Application of Catalytic Desulfurization to Group Sulfur Analysis of Petroleum Fractions

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Previous methods for the group sulfur analysis of petroleum oils have been fully applicable only to low-boiling distillates, such as gasoline, since the mercury salt techniques employed for differentiating nonthiophenic from thiophenic sulfur are limited to sulfur compounds in the lower molecular weight range. This limitation has been overcome, to a considerable extent, by employing selective catalytic decomposition to differentiate nonthiophenic from thiophenic sulfur. The nonthiophenic sulfur compounds are decomposed over alumina at 450° C. to hydrogen sulfide and, presumably, the corresponding olefin, while the thiophenic sulfur compounds are stable under these conditions. Titration of the hydrogen sulfide, which is generally recovered to the extent of 90 to 95% from pure nonthiophenic sulfur compounds, provides a rapid and reasonably quantitative means of determining the content of nonthiophenic sulfur. Thiophenic sulfur is calculated as the difference between the total sulfur content of the sample and the value obtained for nonthiophenic sulfur. This distinction, in connection with conventional methods for determination of elemental sulfur, hydrogen sulfide, mercaptans, and disulfides, enables group sulfur analyses to be made on heavier petroleum fractions than was previously possible. The method has been applied to a wide variety of petroleum fractions, including light and heavy distillates, lubricating oils, crude oils, residues, and shale oils.

THE necessity for economical utilization of "high-sulfur" crude oils, being produced in increasing quantities (*3*, *14*) for the manufacture of products containing relatively small amounts of sulfur, is becoming increasingly important. In order to evaluate properly the effects of refining processes on the sulfur content of products and the effects of the sulfur compounds present on the performance of the products, methods are required for the group sulfur analysis of crude oils, distillates, and residues.

A method for the group sulfur analysis of petroleum distillates, fully applicable only to saturated hydrocarbons in the gasoline range, was developed by the U. S. Bureau of Mines (*1*). A critical review of other proposed methods was included in their development work and other studies concerned with the nature of the sulfur compounds present are in progress (*2*). The Bureau of Mines method involves determination of the sum of the hydrogen sulfide and mercaptans by silver nitrate titration, extraction of hydrogen sulfide from a fresh sample with acidic cadmium chloride solution, and titration of the mercaptan (thiol). Elemental sulfur is determined by doctor treating in the presence of added mercaptan, hydrogen sulfide formed being removed by extraction and the excess mercaptan determined by titration. Disulfides are determined from titration of the mercaptans produced by reduction with zinc and acetic acid. Aliphatic plus alicyclic sulfides are measured by the change in sulfur content of the gasoline upon treatment with powdered mercurous nitrate. The same portion of the sample is then treated with powdered mercuric nitrate and the resultant reduction in sulfur content is considered to be aromatic sulfides and thiophenes. A fresh portion of sample is extracted with water to determine water-soluble sulfur compounds. Although this method is intended to give a complete group sulfur analysis of gasolines there is generally some residual sulfur, especially with heavy naphthas (*9*), not determined by the method.

Those portions of the above methods which involve determination of elemental sulfur, hydrogen sulfide, mercaptans, and disulfides are generally applicable to oils regardless of source or degree of refining because of the high reactivity of these sulfur compounds. However, the determination of organic sulfides by extraction with mercuric and/or mercurous nitrate limits the applicability of the group sulfur analysis. The studies made in connection with the Bureau of Mines method (*1*, *2*, *4*) showed that:

> Mercurous nitrate does not completely remove aliphatic sulfides above dibutyl sulfide and the extent of removal decreases as the molecular weight increases.
> Mercuric nitrate will remove most of the aliphatic sulfides not completely removed by mercurous nitrate.
> Mercuric nitrate will not completely remove diphenyl sulfides and will not remove tetra-substituted thiophenes.
> Mercurous and mercuric nitrate are successively stronger reagents which produce results not based entirely on actual structural differentiations.

The mercury salt procedures can be applied to fractions in the gasoline range because the sulfur compounds present are of low molecular weight. Extension of the mercury salt methods to higher molecular weight fractions has not been successful; the amount of sulfur not classified by these methods progressively increases with fractions of higher molecular weight (*9*). In addition, extraction of olefinic or aromatic materials with mercuric nitrate can be hazardous (*1*).

