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Determination of sulfur components in light petroleum streams by high-resolution gas chromatography with chemiluminescence detection

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ABSTRACT

A versatile high-resolution gas chromatographic system utilizing universal sulfur chemiluminescence detection (USCD) coupled with flame ionization detection (FID) was optimized for the determination of sulfur components in light petroleum process streams. The normalized area precision for individual species was *ca.* 1.5–6.0% (relative standard deviation) for the major components at a total 1.7 (w/w) of sulfur level. The system is capable of speciating sulfur components in petroleum process streams containing 0.01–3.13% (w/w) of sulfur. The linear relationship (r^2 = 0.998) between the USCD absolute sulfur response and the total sulfur content of several samples of petroleum process streams clearly indicated that, in addition to speciation, total sulfur can simultaneously be determined with reasonable accuracy.

INTRODUCTION

Sulfur compounds are one of the most important heteroatom constituents of petroleum and are often determined by gas chromatography (GC) using flame photometric detection (FPD). FPD was introduced in 1966 by Brody and Chaney [1] and it continues to have widespread use [2,3]. Other commercially available detectors for sulfur determination are the electrolytic conductivity (Hall) detector [2,4,5], atomic emission detector [2,6,7] and electron-capture detector [8].

Although FPD is widely used, it has several major drawbacks. FPD is based on the S_2^* chemiluminescence emission bands at 384 and 394 nm [3]. The electronically excited S_2^* species are formed by the sulfur atoms produced in a hydrogen-rich flame. The intensity (I) of this emission which is due to the molecular band, is of the form $I = [S]^n$. The exponent n is theoretically 2, but the response to sulfur ranges between first and second order, depending on the heteroatom environment [9]. The FPD response is also affected by co-eluting water or hydro-carbons, which can quench the chemiluminescence to a significant extent [10,11]. Although dual-flame photometric detectors have been developed to overcome some of these problems, they generally suffer from hydrocarbon interference at trace sulfur levels.

During the last decade, several attempts have been made [12–15] to develop a system for "universal" sulfur-selective chemiluminescence detection (USCD). Recently, such a detector has become commercially available. The USCD instrument is coupled directly to the flame housing of a flame ionization detection (FID) instrument. Benner and Stedman [16] demonstrated that the USCD responses to individual sulfur compounds were equal on a sulfur weight basis and hydrocarbon interferences were minimal. Further, there was no decrease in the detector response or any interferences from carbon dioxide and water vapor. It was also shown that USCD was very sensitive and provided detection limits that are at least 10–15 times lower than that of FPD.

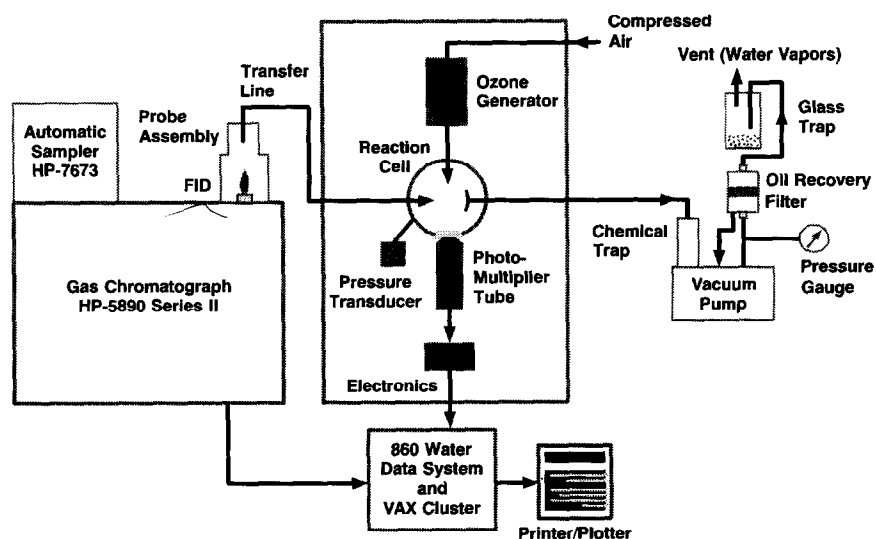This paper describes the optimization and oper-

Fig. 1. Schematic diagram of the major components of a universal sulfur chemiluminescence detection system.

ational characteristics (linear response, sensitivity and stability) of a universal sulfur chemiluminescence detector coupled to a gas chromatograph. The identification of a series of sulfur components such as thiophene (TH), benzothiophene (BTH), dibenzothiophene (DBTH) and their alkyl-substituted homologs present in various light petroleum process streams (catalytically cracked gasolines, kerosenes and diesels) are also reported. The sulfur content of the samples investigated covers a wide range of 0.01–3.13% (w/w).

