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DETERMINATION OF THE TOTAL AMOUNT SULFUR IN PETROLEUM FRACTIONS BY CAPILLARY GAS CHROMATOGRAPHY IN COMBINATION WITH COLD TRAPPING AND A TOTAL SULFUR ANALYZER

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SUMMARY

The distribution of sulfur compounds among fractions of a petroleum liquid has been quantitatively determined by capillary gas chromatographic techniques, including on-column injection, cold-trapping of effluent, and measurement of effective recovery. In this study the amount of sulfur was determined in the gasoline (0–450°F), light cycle oil (450-650°F), and heavy cycle oil (650–1100°F) fractions of a refinery stream liquid. Knowledge of the amount of sulfur in the various fractions of this material can be valuable in determining how to process this material in the refinery. The petroleum liquid was separated by an on-column injection into a fused-silica capillary column, and the sulfur in each of the three cold-trapped fractions was measured by a hydrogen sulfide total sulfur analyzer. A detection limit of 50 ppm was achieved with quantitative recoveries of almost 100%. The sulfur distributions determined for a series of these petroleum liquids were 0.01–0.02 wt.-% in the 0–450°F fraction, 0.13–0.23 wt.-% in the 450–650°F fraction, and 0.50–1.20 wt.-% in the 650–1100°F fraction. The reproducibility for duplicate samples was 3%, and the reproducibility for the same sample with multiple cold-trap separations was also within 3%. This method obviates the complicated calibration step, which is necessary when sulfur-specific detectors, such as the flame-photometric detector and the Hall electrolytic conductivity detector are used.

INTRODUCTION

Sulfur compounds are responsible for problems in storage, blending, and processing of crude petroleum fractions in refinery operations. Typical problems caused by sulfur compounds are catalyst poisoning and deactivation, high hydrogen consumption in processing, and corrosion of equipment[1]. In recent years, the supply of petroleum for refinery feedstocks has gradually shifted towards heavier crudes, containing more sulfur compounds, and the presence of the sulfur in the various refinery streams needs to be known in order to efficient operations and to avoid problems.

In the present study, it was of interest to investigate a series of catalytic cracker products that has been produced from a microconfined catalyst bed unit. An atmos-

pheric residual desulfurization-treated heavy oil was cracked over a wide variety of artificially deactivated commercial catalytic cracking catalysts. The artificially aged catalysts were impregnated either with metal levels characteristic of refinery A or metal levels characteristic of refinery B. Additionally, two of the test samples were produced with equilibrium cracking catalysts. One important piece of information concerning these materials is how sulfur is distributed in the fractions with various boiling points. It is of value to know this for a catalytic cracker product so that it can best be further processed in the refinery. Also, the sulfur distribution will provide useful information on whether the particular catalyst preferentially concentrates sulfur compounds in any of the fractions. Thus, analytical procedure was sought to determine the sulfur distribution in petroleum liquids, such as these catalytic cracker products.

A number of gas chromatographic (GC) methods have been developed for the quantitative analysis of sulfur compounds in various matrices through the use of specific sulfur detectors. Among available sulfur detectors, both the flame-photometric detector (FPD) and the Hall electrolytic conductivity detector (HECD) have enjoyed popularity in interfacing with GC columns[2-5]. However, existing GC methods, associated with these detectors, were found to be unsuitable for quantitating the more than hundred sulfur compounds that are present in a catalytic cracker products, due to several drawbacks of sulfur-selective detectors. The quantitative analysis of sulfur compounds which are present over a wide boiling range (0°F to 1100°F) is very difficult to perform with specific sulfur GC detectors, such as the FPD or the HECD due to the non-linearity of the FPD and the unstable character of the HECD[6].

When a FPD is used, each sulfur compound needs to be individually calibrated, because this detector is not linear and its response varies among compounds. The maximum operating temperature for a detector is generally about 250°C which is well below the oven temperature of 350°C required to elute all sulfur compounds. Also, a quenching effect, which reduces the intensity of response to sulfur compounds, has frequently been found when hydrocarbons are eluted together with sulfur compounds[5].