A suggestion for a possible method of differentiating between organic sulfides and thiophenes was obtained from studies in connection with the mechanism of catalytic cracking (*7*, *8*). Thermodynamic calculations (*8*) by Greensfelder and Voge indicated that, in the absence of hydrogen, aliphatic mercaptans and sulfides would either decompose to olefins and hydrogen sulfide or be cyclized to thiophenes at temperatures above 300° C., but that thiophenes would be stable at these temperatures and higher. Faragher, Morrell, and Comay (*5*) found that thiophene was unchanged when passed through a tube at 870° C. Experiments (*8*) had shown that gasolines containing added aliphatic mercaptans and aliphatic sulfides were substantially desulfurized at 450° C. over bauxite or alumina catalyst. Thiophene solutions showed substantially no reduction in sulfur content at 450° C. over alumina but their sulfur content was reduced by about 20% when bauxite (typical composition, 83% alumina, 7% ferric oxide, 7% silica, and 3% titania) or alumina containing added iron salts were used as catalysts.

A method has been developed for differentiating between thiophenic and nonthiophenic sulfur compounds based on the principle of differential thermodynamic stability. Catalytic decomposition of nonthiophenic sulfur compounds over heated alumina produces hydrogen sulfide, and, with certain compounds, mercaptans, which provide a direct measure of the nonthiophenic sulfur content of the sample. A more complete group sulfur determination can be made by employing direct procedures for the determination of total sulfur, elemental sulfur, hydrogen sulfide, mercaptan, and disulfide. Thiophenes are calculated by difference between total sulfur and nonthiophenic sulfur.

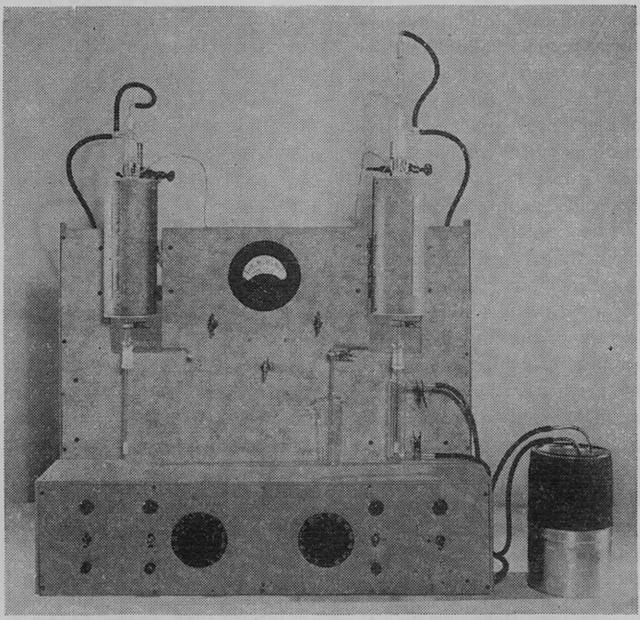


Figure 1. Dual Catalytic Desulfurization Apparatus

About the time the development of this method was completed, a somewhat similar technique for differentiating between thiophenic and nonthiophenic sulfur was reported by Hammar (*10*). The thiophene in the condensed liquid product, after removal of hydrogen sulfide, was determined from its sulfur content.

APPARATUS AND REAGENTS

A photograph of the assembled catalytic decomposition apparatus is shown in Figure 1 and a schematic diagram in Figure 2. A dual unit was constructed to enable more efficient use of operator time.

The purge gas was commercial purified nitrogen (99.9%) and was brought to constant humidity by bubbling through water. To remove possible traces of oxygen, the nitrogen was passed through a tube containing copper maintained at 350° C., mounted on the back of the apparatus. The borosilicate glass reaction tube, shown in Figure 2, was 370 mm. long and consisted of a catalyst section, 18-mm. inside diameter, and 220 mm. long filled to a depth of 100 to 120 mm. with 0.125-inch alumina pellets (Harshaw Chemical Co., Al-0104T) and an exit section 5-mm. inside diameter and 150 mm. long. A glass wool plug was placed at the bottom of the catalyst section to serve as a catalyst support. The upper end of the reaction tube was fitted with a standard taper 24/40 joint, a 3-mm. inside diameter thermocouple well was placed near the top of the catalyst filling, and the exit end was provided with a 12-mm. radius spherical joint for connection to the absorber system. A standard taper 24/40 joint fitted with a sidearm and a standard taper 10/30 joint placed concentric with the reaction tube was used for the cap. A weighing pipet, fitted with standard taper 10/30 joints to fit the cap and bypass, was used for introducing the sample.

The dimensions are not considered critical except that the entire catalyst zone must be maintained at a uniform temperature and the thermocouple well should be placed in the upper part of the catalyst zone. The bypass line was necessary to equalize pressure and enable the sample to be admitted at a uniform rate. Tubular electric furnaces, similar to those used by Tunnicliff, Peters, Lykken, and Tuemmler (*17*) except for uniform spacing of the heating coils, were employed for heating the catalyst. Variable transformers and a multiposition pyrometer were used to adjust and measure the catalyst temperature.