EXPERIMENTAL

A schematic diagram of the major components of the Model 350 universal sulfur-selective chemiluminescence detector (Sievers Research, Boulder, CO, USA) coupled to a gas chromatograph is shown in Fig. 1. A probe assembly was mounted on top of a flame ionization detector. The probe was preset high (ca. 5 mm) above the flame to avoid being damaged when inserted. The optimum position of the probe was determined by adjusting the Allen screw on top of the flame interface housing. At the optimum probe position, the FID background signal as monitored by a Hewlett-Packard Model 5890 GC digital display was ca. 250 ± 50 pA at a range of 2.

The combustion products formed in the flame were transferred under a reduced pressure of about 9 ± 2 Torr to the chemiluminescence reaction chamber. A high-capacity vacuum pump (Model E2M5; Edwards High Vacuum, West Sussex, UK) was used. To minimize oil loss, a large coalescing oil return/recovery filter (P/N 18/18-371H; Ditto, Mount Laurel, NJ, USA) was fitted to the pump exhaust outlet to trap vaporized oil. A pressure gauge was also installed between the oil return/recovery filter and the pump (see Fig. 1) to monitor potential plugging of the filter during its continuous use. The outlet of the oil filter was then atttached to a glass trap for collecting the outgoing water–oil emulsion and then finally to a vent line. During method development, no clogging of the oil return/ recovery filter was observed over a period of 2–3 months. The pump was filled with Mobil 1 oil and remained in continuous use (24 h per day) for about 2–3 months without requiring an oil change or any replacement of the oil return/recovery filter. In order to remove unreacted ozone, nitrogen oxides and other potentially oil-destructive gases, a trap containing Hopcalite (Callery Chemical, Pittsburgh, PA, USA) and soda-lime (7:3, v/v) was placed between the reaction cell and the vacuum pump.

A Hewlett-Packard Model HP-5890 Series II gas chromatograph, equipped with a split/splitless in-

jection port, an automatic sampler (HP-7673) and a flame ionization detector was employed under the following operating conditions: column, DB-1 (60 m × 0.25 mm I.D.), 0.25-μm film thickness (J & W Scientific, Folsom, CA, USA); oven temperature, programmed from 35 to 100°C at 10°C/min and then to 225°C at 2°C/min, with a final hold for 20 min; injector, split/splitless, used in split mode at 275°C; injector insert, capillary liner (unpacked), HP P/N 18740-80190; injection volume 0.5–1.0 μl (neat sample); FID range, 2; carrier gas, helium; split vent, 100 ml/min; purge vent, 1.4 ml/min; column-outlet flow-rate, 2.0 ml/min (ambient temperature); linear velocity, 30 cm/s (methane at 35°C); air flow-rate, 375 ml/min (38 p.s.i.g.); hydrogen flow-rate, 180 ml/min (60 p.s.i.g.); column head pressure, 35 p.s.i.g.; run time, 95 min; USCD probe, ceramic, 105 mm × 1.3 mm O.D. × 0.5 mm I.D. (Sievers); probe conditioning: 3–4 h at air flow-rate 600 ml/min (50 p.s.i.g.), hydrogen flow-rate 230 ml/min (70 p.s.i.g.) and pump exhaust line pressure 0–1 p.s.i.g.; and USCD signal control, 0.06 s (integrated time for photon counts).

Proper positioning of the probe in the flame ionization detector is critical for long-term USCD stability. The probe is correctly positioned if the last 2–3 mm of the probe tip are glowing when the probe is rapidly but carefully removed from the FID tower assembly. The position of the probe is adjusted by using the two Allen screws on the probe assembly.

Data acquisition, processing, storage and retrieval were performed using a Waters Assoc. 860 Networking Computer System coupled with an in-house VAX cluster.