A HECD may eliminate some of the problems associated with the operation of a FPD. Extensive calibration is not necessary with a HECD because it is a linear detector. The detector temperature is easily increased to 350°C without any problems[6]. Unfortunately, poor reproducibility has been a problem when a HECD was used with the wide temperature programming which is required in simulated distillation type GC analysis of crude oils and other heavy hydrocarbon feedstocks[7]. Recently, Bradley and Schiller[8] reported a method for assessing the sulfur distribution in heavy oils by means of a pyrolyzer and a FPD. Although this method utilized the FPD in a manner that eliminated several problems, such as the detector temperature limit and the need of extensive calibrations for individual sulfur compounds, it still required a time-consuming calibration of sulfur dioxide. Thus, there is still a need for a simple and reliable method of determining the distribution of sulfur compounds in petroleum.

Knowledge of the amount of sulfur present in each of three boiling point fractions of the catalytic cracker products (gasoline at 0–450°F, light cycle oil at 450–650°F, and heavy cycle oil at 650–1100°F) would provide the type of information valuable in processing these materials and in evaluating the catalysts. This report

describes the development of a new method for the determination of total sulfur compounds in each of these fractions in petroleum liquids, such as the catalytic cracker products.

This method combines on-column injection with cryogenic trapping of effluents in capillary tubing. A hydrogen sulfide-type total sulfur analyzer was used to measure the sulfur compounds recovered. The Houston–Atlas hydrogen sulfide analyzer has been found to be reliable and sensitive, without interference from nitrogen and halogens[9]. The on-column injection into a fused-silica capillary column is becoming increasingly popular for quantitation[10]. The use of a fused-silica capillary column in our work had the advantage over a packed column of reducing the adsorption of sulfur compounds.

EXPERIMENTAL

Simulated distillation capillary GC with a cold-trap loop

The GC equipment utilized for this work was a Varian Model 3700 (Walnut Creek, CA, U.S.A.), equipped with a FID and a dual flame photometric detector. An additional on-column injector, Model OCI-2 (SGE, Austin, TX, U.S.A.) was installed on the GC oven wall, and the carrier gas, helium, for an unused packed-column injection port was diverted into the on-column injector. A fused-silica capillary column, DB-5 25 m × 0.32 mm I.D. with 1-μm film thickness (J&W, Folsom, CA, U.S.A.) was connected to the on-column injector. The outlet end of the capillary column was connected to a cross (Valco, Houston, TX, U.S.A.) which diverts the column effluents into three capillary trap loops, made of 0.031-in. stainless-steel tubing.

The analytical column, the cross, and a portion of the sample trap loop were located inside the GC oven, while one third of the trap loop which was located outside the GC oven was submerged in liquid nitrogen. Two cold-traps were connected in series from each of the three cold-trap loops. The first trap loop (which will trap the low-boiling compounds along with the solvent) was prepared by inserting a stainless-steel tube, 10 cm × 0.1 in. I.D., in the middle of a capillary tube in order to prevent clogging by a large amount of solvent being eluted. The 0.31-in. capillary stainless-steel tube was connected with a 0.1-in. stainless-steel tube by means of a capillary butt connector and double-tapered ferrule (Supelco, Bellefonte, PA, U.S.A.).

The sample was first diluted with ten volumes of toluene. A 3-μl sample was then introduced, using an on-column injection syringe with a fused-silica needle (12 cm × 0.17 mm I.D.). The oven temperature was programmed from 30°C to 350°C at 8°C/min. The first fraction (0–450°F) was eluted when the oven temperature reached 140°C, the second fraction (450–650°F) when it reached 220°C, and the third fraction (650–1100°F) when it reached 340°C. The oven temperature for each fraction was calibrated using the boiling points of hydrocarbons and sulfur compounds with both FID and FPD. While the first fraction was being collected on the first trap-loop, the other two trap-loops were plugged with septa.

Sulfur compounds (along with other trapped components) were recovered by passing approximately 400 μl of toluene (a rinse volume that was several times the volume of the loop in order to recover all material efficiently through the capillary trap-loop). The glass injection reservoir, containing the toluene, was pressurized to

1 lb./in.[2] with nitrogen, and the flow-rate of toluene was controlled with a needle valve so as not to exceed 0.1 ml/min.

