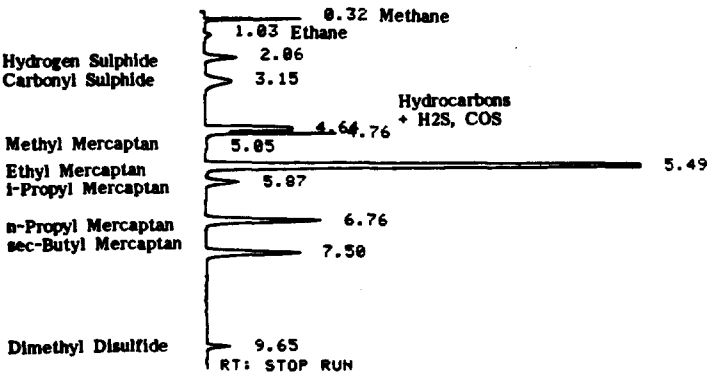

Fig. 3. Analysis of hydrogen sulphide, carbonyl sulphide, and organic sulphur compounds in natural gas. Columns: (1) 3 ft. × 1/8 in. I.D. PTFE, Porapak QS, 60–80 mesh, acetone-washed, 0.5% phosphoric acid; (2) four 10-m fused-silica, 0.53-mm film of 50% phenyl methyl silicone. Column temperature, 40°C (for 6.2 min) to 120°C (at 15°C/min); carrier gas, nitrogen; flow-rate in column 1, 17 ml/min; flow-rate in column 2, 13 ml/min.

TABLE II

STATISTICAL DATA OF TEN CONSECUTIVE RUNS

Compound	*Amount (ppm)*	*Standard deviation*	
		ppm	*%*
Methyl mercaptan	28.6	0.29	1.03
Ethyl mercaptan	05.55	0.056	1.01
Dimethyl sulphide	08.43	0.079	0.94
Isopropyl mercaptan	08.77	0.032	0.36
n-Propyl mercaptan	11.70	0.042	0.36
Isobutyl mercaptan	10.30	0.128	1.25
n-Butyl mercaptan	20.8	0.241	1.16
sec.-Butyl mercaptan	11.0	0.148	1.35
tert.-Butyl mercaptan	05.18	0.024	0.46

calibration runs will be performed until the deviation of the last five runs is within the limit.

After each sample analysis a single line report is printed, together with the sampling time (Table I). The report contains information on the amounts of individual sulphur compounds as well as on the total sulphur content.

Mercaptans have been analysed by the same chromatographic system, as have low-molecular-weight sulphur compounds (see Fig. 3). The column temperature was programmed from 40 to 120°C, and four 10-m columns were necessary to obtain a complete separation. The columns were interconnected with zero-dead-volume unions (HP P/N 0100-0900). The analysis cycle time for this analysis was 15 min. The accuracy and precision of the analysis are shown in Table II for ten consecutive runs.

REFERENCES

1 C. D. Pearson, *J. Chromatogr. Sci.*, 44 (1976) 154–158.
2 *Hewlett-Packard Application Note AN 228-25*, Hewlett-Packard, Avondale, PA, 1983.