A dual absorber system was found necessary to separate most of the hydrogen sulfide produced from traces of mercaptan and thus enable small amounts of mercaptans to be detected. The first absorber contained 10 ml. of ethyl alcohol and consisted of a 16-mm. inside diameter tube, 200 mm. long, jacketed for circulation of water and fitted with a coarse gas dispersion thimble as shown. The second absorber was a 250-ml. tall-form beaker containing 100 ml. of oxygen-free 4% aqueous sodium hydroxide solution. Tap water, cooled by passage through an iced copper coil, was circulated through the jacket of the first absorber; the second absorber was cooled by placing it in a container of ice. Nitrogen was passed through the system at a rate, viewed in the last absorber, of 3 to 5 bubbles per second.

Solutions of isoamyl (or other similar) sulfide and thiophene, of known concentration in sulfur-free white oil and containing about 1% sulfur, are used to test the performance of each lot of alumina catalyst. A satisfactory catalyst will produce over 90% of the theoretical amount of hydrogen sulfide from the aliphatic sulfide solution, and less than 2% of the sulfur from the thiophene solution will appear as hydrogen sulfide.

Potentiometric titration apparatus and reagents used for the determination of hydrogen sulfide and mercaptans have been described previously (*12, 16*).

CATALYTIC DESULFURIZATION PROCEDURE

Nonthiophenic Sulfur. Bring the furnaces to a temperature of 450° ± 10° C., connect the filled absorbers, and turn on the nitrogen. Fill a weighing pipet with sample, weigh, remove the bypass from the reaction tube cap, place the pipet in the cap, and place the bypass in the joint on the top of the pipet. Allow the system to purge for a few minutes. Drop a quantity of sample containing from 2 to 10 mg. of nonthiophenic sulfur directly onto the catalyst at such a rate that the catalyst temperature does not drop over 20° C. Remove the pipet and replace the bypass.

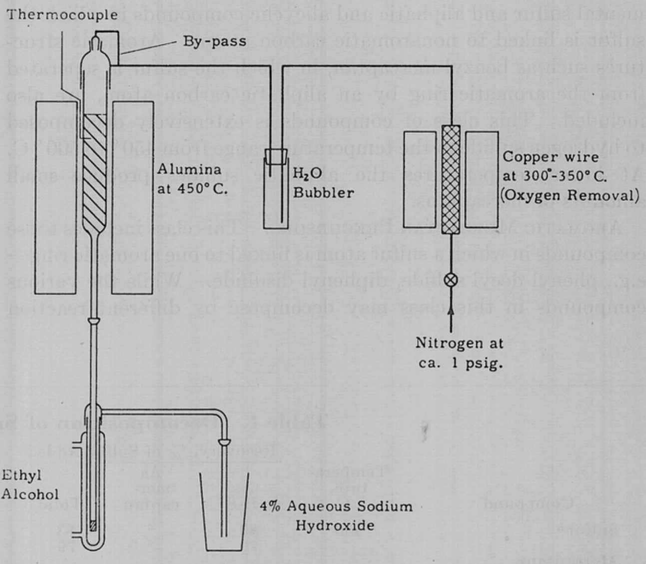


Figure 2. Schematic Diagram of Catalytic Desulfurization Apparatus

Allow the system to purge for 30 minutes after addition of the last portion of sample, transfer the copper cooling coil to a container of water at room temperature, and increase the nitrogen flow somewhat. Purge for an additional 5 minutes and remove the absorbers. Transfer the contents of the first absorber to a 250-ml. tall-form beaker containing 100 ml. of 0.1*N* alcoholic sodium acetate solution and rinse the absorber with a few milliliters of benzene. Add 1 ml. of ammonium hydroxide to the second absorber. Protect these solutions from exposure to air and immediately titrate potentiometrically (*12, 16*) using 0.01 and 0.1*N* silver nitrate solutions, respectively, for the first and second absorbers. Plot the titration curves and select end points for hydrogen sulfide and mercaptan in the first absorber and for hydrogen sulfide in the second absorber. Calculate the nonthiophenic sulfur content of the sample from the sum of the hydrogen sulfide and mercaptan sulfur found.