Measurement of total sulfur content of separated fractions

A Houston–Atlas total sulfur analyzer, Model 856 Tracor Atlas, Houston, TX, U.S.A.) was used to measure the total sulfur content of each fraction recovered from the cold-traps. This instrument consists of a total sulfur hydrogenator (Model 856) and a total hydrogen sulfide analyzer (Model 825R-D). Approximately, 80 μl of the toluene solution from the cold-trap was injected into the Model 856 pyrolyzer at 1250°C. The analyzer was operated at a hydrogen flow-rate of 30 ml/min and a sample injection rate of 5 ml/min. For the injection of a large amount of sample at a constant rate, a micro-jet automatic injector (Tracor Atlas, Model 1001) was used. A 0.4-μg/ml solution of butyl sulfide in toluene was used to calibrate the first and second fractions. A dodecyl sulfide (boiling point, 485°C) solution of 0.4 μg/ml was used to calibrate the third fraction.

Recovery of sulfur compounds

In order to determine the recovery of sulfur compounds by the cold-trap and Houston–Atlas analyzer, standard solutions of sulfur in toluene at concentrations of 10–100 ng/μl were prepared and analyzed. Thirteen groups of sulfur compounds with boiling points ranging from 289 to 657°F were used individually to evaluate the sulfur response for this study. These are shown along with their boiling points in Table I. The fourth column in Table I shows the amount of sulfur known to be introduced into the column as the standard, and the fifth column shows the amount of sulfur recovered. Most of the compounds, except the dibenzothiophenes and some disulfides showed almost 100% recovery (sixth column of Table I).

The seventh column in Table I shows recoveries obtained when the Houston–Atlas hydrogen sulfide analyzer was calibrated in each case with a standard, made from the same compound as that being analyzed, rather than by using the single calibration with the butyl sulfide standard for all compounds. The recoveries then approach 100% in all cases, with particular improvement in the dibenzothiophenes and disulfides. This type of external calibration compensates for hydrogenator efficiency and sulfur detector response to the individual sulfur compounds and results in recoveries of almost 100%. The reason for the improvement when such self-calibration is carried out is seen in Fig. 1, which shows the response of the Houston–Atlas hydrogen sulfide analyzer to a number of sulfur compounds. There is clearly a variation among these compounds, some groups, such as the dibenzothiophenes, showing much lower response than the majority of the others. A low response of this analyzer to dibenzothiophenes has been reported previously by Drushel[9], who showed that an improved response could be obtained by increasing the temperature of a pyrolyzer. It therefore follows that such compounds would show a low recovery when calibrated with a compound like butyl sulfide, which shows a significantly higher response in the Houston–Atlas analyzer. Low Houston–Atlas response and low recoveries in these cases are not due to the boiling points of the compounds, because their boiling points are close to those of others which show high response. The excellent recoveries obtained with self-calibration indicate that components are not being lost or discriminated against in the overall procedure involving GC separation, cold-trapping, and sulfur analysis.

TABLE I

PERCENT SULFUR RECOVERY FOR SULFUR COMPOUND BLEND

Amount of sulfur present and recovered includes all compounds in group.

Compound	b.p. ($°F$)	Group no.	Test no.	Calc. (ng)	Recovery[a] (ng)	Recovery (%)	Direct compound recovery[c] (%)
n-Propyl sulfide	289	1	1	68	70.2	103	100
			2	68	63.0	93	95
n-Pentyl sulfide	527	2	1	82	65	79.2	100
			2	82	62.5	77	96
			3	170	205	122	100
Dibenzothiopene	640	3	1	181	114	63	92
			2	181	132	73	100
Thiophene	183	4	1	60	65	107	100
			2	60	83	138	128
Dodecyl mercaptan	530	5	1	23	21	91	100
			2	46	50	108	100
Multicomponent groups							
Dibenzothiophene	640						
1-Benzothiophene	428	6	1	140	62	44.3	100
2-Ethylthiopene	273		2	140	68	48.5	100
Amyl mercaptan							
Hexyl mercaptan	280	7	1	81.2	93.7	109	115
Heptyl mercaptan	325		2	81.2	94	116	110
Butyl disulfide	448						
Pentyl disulfide	527	8	1	207.9	198.9	96	102
Phenyl disulfide	657		2	207.9	204	98	103
Ethyl sulfide	198						
n-Propyl sulfide	289	9	1	98	111	113	99
n-Butyl sulfide	372		2	98	110	113	99
Dimethyl disulfide	99.2						
Dibutyl disulfide	448	10	1	121.7	104	88	100
Dipropyl disulfide	388		2	121.7	97	80	100
2-Ethyl thiophene	273						
Propyl disulfide	388	11					
Dodecyl mercaptan	530		1	62.2	66.9	107	100
Phenyl sulfide	565		2	62.2	65.9	103	100
Diallyl sulfide	280.4						
Methyl n-octyl sulfide	651						
Methyl n-nonyl sulfide		12	1	262.2	355	135	98
Heptyl sulfide			2	262.2	251[b]	96	100
Phenyl sulfide	565		3	262.2	257[b]	98	100
Octyl mercaptan	390						
t-Dodecyl mercaptan	509						
t-Decyl mercaptan	442	13					
sec-Amyl mercaptan	234		1	350.7	331	94.3	107
Hexyl mercaptan	306		2	350.7	315.8	91	103