RESULTS AND DISCUSSION

Optimization of sulfur chemiluminescence detector

A dilute solution of dibenzothiophene (1.28 · 10^{-6} mol/ml) in n-heptane was used to optimize the air and hydrogen flow-rates (Figs. 2–5). The optimum conditions for USCD were air at 38 p.s.i.g. (375 ml/min) and hydrogen at 60 p.s.i.g. (180 ml/min) (Figs. 2 and 4). The maximum FID and USCD responses were attained at similar air flow-rates (Figs. 2 and 3). However, the FID response decreased linearly with increasing hydrogen flow-rate (Fig. 5) and, at the USCD-optimized hydrogen
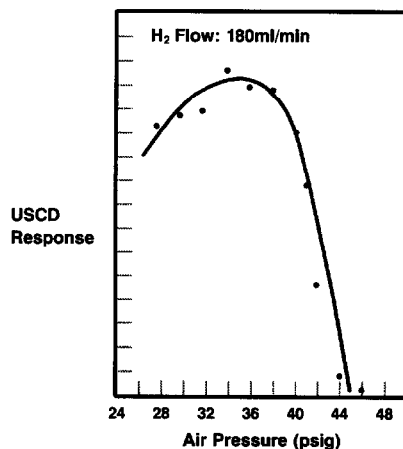

Fig. 2. USCD response *vs.* air pressure (hydrogen flow-rate 180 ml/min).

flow-rate the FID response was less than the FID response when operated under conventional conditions.

Optimization of GC separation

Three fused-silica capillary columns were investigated for the GC separation of light petroleum streams: (i) Petrocol DH (100 m × 0.25 mm I.D.), 0.50-μm film thickness (Supelco, Bellefonte, PA, USA); (ii) DB-1301 (30 m × 0.25 mm I.D.), 0.25-μm film thickness (J&W Scientific, Folsom,
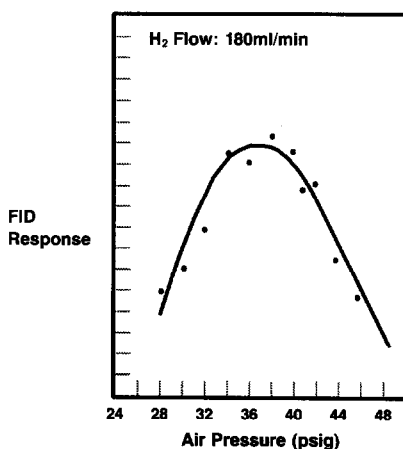

Fig. 3. FID response *vs.* air pressure (hydrogen flow-rate 180 ml/min).

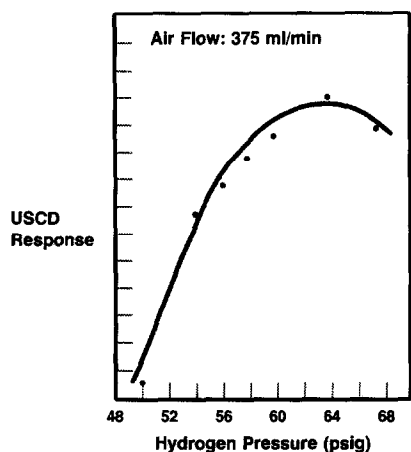Fig. 4. USCD response vs. hydrogen pressure (air flow-rate 375 ml/min).

CA, USA); and (iii) DB-1 (60 m × 0.25 mm I.D.), 0.25 μm film thickness (J&W Scientific). Although the 100-m column gave satisfactory separations of sulfur species in gasoline and diesel range streams, it encountered two difficulties. First, the column bled excessively at the final column temperature of about 300°C. As the USCD probe was very sensitive to column bleeding, the 100-m column was found to be unsuitable for quantitative work. Second, the analysis time was relatively long (ca. 160 min). The 30-m (DB-1301) column did not yield satisfactory resolution of the sulfur species. The 60-m (DB-1) column gave acceptable resolution in the shortest analysis time.
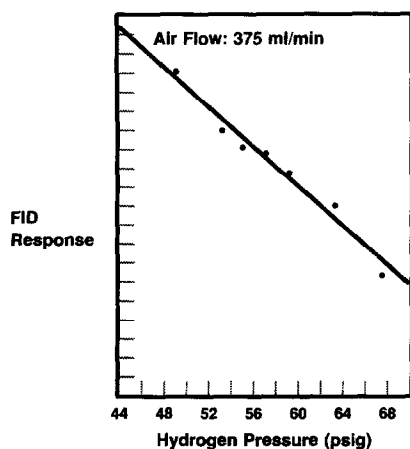