DIFFERENTIATION OF SULFUR GROUPS BY CATALYTIC DECOMPOSITION

Catalytic Decomposition of Pure Sulfur Compounds. Decomposition tests were made at various catalyst temperatures to determine the extent of decomposition of known sulfur compounds to hydrogen sulfide in the presence of oils. The sulfur compounds were commercial materials or laboratory preparations and, in cases of doubtful purity, were fractionally distilled before use. The tests were performed on white oil solutions of these compounds, prepared to contain about 1% sulfur. In some cases it was necessary to add xylene or a similar solvent to dissolve the compound completely. The sulfur contents of these solutions (*13*) were used to calculate the theoretical hydrogen sulfide production. A purge time of 30 minutes after the sample was added was found sufficient for completion of the reaction and sweeping of the reaction products into the absorbers. The amounts of hydrogen sulfide and mercaptan produced by the compounds tested are shown in Table I. It was found that 325° C. was the lowest practicable catalyst temperature because mercaptans produced were not readily purged from the reaction tube at lower temperatures. Analysis of used catalyst showed only a negligible sulfur content. In general, fresh catalyst was used after each five to 10 tests.

Results thus obtained showed that the stabilities of the sulfur compounds tested, as measured by the hydrogen sulfide and mercaptans produced, fall into three general classifications which correlate with the structures of the compounds. These classifications, outlined in Figure 3, are summarized and defined as follows:

ALIPHATIC AND ALICYCLIC SULFUR. This class includes elemental sulfur and aliphatic and alicyclic compounds in which the sulfur is linked to nonaromatic carbon atoms. Aromatic structures such as benzyl mercaptan, in which the sulfur is separated from the aromatic ring by an aliphatic carbon atom, are also included. This class of compounds is extensively decomposed to hydrogen sulfide in the temperature range from 450° to 500° C. At lower temperatures the aliphatic sulfides produce small amounts of mercaptans.

AROMATIC MERCAPTAN PRECURSORS. This class includes those compounds in which a sulfur atom is linked to one aromatic ring—e.g., phenyl decyl sulfide, diphenyl disulfide. While the various compounds in this class may decompose by different reaction mechanisms, similar reaction products are obtained and thus they are included in a single classification. These compounds are less completely decomposed to hydrogen sulfide than the aliphatic and alicyclic sulfur compounds. At 450° C. from 10 to 80% of the sulfur appears as hydrogen sulfide while most of the remaining sulfur appears as mercaptans, presumably of the phenyl mercaptan type because aliphatic mercaptans produce only hydrogen sulfide under these conditions.

THIOPHENIC SULFUR. This class includes the thiophenes and their analogs. In addition, for purposes of classification, structures in which the sulfur atom is linked to two aromatic rings (as in diphenyl sulfide) are included since their behavior is similar to that of the thiophenes. These materials produce only a small amount of hydrogen sulfide even at 500° C. However, as the temperature increases, the extent of decomposition increases rapidly. The data in Table I indicate that these materials would be more extensively decomposed to hydrogen sulfide at higher temperatures. No mercaptans were detected at any of the temperatures tested.

OXYGENATED SULFUR COMPOUNDS. The results obtained with the few compounds tested indicate that when the sulfur and oxygen are not present in the same functional group the thermal stability is dependent on the way the sulfur atom is linked to the molecule but when the sulfur is oxygenated, the linkage is stable. Further tests with additional compounds are necessary for verification of this trend.

The results in Table I show that the amount of hydrogen sulfide produced by the aliphatic and alicyclic sulfur class is apparently never complete, reaches a maximum in the region of 450° to 500° C., and decreases rapidly above 500° C. The somewhat lower recoveries of hydrogen sulfide found for elemental sulfur (80%) were caused by distillation of part of the sulfur into the cooler top of the reaction tube where crystallization occurred.

The differences in stability between types of sulfur compounds are sufficiently great to be used as the basis for distinguishing the

Table I. Decomposition of Sulfur Compounds over Alumina[a]