[a] Butyl sulfide (0.4 mg/ml) was used to calibrate the concentration on a Houston–Atlas total sulfur analyzer.

[b] Heptyl sulfide (0.4095 mg/ml) was used to calibrate this concentration.

[c] Direct compound recovery was compared with its own solution instead of butyl sulfide solution.
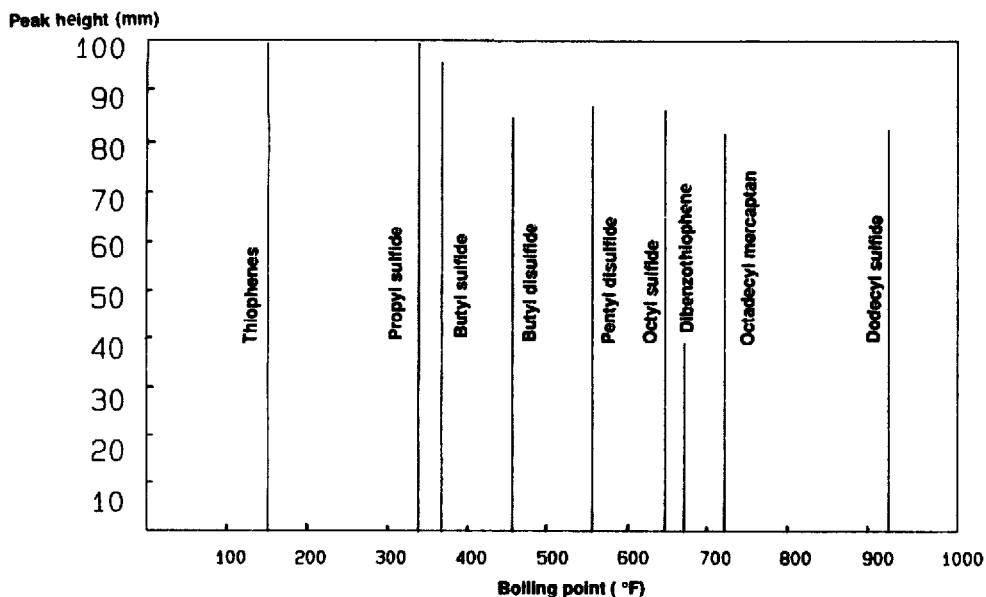
Peak height (mm)

Fig. 1. Different responses of Houston–Atlas total sulfur analyzer to various compounds.

Calibration for individual compounds is time-consuming and is not even possible for samples where the specific sulfur compounds are not known. Examination of the results for the butyl sulfide calibration in Table I shows that overall the recovery for the various compounds is quite good and that acceptable results should be obtainable with this procedure.

The response (peak height) of the Houston–Atlas analyzer was found to be linear with sulfur concentration between 30 and *ca.* 200 ng. The error in measuring peak heights in the analyzer with a signal-to-noise ratio of about 2–8 was estimated to be below 4 5 ng. Most reading fall in the 100 220 ng range, so that the signal-to-noise ratio for these was between 2 and 4%.