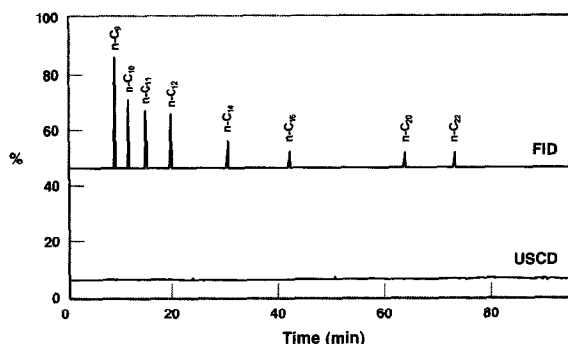Fig. 5. FID response vs. hydrogen pressure (air flow-rate 375 ml/min).

Fig. 6. FID and USCD chromatograms for a mixture of n-alkanes.

In order to obtain quantitative results from the GC separations, it was essential to minimize injection port sample discrimination. A mixture containing C_9–C_{22} n-alkanes was analyzed using FID (Fig. 6). It was found that extending the capillary column 6–7 mm rather than the 2–4 mm recommended by Hewlett-Packard from the end of the ferrule into the injection port splitter gave the best quantitative results. Excellent agreement was obtained between the actual % (w/w) and the experimentally observed % (w/w) for each of the n-alkanes present in the mixture (Table I).

TABLE I

MASS DISCRIMINATION OPTIMIZATION OF THE GC SYSTEM

n-Alkane	Retention time (min)	Concentration (%, w/w)			
		Actual	Experimental		
			FID (300°C)[a]	FID[b]	
				300°C	275°C
C_9	9.60	26.53	26.63	27.21	27.07
C_{10}	12.19	11.63	11.54	11.78	11.67
C_{11}	15.69	13.84	13.62	13.88	13.60
C_{12}	20.20	20.83	20.36	20.67	20.52
C_{14}	30.89	10.56	10.14	10.13	10.14
C_{16}	42.27	6.25	6.30	6.11	6.08
C_{20}	63.64	5.91	6.26	5.69	5.93
C_{22}	72.93	4.45	4.90	4.20	4.57

[a] GC–FID results obtained under normal FID hydrogen/air conditions at an injector temperature of 300°C.

[b] GC–FID results obtained under FID hydrogen/air conditions optimized for maximum USCD sulfur response at two injector temperatures.
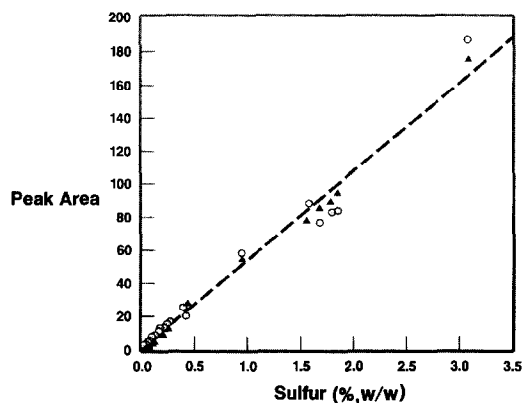
Fig. 7. USCD response at two injector temperatures. ○ = 300°C, area × 10^{-6} = 52.665 [S] + 0.4095, r^2 = 0.976. ▲ = 275°C, area × 10^{-6} = 52.808 [S] − 0.3855, r^2 = 0.993.

Fig. 8. FID and USCD responses for a dilute solution of dibenzothiophene.

Effect of injector temperature on USCD linear response

The USCD has been shown to have a linear response [17,18] which is generally independent of the sample compound. In order to establish its linear response and its detection limits, 22 samples of light petroleum streams (gasoline, kerosene, diesel boiling point range) with various sulfur contents from 0.03 to 3.13% (w/w) were analyzed under the same chromatographic operating conditions. The USCD response for all these samples in terms of total area under the resulting peaks was plotted against the total sulfur content. These samples were analyzed at two different injector temperatures, 300 and 275°C. The linear fits for the data obtained at two temperatures are presented in Fig. 7. The USCD response increases linearly with increasing sulfur content. The linear fit was better when the injector temperature was 275°C (r^2 = 0.993 *versus* 0.976 at 300°C), perhaps because of improved injector splitter performance and/or decreased losses of the more reactive sulfur species (sulfides, thiols) present in some of the samples. It was decided to use 275°C as the injector temperature for subsequent work.