Compound	Temperature, ° C.	Recovery, % of Sulfur Added		
		As H_2S	As mercaptan	Total
Sulfur[b]	450	83	[c]	83
		79	[c]	79
Mercaptans				
n-Amyl	450	93	[c]	93
		94	[c]	94
n-Dodecyl	400	90	[c]	90
	450	91	[c]	91
	500	93	[c]	93
	540	59	[c]	59
tert-Hexadecyl	450	90	[c]	90
		92	[c]	92
Benzyl	450	84	[c]	84
		87	[c]	87
Phenyl	450	11	50	61
Sulfides				
Diethyl	450	95	[c]	95
Diisoamyl	450	93	[c]	93
		95	[c]	95
		96	[c]	96
Isobutyl-*n*-octyl	350	55	25	80
	400	86	[c]	86
	450	92	[c]	92
		94	[c]	94
		96	[c]	96
	500	97	[c]	97
	560	72	[c]	72
		85	[c]	85
Dibenzyl	450	92	[c]	92
		94	[c]	94
Phenyl decyl	450	73	13	86
		77	11	88
Thiophane[d]	450	90	[c]	90
		94	[c]	94
Sulfides (*continued*)				
Diphenyl	450	2	2	4
		4	3	7
Disulfides				
Diamyl	450	85	[c]	85
		88	[c]	88
Di-*tert*-octyl	450	87	[c]	87
		91	[c]	91
Dibenzyl	450	87	[c]	87
		89	[c]	89
Diphenyl	450	55	42	97
		73	26	99
Thiophenes				
Thiophene	450	0.7	[c]	0.7
		1.0	[c]	1.0
	500	1.5	[c]	1.5
	560	10.7	[c]	10.7
2-Methylthiophene	450	1.4	[c]	1.4
3-Methylthiophene	450	1.1	[c]	1.1
Benzothiophene	450	<0.5	[c]	<0.5
Dibenzothiophene	450	<0.5	[c]	<0.5
	500	1	[c]	1
	515	4	[c]	4
	540	22	[c]	22
Oxygenated compounds				
Thioglycolic acid	450	71	[c]	71
		80	[c]	80
Diphenyl sulfoxide	450	5	4	9

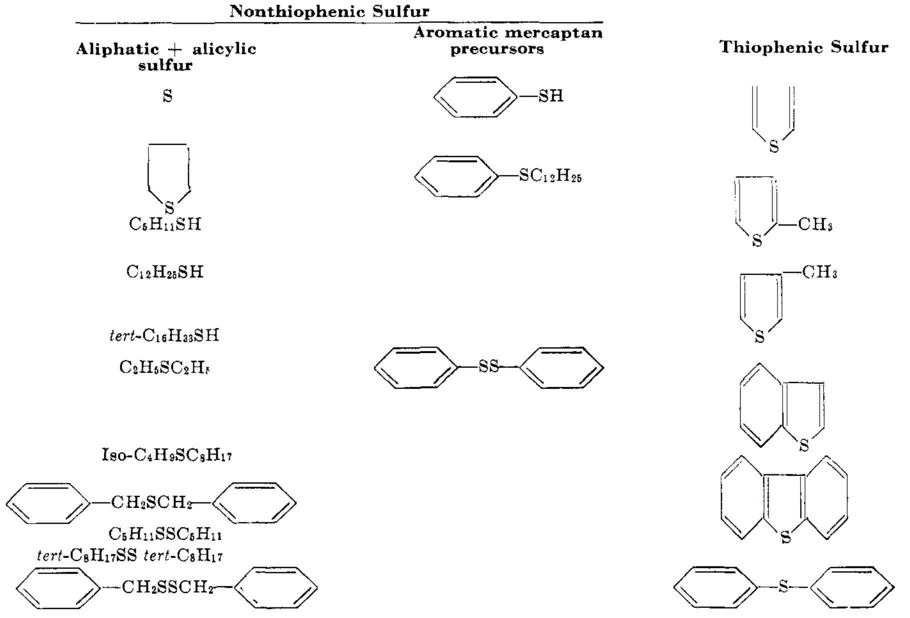
[a] Sulfur compounds dissolved in white oil to give approximately 1% sulfur.

[b] Recoveries low because sulfur vapor partially crystallized in cooler top portion of reaction tube.

[c] None detected; generally less than 1%.

[d] Standard solution unstable after 4 days; only 56% of the sulfur was produced as hydrogen sulfide.

Figure 3. Classification of Sulfur Compounds by Reaction over Alumina at 450° C.



Aliphatic + alicylic sulfur compounds decompose to produce hydrogen sulfide.
Aromatic mercaptan precursors produce a mixture of hydrogen sulfide and mercaptan.
Thiophenic sulfur compounds produce no hydrogen sulfide or mercaptan.

thiophenic group from the aliphatic and alicyclic sulfur group and the aromatic mercaptan precursors. At a catalyst temperature of 450° C. the aliphatic and alicyclic sulfur compounds are almost completely cracked to hydrogen sulfide, the aromatic mercaptan precursors are cracked to a mixture of hydrogen sulfide and mercaptan, and the thiophenic sulfur compounds produce only a negligible amount of hydrogen sulfide. Fortunately for the purpose of simple classification of sulfur groups, aromatic mercaptans and mixed aromatic-aliphatic sulfides and disulfides are uncommon in petroleum products as is shown by the fact that negligible or very low concentrations of aromatic mercaptans are generally found in passing petroleum fractions over alumina at 450° C. Consequently, the hydrogen sulfide produced usually serves as a measure of the amount of "aliphatic plus alicyclic sulfur" present and the difference between this sulfur and the total sulfur content of the material is a measure of the "thiophenic sulfur." If mercaptans are found in the cracked products, they are considered as "nonthiophenic sulfur," but determination of the "aromatic mercaptan precursors" from the amount of mercaptan produced is not feasible because the extent of decomposition is not constant.