RESULTS AND DISCUSSION

Sulfur distributions were determined for eleven catalytic cracker products and one reference liquid product which was not treated, and the results are shown in Table II. The catalytic cracker products were all produced by a microconfined catalyst bed unit which was fed an atmospheric residual desulfurization-treated heavy oil. The catalysts for nine of the samples (1–9) were artificially aged in the laboratory. Five of these (1, 3, 5, 7 and 9) were impregnated with metal levels (1200 ppm Ni, 1800 ppm V and 600 ppm Sb) characteristic of refinery A, and these are designated as (A) in Table II. Four of these (2, 4, 6 and 8) were impregnated with metal levels (2500 ppm Ni, 3500 ppm V and 1200 ppm Sb) characteristic of the refinery B, and these are designated as (B) in Table II. The catalysts impregnated to the refinery A metal levels were used to crack an atmospheric residual desulfurization-treated refinery A crude containing 0.31 wt.-% sulfur. The catalysts that were impregnated to the refinery B

TABLE II

SULFUR DISTRIBUTION IN CAT CRACKER PRODUCTS

Sample [c]	Catalyst [d]	wt.-% Sulfur in fractions [a]			wt.-% Hydrocarbon in fractions [b]		
		F-1 (Gasoline) (0–450°F)	F-2 (Light cycle oil) (450–650°F)	F-3 (Heavy cycle oil) (650–1100°F)	F-1 (Gasoline) (0–450°F)	F-2 (Light cycle oil) (450–650°F)	F-3 (Heavy cycle oil) (650–1100°F)
1(A)	P	0.01	0.23	0.57	59.17	25.11	15.72
2(B)	C1	0.01	0.15	0.50	62.40	22.00	15.60
3(A)	C2	0.01	0.22	0.83	67.73	22.01	10.28
4(B)	C1	0.01	0.15	0.50	62.40	22.00	15.60
5(A)	C2	0.01	0.26	0.70	62.73	22.01	15.26
6(B)	D1	0.02	0.17	0.78	66.07	24.10	9.83
7(A)	D2	0.01	0.19	1.07	69.21	23.02	7.77
8(B)	E1	0.02	0.13	0.62	61.51	25.56	12.93
9(A)	E2	0.01	0.21	0.92	65.38	24.50	10.12
10	F1	0.02	0.17	1.20	68.29	23.76	7.95
11	F2	0.02	0.22	0.70	63.68	23.80	12.52
12	Ref.liq.prod.	0.03	0.19	0.35	54.12	22.00	23.88

[a] Sulfur content as a percentage of weight in each fraction. wt.-% sulfur = $\dfrac{\text{wt. of sulfur in fraction}}{\text{total wt. in fraction}}$

[b] Percentage of total hydrocarbon sample present in each fraction (determined by simulated distillation analysis).

wt.-% hydrocarbon = $\dfrac{\text{wt. hydrocarbon in fraction}}{\text{total sample weight}}$

[c] A = refinery A; B = refinery B.

[d] Real catalyst name is not shown.

metal levels were used to crack an atmospheric residual desulfurization-treated refinery B fresh feed, containing 0.3 wt.-% sulfur. The remaining two samples (10 and 11) were prepared by using equilibrium catalysts. Sample 12 is a reference liquid product, which is used to calibrate the hydrocarbon boiling point distribution in the simulated distillation test procedure. The first three columns in Table II show the concentration of sulfur in each of the three fractions. This is given as weight percent of the amount of material in the particular fraction, so that the numbers shown represent the sulfur levels that would be present in a stream consisting of that fraction alone. In order to determine the weight percent for each fraction from the amount of sulfur measured in the cold-trap, it was necessary to know the distribution of the hydrocarbon in the sample among the fractions. This was obtained from a simulated distillation GC analysis, and the results are shown in the last three columns of Table II.

The results in Table II show that in the catalytic cracker products, the sulfur levels were 0.01–0.02 wt.-% in the gasoline fraction (0–450°F), 0.13–0.23 wt.-% in the light cycle oil fraction (450–650°F), and 0.50–1.20 wt.-% in the heavy cycle oil fraction (650–1100°F). Samples 2 and 4 were duplicates, as were samples 3 and 5. Comparison of results in Table II for those duplicate sample pairs shows that reproducibility obtained with this technique was good.

We have noted that the sulfur levels measured in the light cycle oil cut (450–650°F) and heavy oil cut (650–1100°F) of the microconfined catalyst bed unit (MCBU) products are consistently *ca.* 1.5 times higher for the products from the experiments made by using a catalyst impregnated to refinery A metals level and a refinery A feedstock than those made by using a catalyst impregnated to refinery B metals levels and a refinery B feedstock. Specifically, we are referring to analyses runs 2 and 3, 4 and 5, 6 and 7, and 8 and 9 for catalyst C, D, and E as shown in Table III. Samples 2 and 4 were identical and treated with the same catalyst as were samples 3 and 5. The wt.-% of sulfur in the fractions were surprisingly reproducible, as shown in Table IV. When the analyses were performed, the analyst did not have any information on these samples. These results proved that the procedure itself is very reproducible and applicable to routine analysis. From the MCBU experiments we know that the experiments on refinery B-metal and feed material resulted in lower conversions and greater selectivities towards hydrogen and coke than those on refinery A-catalyst materials.