Identification of organosulfur compounds in petroleum process streams

A dilute solution (1.28 · 10^{-6} mol/ml) of dibenzothiphene in *n*-heptane was used to confirm the USCD selectivity (Fig. 8). Under USCD-optimized operating conditions, only DBTH was detected.
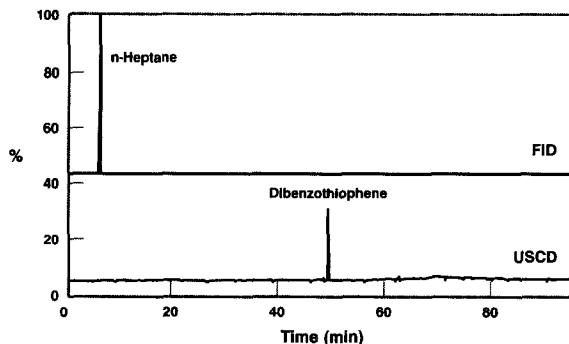
The USCD/FID chromatograms for a diesel range petroleum stream and a catalytically derived FCC gasoline range stream are shown in Figs. 9 and 10, respectively. The sulfur-containing compounds were identified by comparision of their retention times with those of reference standards (Table II) and/or by GC–mass spectrometry (MS).

Precision

The short-term precision of the USCD response in terms of absolute total peak area was determined by making several independent injections of a light petroleum process stream. The precision of the USCD data was found to be better than 3%, indicating that the USCD has good short-term stability when properly optimized.

The precision of the normalized sulfur weight percentage of several selected thiophene groups was determined for a diesel range sample (Fig. 9, Table III). The USCD data showed that 70% of the thiophene groups had a precision of better than 3%. The precision of relatively smaller amounts of unsubstituted benzothiophene and dibenzothiophene was *ca.* 8% and that of a "sulfides and thiophenes" group, which was spread over a section of the initial 18 min of the chromatogram and was only *ca.* 0.5% (w/w) of the total sample, could be obtained with a precision as high as 24%.

Because of the long-term drift in the USCD absolute response, frequent calibrations are necessary. Although not investigated here, the use of an internal standard may resolve the drift in response provided that a reasonable wide "window" is available in the chromatogram. If only the normalized
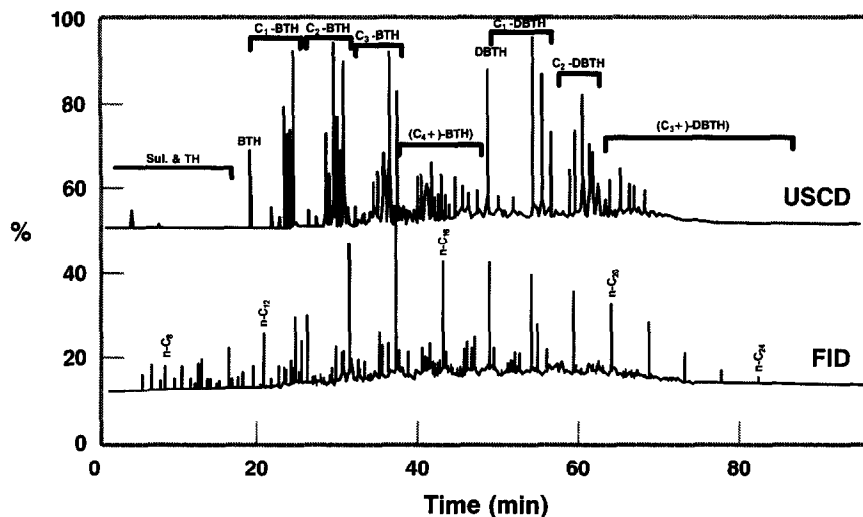
Fig. 9. Comparison of USCD and FID chromatograms obtained from a single injection of a light petroleum stream (1.73%, w/w, S).

area percentage response is required, then the long-term drift problem is not critical as long as the USCD instrument is properly installed and optimized.