Detection of Aromatic Mercaptan Precursors by Catalytic Desulfurization. The potentiometric titration methods using silver nitrate solution for the determination of hydrogen sulfide and mercaptans in aqueous or nonaqueous solution become progressively less reliable for the determination of mercaptans in the presence of hydrogen sulfide as the ratio of hydrogen sulfide to mercaptan increases and as the molecular weight of the mercaptans increases. This effect is similar to that found in the titration of mixtures of halides (*11*). Tests were made to determine the limits of detection of aromatic mercaptan precursors in the presence of a model aliphatic sulfur compound. These tests, made by treating various solutions of phenyl decyl sulfide and *n*-dodecyl mercaptan (1-dodecanethiol) in white oil at 450° C. showed that the mercaptan produced by phenyl decyl sulfide could not be detected in the presence of appreciable amounts of hydrogen sulfide when a single aqueous sodium hydroxide absorber was used.

Further tests showed that separation of the aromatic mercaptans from the hydrogen sulfide by absorption of the former in ethyl alcohol enabled the mercaptan produced by phenyl decyl sulfide to be detected even when the mole ratio of the *n*-dodecyl mercaptan to the phenyl decyl sulfide was as large as 100 to 1. By warming the alcohol absorber and increasing the flow rate in the latter part of the procedure, almost all of the hydrogen sulfide was removed from the alcohol.

Catalyst Behavior. The most selective catalyst found was a purified alumina. According to the manufacturer a typical analysis of the catalyst is as follows:

	Weight %
Al_2O_3	99
Na_2O	0.5
SiO_2	0.03
Fe_2O_3	0.03

The catalyst is pure white in color and comes in the form of 1/8-inch pellets. This catalyst was employed in obtaining the majority of the data on pure materials listed in Table I. In the early stages of this investigation a sample of alumina from another supplier was used that had the desired selectivity, but subsequent lots of the same catalyst proved to be unsatisfactory. A number of other types of aluminas from various sources were tested but none of these were found to have the desired degree of selectivity. Low recoveries of hydrogen sulfide were obtained with nonthiophenic sulfur compounds, and occasionally appreciable amounts of hydrogen sulfide were produced from thiophenes. The poor selectivity was tentatively attributed to excessive amounts of iron oxide in the catalyst. Another alumina, which apparently had been acid treated in manufacture to produce a low iron content, gave improved recoveries of hydrogen sulfide with nonthiophenic sulfur compounds, but showed a disadvantage in releasing chloride ion to the first absorber, which interfered in the titration of small amounts of mercaptan. Since the proper application of the method is dependent on the catalyst, it is considered necessary to test each lot of catalyst with known solutions of suitable sulfur compounds in white oil before accepting the batch for use.

GROUP SULFUR DETERMINATION

Application of the proposed method for differentiation between thiophenic and nonthiophenic sulfur, based on the above experiments, together with available procedures for the direct determination of elemental sulfur, hydrogen sulfide, mercaptans, and disulfides enables the group sulfur analysis of a wider variety of petroleum products than was previously possible.

In this work the potentiometric titration procedure of Tamele and Ryland for the determination of mercaptans (*16*) was used for the determination of both hydrogen sulfide and mercaptan. This mercaptan procedure gives accurate and precise results for the determination of hydrogen sulfide alone when a silver sulfide coated indicating electrode is used and when the end point is selected at the bottom part of the steep portion of the titration curve. The procedure may also be applied to the simultaneous determination of mixtures of hydrogen sulfide and mercaptans,

Table II. Typical Results Obtained for Group Sulfur Analyses[a]