TABLE III

FEED PROPERTIES

		Refinery A topped crude	Refinery B fresh feed
American Petroleum Institute (API) at 60°F		19.5	22.1
Carbon residual	(wt.-%)	4.7	3.1
Sulfur	(wt.-%)	0.30	0.31
Total nitrogen	(wt.-%)	0.14	0.17
Basic nitrogen	(ppm)	830	658
Saturates	(wt.-%)	57.4	55.0
Aromatics	(wt.-%)	26.3	30.4
Resins	(wt.-%)	11.8	10.6
Asphaltenes	(wt.-%)	4.4	3.4

TABLE IV

WEIGHT PERCENT SULFUR IN HEAVY CYCLE OIL FRACTION

wt.-% sulfur in heavy cycle oil A/B = C 1.58, D 1.37, E 1.48.

Sample [a]	Catalyst	wt.-% sulfur in fraction
2 (B)	C1	0.50
3(A)	C2	0.83
4(B)	C1	0.50
5(A)	C2	0.70
6(B)	D1	0.78
7(A)	D2	1.07
8(B)	E1	0.62
9(A)	E2	0.92

[a] A = refinery A, B = refinery B.

Since the sulfur from the feeds could turn up in any of three product stream (the liquid product, the gas products, or the coke), the sulfur unaccounted for in the liquid products of the refinery B experiments must have been converted to hydrogen sulfide or deposited as coke. Several explanations of this phenomenon are possible and, most likely, they all contributed to the overall result. One explanation could be that the higher nickel concentrations resulted in dehydrogenation and condensation of heavier sulfur-bearing hydrocarbon components and resulted in the selective concentration of the incremental sulfur in the coke. Another explanation could be that the feedstocks and/or the differences in the feed pretreatment (atmospheric residual desulfurization processing) between the two facilities (refineries A and B) could account for the sulfur-containing fraction of the refinery B feed being more refractory than the sulfur-containing fraction of the refinery A feed, resulting in preferential condensation of the incremental sulfur-bearing material as coke. In any case, we do not have the information necessary to determine why the recovery of sulfur in the liquid products differed in such a consistent manner, and additional experiments would be necessary to confirm these results and determine the reasons for them. What is important to note is that this analysis technique allowed us to observe these differences.

Table V shows the amount of sulfur in each of the samples found by various techniques. The first three columns show the amount of sulfur in nanogram, found in each fraction for a given total sample volume (in 3 μl of diluted sample) by the present GC–cold-trap method, and the fourth column gives the total of the three fractions. In addition to this method, the total amount of sulfur for this same volume of each sample was measured by X-ray fluorescence, and this result is shown in the fifth column. The X-ray fluorescence technique determines the weight percent of sulfur in the sample, and this number can then be converted to nanogram in the injected volume of sample in the GC–cold-trap method. This is the number shown in the fifth column, while the weight percent is shown in parentheses. The sixth column shows the recovery for the GC–cold-trap method relative to the sulfur amount determined by X-ray fluorescence. The last column in Table V shows the amount of elemental sulfur as determined by the polarographic method. The amount of elemental sulfur