Comparison between different probes

After 2 months of continuous use, the USCD response had decreased by a factor of approximately ten. A new probe was installed and conditioned as

TABLE II

RETENTION TIME DATA FOR SELECTED THIOPHENES
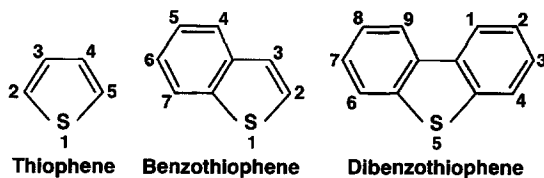
| Compound	Retention time (min)	Compound	Retention time (min)
Thiophene	5.26	3,6-Dimethyl-	60.15
2-Methyl-	6.71	3-Ethyl-	60.18
3-Methyl-	6.81	3,7-Dimethyl-	60.91
2,5-Dimethyl-	8.56	2,8-Dimethyl-	60.94
Benzothiophene	18.43	3,8-Dimethyl-	60.98
3-Methyl-	24.08	1,4-Dimethyl-	61.17
Dibenzothiophene	48.25	1,6-Dimethyl-	61.25
4-Methyl-	53.71	1,8-Dimethyl-	61.40
3-Methyl-	54.77	1,3-Dimethyl-	61.82
2-Methyl-	54.74	3,4-Dimethyl-	61.95
1-Methyl-	55.89	1,9-Dimethyl-	62.04
4,6-Dimethyl-	59.01	2,4-Dimethyl-	62.07
2-Ethyl-	59.59	1,7-Dimethyl-	62.08
2,6-Dimethyl-	60.04	1,2- and 2,3-	62.79
1-Ethyl-	60.14	Dimethyl-	
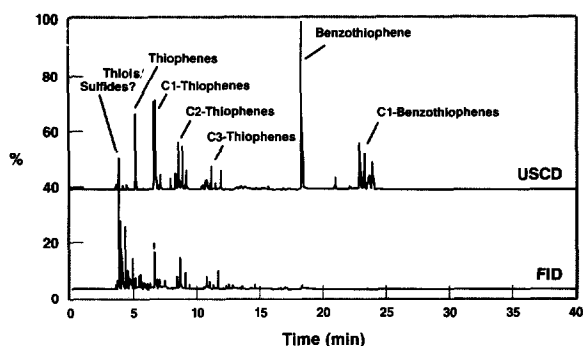
Fig. 10. Comparison of USCD and FID chromatograms obtained from a single injection of an FCC gasoline.
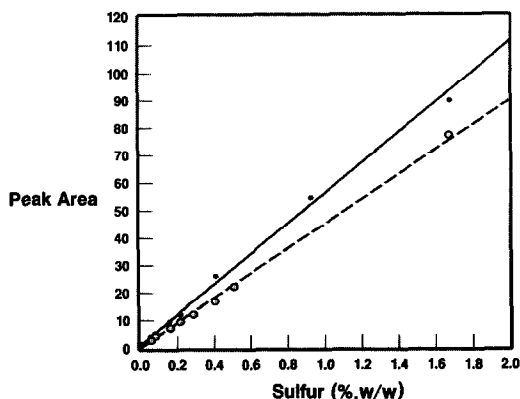

Fig. 11. USCD response with two different probes. ● = First probe, area $\times$ 10^{-6} = 55.362 [S] $-$ 0.0304, r^2 = 0.997. ○ = Second probe, area $\times$ 10^{-6} = 46.075 [S] $-$ 0.8645, r^2 = 0.998.

described above. Ten light petroleum stream samples were analyzed and the results were compared with those obtained with the old probe when new. The excellent linear fits obtained by plotting the USCD response against the sulfur content of the samples are shown in Fig. 11.

The precision of the data obtained using the two different probes remained approximately the same. However, the absolute USCD response obtained using the first probe immediately after conditioning

TABLE III

PRECISION OF THE USCD RESPONSE FOR SELECTED THIOPHENE GROUPS[a] PRESENT IN A LIGHT PETROLEUM STREAM (1.73%, w/w, S)