Material	Sulfur, Weight %						Nonthiophenic Sulfur, % of Total Sulfur	Aromatic Mercaptan Precursor Sulfur, Weight %
	Mercaptan	Disulfide	Sulfide	Nonthiophenic	Thiophenic	Total		
Commercial gasoline	<0.001	0.007	0.01, 0.01	0.02, 0.02	0.09, 0.09	0.11	18, 18	None detected
Catalytically cracked gasoline	0.003	0.001	0.014	0.018	1.18	1.20	2	None detected
Thermally cracked gasoline	0.12	0.03	0.39	0.54	1.52	2.06	26	0.018
Jet fuel	<0.001	<0.002	0.072	0.072	0.13	0.20	36	None detected
Catalytic gas oil	<0.001	<0.001	0.002	0.002	0.10	0.10	2	None detected
California lubricating oil	0.0025	<0.001	0.016, 0.017	0.18, 0.19	0.10, 0.09	0.28	64, 68	None detected
Mid-Continent lubricating oil	0.025	0.012	0.050, 0.052	0.087, 0.089	0.053, 0.051	0.14	62, 64	Approx. 0.003 to 0.004
Shale oil	...	0.04[b]	0.18	0.22	0.48	0.70	31	None detected
Thermal distillate	0.004	0.005	0.47	0.48	0.85	1.33	36	Approx. 0.01 to 0.02
Thermal distillate	...	...	...	0.78, 0.80	1.62, 1.60	2.40	32, 33	None detected
Straight-run short residue[c]	0.01	0.01	1.0	1.0	1.1	2.08	49	None detected
Asphalt[c]	...	...	...	0.16	1.42	1.58	10	None detected
Straight-run long residue[c]	0.006	0.007	0.88, 0.89	0.89, 0.90	0.81, 0.80	1.70	52, 53	None detected

[a] No elemental sulfur or hydrogen sulfide found in these materials.
[b] Sum of mercaptan and disulfide sulfur.
[c] Sample admitted as pellet rolled with powdered alumina.

but coprecipitation effects result in less accurate determinations of the individual materials. A typical titration curve for this determination was shown by Lykken and Tuemmler (*12*). When more accurate determinations in mixtures of the two are necessary a second titration is made on a fresh portion of sample after removal of hydrogen sulfide as in the Bureau of Mines procedure (*1*). Experimental work concerning the potentiometric titration of hydrogen sulfide (*15*) and mixtures of hydrogen sulfide and mercaptans (*15*) is being studied and publication in a subsequent paper is anticipated.

In the titration procedure used, the presence of elemental sulfur is indicated by the appearance of a hydrogen sulfide inflection point after removal of hydrogen sulfide from the sample. Since neither hydrogen sulfide nor elemental sulfur was found in the particular samples to which the catalytic desulfurization procedure was applied, the procedure used was adequate.

Disulfides were determined by potentiometric titration of the mercaptans formed by a conventional reduction procedure using zinc and acetic acid (*6*). Benzene was added as solvent for the heavier materials and the reduction was carried out at room temperature in stoppered pressure bottles which were shaken vigorously to reduce the reaction time. A suitable aliquot was neutralized with ammonium hydroxide and titrated directly. The applicability of the disulfide reduction technique and the argentometric determination of mercaptans to the heavier materials analyzed was not tested but the results obtained are reported for information.

Other procedures, such as that recommended by the Bureau of Mines (*1*), for the determination of the individual sulfur type compounds may also be used in conjunction with the catalytic decomposition procedure for differentiation of thiophenic and nonthiophenic sulfur.

Use of suitable methods for the determination of elemental sulfur, hydrogen sulfide, mercaptans, and disulfides in conjunction with the determination of nonthiophenic sulfur by catalytic desulfurization enables a complete group sulfur analysis to be made. The difference between the nonthiophenic sulfur, as calculated from hydrogen sulfide and mercaptan production, and the sum of the elemental sulfur, hydrogen sulfide, mercaptan, and disulfide sulfur in the original sample is considered to include all the aliphatic and alicyclic sulfides. Likewise, the difference between the nonthiophenic sulfur and the total sulfur content of the original sample is considered to be due to materials such as thiophenes and diphenyl sulfides.

Sensitivity of Group Sulfur Method. The methods for determination of elemental sulfur, hydrogen sulfide, mercaptans, and disulfides are generally sensitive to at least 0.01% sulfur. A limited number of tests by the catalytic decomposition procedure on pure aliphatic sulfur compounds in white oil solution at concentrations as low as 0.01% sulfur indicate that recoveries of hydrogen sulfide of approximately 90% can be obtained.

Applicability of the Catalytic Desulfurization Procedure. The method has been applied to a wide variety of petroleum fractions ranging from distillates to heavy residues and crudes. Typical data obtained are listed in Tables II and III. Gasolines and light naphthas were handled without difficulty and a limited number of such materials have been analyzed on a service basis. The main emphasis of the application in the past several years has been to heavier distillates and residuals. Medium and heavy distillates are readily passed into the catalytic reactor. Those boiling above the temperature of the system allow a more rapid throughput since pressure and temperature surges, due to volatilization, are lessened. The ratio of nonthiophenic to total sulfur was found to vary over a wide range as would be expected from the history and nature of the materials. Catalytic gas oils contain only a small proportion of nonthiophenic sulfur because the treating conditions are similar to, but more drastic than, the catalytic desulfurization conditions used in this method. The largest fraction of nonthiophenic sulfur was found in the lubricating oils. Aromatic mercaptan precursors were found in but a few cases and only in minor amounts.