TABLE V

SULFUR CONTENT IN CAT CRACKER PRODUCTS BY DIFFERENT TECHNIQUES

| Sample | Catalyst | Total sulfur by cold trap (ng) [a] | | | | Total sulfur[b] by X-ray fluorescence | | Recovery (%) | Elemental sulfur[c] by polarographic method | |
		F-1 (Gasoline) (0–450°F)	F-2 (Light cycle oil) (450–650°F)	F-3 (Heavy cycle oil) (650–1100°F)	Total	ng	wt.-% in sample		ng	wt.-% in sample
1(A)	P	18.2	152.3	233.1	403.6	369.2	(0.14)	109	3.4	(0.0013)
2(B)	C1	22.0	84.3	203.6	309.9	316.4	(0.12)	97.9	1.8	(0.0006)
3(A)	C2	10.6	124.9	220.4	355.9	394.2	(0.15)	94.3	3	(0.0010)
4(B)	C1	19.5	85.3	203.5	308.3	342.8	(0.23)	90	0.6	(0.0002)
5(A)	C2	24.4	150.3	276.5	451.2	395.5	(0.15)	114	2.4	(0.0008)
6(B)	D1	31.9	103.9	199.9	335.7	263.7	(0.10)	127	3	(0.0010)
7(A)	D2	23.9	111.9	216.6	352.4	369.2	(0.14)	95.5	2.7	(0.0009)
8(B)	E1	25.2	87.7	206.9	319.8	316.4	(0.12)	101	2.7	(0.0009)
9(A)	E2	18.2	136.0	241.2	395.4	395.5	(0.15)	100	3.3	(0.0011)
10	F1	30.5	107.4	249.0	386.9	369.2	(0.14)	104.8	2.1	(0.0007)
11	F2	26.8	134.1	226.8	387.7	316.4	(0.12)	123	3.3	(0.0011)
12	Ref.liq.prod.	36.6	107.0	215.4	359.0	321.0	(0.63)	112	<0.6	(<0.0002)

[a] Samples were diluted with toluene in 1:10 ratio prior to injection. Sample 12 was diluted 1:50. Amount of sulfur shown is that found in 3 μl injected volume of the diluted sample.

[b] X-Ray fluorescence data given result as wt.-% of sulfur in sample. Amount of sulfur shown is that which would be contained in the injected volume of diluted sample for the corresponding GC–cold trap test in preceding columns.

[c] Polarographic data given result as wt.-% of elemental sulfur in sample. Amount of sulfur shown is that which would be contained in the injected volume of diluted sample for the corresponding GC–cold trap test in the preceding columns.

was generally found to be less than or equal to 0.0010 wt.-% in three catalytic cracker products.

The largest discrepancies between the X-ray method and the GC–cold-trap method were 14%, 23%, and 27% (Table V). The remaining nine samples showed agreement within 10%, which is considered reasonable for comparisons between two completely different procedures. The precision of sulfur analyses by X-ray fluorescence is generally about ±5%[11]. Differences may be due to several reasons in the cold-trap method, such as inaccurate injection volumes, unusually high response of the sulfur analyzer, and misuse of the correction factors. The error in the 3-μl volume of sample injected was *ca.* ±0.15 μl. The detector, consisting of a lead acetate tape in the Houston–Atlas analyzer often gives a little different response in repeated use without good conditioning, and this can also introduce some error. All these factors may lead to *ca.* 5% uncertainty in the results.

Excluding the two samples which showed more than 20% difference, the total sulfur contents of catalytic cracker samples obtained by this method differed by about 5% from those obtained by X-ray fluorescence method. This might indicate the accuracy obtainable in the cold-trap method. Thus, it is apparent that the cryogenic trapping of effluents in the capillary tubing and their subsequent recovery was quantitative. Cryogenic trapping in a capillary tubing was originally used in the purge-and-trap method for the analysis of volatile organics. The trapping efficiency is controlled by using a different film thickness when trapping is performed at room temperature[12]. The present method is novel in that it involves the trapping of three fractions in series, cut from column effluents covering a wide boiling range. The use of an inert fused-silica capillary column eliminates the adsorption of polar sulfur compounds that occurs in a packed column. Non-reproducible recovery of some mercaptanes was thought to be due to such adsorption[8]. The recovery for mercaptans in this method was quite reproducible.

The good overall agreement between this procedure and X-ray fluorescence obtained in this study is ascribed to the nature of the present samples. Even though large discrepancies were observed for some individual sulfur components in this method, the overall blend of sulfur compounds present in the samples themselves resulted in a good determination of the total sulfur content. When samples were analyzed in triplicate by this method, the standard deviation for the values determined was *ca.* 3%. These replicate analysis results show that the precision for sulfur determination in fractions of catalytic cracker products by this method is *ca.* 3%.