Injection No.	Contribution (wt.%)									
	Sul. and TH[b]	BTH	C_1-BTH	C_2-BTH	C_3-BTH	C_{4+}-BTH	DBTH	C_1-DBTH	C_2-DBTH	C_{3+}-DBTH
1	0.68	0.80	6.47	10.96	11.80	16.42	2.69	16.76	15.43	17.96
2	0.71	0.67	5.43	10.70	10.69	17.41	2.77	17.53	16.11	17.96
3	0.45	0.66	5.93	10.82	11.79	17.09	2.55	16.77	15.83	18.11
4	0.42	0.65	5.61	10.54	11.40	16.98	2.78	17.10	16.15	18.36
5	0.35	0.68	5.68	10.27	11.13	17.33	2.31	17.32	16.42	18.51
6	0.44	0.59	5.74	10.51	11.40	17.35	2.70	17.32	15.52	18.43
7	0.62	0.70	5.45	10.43	11.65	17.54	2.67	16.81	16.27	17.85
8	0.67	0.66	5.70	10.29	11.18	17.47	2.53	17.44	15.79	18.28
9	0.62	0.69	5.60	10.33	11.42	17.48	2.70	17.18	15.81	18.18
10	0.42	0.57	5.64	10.55	11.56	17.70	2.39	17.08	16.11	17.98
11	0.45	0.70	5.77	10.59	11.31	17.48	2.67	17.09	16.00	17.94
12	0.41	0.58	5.87	10.72	11.87	17.74	2.67	16.40	15.87	17.88
Mean	0.51	0.65	5.68	10.52	11.40	17.42	2.62	17.10	15.99	18.14
S.D.	0.12	0.05	0.15	0.18	0.33	0.25	0.15	0.33	0.26	0.23
R.S.D.[c] (%)	23.53	7.69	2.64	1.71	2.89	1.44	5.73	1.92	1.63	1.27

[a] See Fig. 9 for peak identifications.
[b] Sulphides and thiophenes grouping consisting of a number of sulfur compounds at low concentrations plus an unidentified peak which is probably due to H_2S.
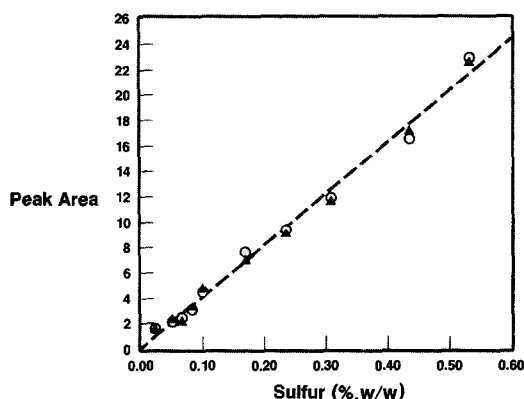[c] Relative standard deviation.

Fig. 12 Reproducibility of the USCD response with several light petroleum streams. $\bigcirc$ = Day 1, area × 10^{-6} = 41.478 [S] − 0.1070, R^2 = 0.999. $\blacktriangle$ = Day 2, area × 10^{-6} = 41.455 [S] − 0.0922, r^2 = 0.998.

Determination of total sulfur by USCD

Ten samples of the light petroleum process streams with various sulfur contents from 0.027 to 0.54% (w/w) were used to evaluate whether the USCD can be used for determining the total sulfur content in addition to speciation. A new probe was installed and two sets of measurements were made on two different days. The USCD response (total peak area) data obtained from these two sets of measurements were plotted against total sulfur content (Elemental determinations). Two excellent and almost precisely overlapping linear relationships were observed between the USCD response and the sulfur content of the petroleum samples (Fig. 12).

The total sulfur contents of these ten samples were determined by treating the linear fit of day 1 as a calibration and using the total-peak-area data from day 2 as "unknown" samples. The results obtained are given in Table IV.

The excellent agreement between the USCD results and the elemental determinations of sulfur content (Table IV) strongly suggests that USCD could be used to determine total sulfur in the light streams within the accuracy indicated in Table IV.

was *ca.* 15–18% higher than that obtained using the new second probe. The difference in absolute responses with the two different probes was probably due to the different inner diameters of the probes and their position in the FID housing. The gaseous sample which is transferred from the flame ionization detector to the USCD reaction cell depends significantly on the probe inner diameter and the probe position in the flame ionization detector.

ACKNOWLEDGEMENTS

TABLE IV

COMPARISON OF USCD AND ELEMENTAL DETERMINATIONS OF TOTAL SULFUR IN LIGHT PETROLEUM STREAMS

USCD area × 10^6 ("unknown")	Sulfur (%, w/w)		Difference (%)
	Elemental	USCD data	
1.263	0.027	0.032	18.52
1.944	0.046	0.046	0.0
1.945	0.056	0.051	8.92
3.006	0.076	0.071	6.58
4.331	0.10	0.104	4.00
7.451	0.18	0.189	5.00
9.686	0.24	0.238	0.83
12.094	0.31	0.297	4.19
17.551	0.43	0.417	3.02
22.832	0.54	0.555	2.79

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