Most of the sulfur compounds in these catalytic cracker products were identified as benzothiophenes and dibenzothiophenes by mass spectrometric analysis. Dibenzothiophenes begin to appear at 600°F (which is the last part of fraction 2), followed by isomers of alkyl group-substituted dibenzothiophenes (mostly methyl, ethyl, propyl, butyl, and amyl substituted). Benzothiophenes begin to appear at 500°F (the first part of fraction 2). The benzothiophenes consist of several families, substituted by alkyl groups, just like the dibenzothiophenes. Longer alkyl chains, such as the decyl group (which is usually found in crudes) were not detected in the mass spectrometric analysis. Dealkylation is believed to occur during the distillation of crudes. Mercaptans and volatile sulfides constitutes less than 1% of the total sulfur, according to the results of both sodium hydroxide and silver nitrate tests. Heavy sulfides and multiple-ring thiophenes apparently predominate. Disulfides were not

TABLE VI

SULFUR DISTRIBUTION IN A CAT CRACKER PRODUCT BY GC WITH SPECIFIC SULFUR DETECTOR (HECD)

	wt.-% sulfur in fractions (by cold trap)			wt.-% sulfur in fractions (by HECD specific sulfur detector)		
Sample 12, ref. liquid product	F-1 (gasoline) (0–450°F)	F-2 (light cycle oil) (450–650°F)	F-3 (heavy cycle oil) (650–1100°F)	F-1 (gasoline) (0–450°F)	F-2 (light cycle oil) (450–650°F)	F-3 (heavy cycle oil) (650–1100°F)
Run 1	0.03	0.17	0.32	0.02	0.16	0.40
Run 2	0.04	0.19	0.29	0.02	0.25	0.33
Run 3	0.03	0.18	0.29	0.01	0.25	0.33
Run 4	0.03	0.14	0.24	0.01	0.18	0.40
Run 5				0.01	0.29	0.30
Run 6				0.02	0.20	0.36
Run 7				0.01	0.22	0.37
Mean	0.03	0.17	0.30	0.01	0.16	0.36
Standard deviation	0.0045	0.021	0.041	0.005	0.045	0.038

Fig. 2. Chromatogram of a references liquid product. Column, DB-1, 30 m × 0.32 mm I.D.; 1-μm film thickness; carrier gas, helium; detector, HECD at 350°C; temperature programming, 30 to 350°C with 6°C/min; on-column injection; sample size, 1 μl, diluted 1:10 in toluene.

found by mass spectrometry. A number of literature references also indicate that disulfides are not found in gas oils[13].

On-column injection into a fused-silica capillary column was verified in this study as a powerful technique for the quantitation of complex samples, such as the sulfur compounds in these catalytic cracker products. It has previously been reported that column injection modes, such as split or splitless injection, can cause component discrimination so that quantitation is not achieved[14]. Many laboratories have reported that on-column injection is superior to injection through a hot injection port[15]. The former was found to be reliable, rugged, and simple to perform by any person familiar sample trapping techniques.

As a comparison of techniques, sample 12 was analyzed with a simulated distillation gas chromatograph (SIMD), interfaced with a HECD. Results of replicate analyses are shown in Table VI. A chromatogram from one of these analyses is shown in Fig. 2. The sulfur distributions for the three fractions are calculated based upon the sulfer area in each fraction divided by the total sulfur area obtained with the HECD. The standard deviation for this SIMD–HECD method (Table VI) is greater than for the cold-trap method. It is interesting to observe that the mean distribution from seven analyses of fraction 3 is 60.8%, compared to the value of 60.0% for the cold-trap method, shown in Table I. However, the poor reproducibility associated with the SIMD–HECD method appeared to be a problem. The response of the HECD also varies with the type of sulfur compound. This means that quantitation of the different compounds in a sample requires knowledge of the identity of each sulfur component and a calibration for each component. For complex samples, such as these catalytic cracker products, calibration for each component is tedious and time consuming. Moreover, it is impossible to perform a complete calibration, since standards for many sulfur containing compounds are not available. The FPD suffers less from response variation. However, the operating temperature of the FPD is much below

the temperature needed to elute many components of interest in samples, such as these catalytic cracker products, and the use of a column temperature above the detector temperature is undesirable due to problems with condensation in the detector.

Further study is necessary to refine the present method in order to reduce the error and automate the entire procedure or make it semi-automatic by use of a microsampling valve. An alternative to the Houston–Atlas hydrogen sulfide-type total sulfur analyzer could be a sulfur dioxide-type sulfur analyzer, which has been claimed to provide better detection.

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