Table III. Hydrogen Sulfide Produced by Catalytic Desulfurization of Crude Oils over Alumina

California Crude Oil	Total Sulfur, Weight %	Hydrogen Sulfide Found as S, Weight %										
		Purge Time at 450° C., Hours					Purge Time at 490° C., Hours					
		0.5	0.75	1	1.5	2	0.5	1	1.5	3	4	5
Crude A	0.57	...	0.18	...	...	...	...	...	...	...	...	...
Crude A + added white oil[a]	...	0.17	...	0.20	0.20	...	...	...	...	...	...	...
Crude B	0.69	...	...	0.26	...	...	...	...	...	...	...	...
Crude B + added white oil[a]	...	0.23	...	0.24	0.26	...	...	...	...	...	...	...
Crude C	5.46	...	0.79 0.87	...	...	...	1.53	1.29 1.70	1.76	2.04	2.14	2.17
Crude C + added white oil[a]	...	...	1.46	1.81	1.94	2.04	1.87 1.96	2.14	2.30	2.37	...	...

[a] Approximately equal weight of white oil added immediately after sample addition and equivalent amount added while purging.

Residues and crude oils can be analyzed, although with more difficulty and less accuracy than with distillates. Solid or viscous materials can either be dissolved in a heavy oil, which does not produce hydrogen sulfide, or, alternatively, can be sampled as pellets dusted with alumina powder (to enable weighing and handling without loss). The residuals which were analyzed were found to produce from 10% to somewhat more than 50% of the possible hydrogen sulfide calculated from the total sulfur content of the material.

A few tests were made to determine the applicability of the catalytic desulfurization procedure to three California crude oils. Two were fluid (A and B) and the third (C) was viscous. In the tests, catalyst temperatures of 450° C. and, with the viscous crude, 490° C. were used, purge times were increased, and, in some cases, white oil was added to the reaction tube to act as a high temperature solvent. These tests, detailed in Table III, show that the decomposition of the viscous crude to hydrogen sulfide is slow and that the decomposition increases at the higher catalyst temperature and when white oil is added to the reaction tube after the crude oil. The lighter crudes required less drastic reaction conditions. Examination of the catalyst after desulfurization of the viscous crude revealed that the upper section of the catalyst and the adjacent portion of the reaction tube were coated with a tarry material. Thus it appears that the slow desulfurization results from the formation of a coating of high molecular weight material on the catalyst which slows or prevents adequate contact between the sample and the catalyst. The increased rate of hydrogen sulfide production found when white oil was added to the reaction tube after the viscous crude is attributed to the solvent action of the hot oil on the catalyst coating.

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Potentiometric Titrations with Controlled Current Input

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The technique of current scanning polarography was extended to include an electrometric titration which is the analog of conventional amperometry. The method consists in applying a small, controlled current from a 1.5-volt dry cell and 1- to 5-megohm resistor to a polarographic electrode and a reference half cell. The resulting polarographic voltages are followed with a continuous indicating pH meter or inexpensive VTVM as a function of volume of titrant. Zinc was titrated with ferrocyanide with satisfactory results. Using a platinum foil in stirred solution, arsenic(III) was titrated with bromide in hydrochloric acid medium. Excellent results were obtained with considerably more ease than by the conventional amperometric method. In the titration of iron(II) with cerium(IV), the new method is no more desirable than conventional potentiometry. The results are interpreted in terms of experimental polarograms and the fallacy of using theoretical polarograms is emphasized. The method was applied to the titration of cadmium with ethylenediaminetetraacetic acid at the dropping mercury electrode and found satisfactory.

THE recently reported technique of current scanning polarography (*1*) has been extended to include the analog of conventional amperometric titrations. The procedure consists in passing a controlled current (ca. 0.1 to 2 μa.) through a polarographic working electrode and a reference half cell. The resulting polarographic voltage is followed with a continuous indicating pH meter or vacuum-tube voltmeter, as a function of the volume of titrant added. Titration curves are obtained which are not unlike those observed in ordinary potentiometric titrations.

Such a technique was used in 1925 by Van Name and Fenwick in their study of polarized bimetallic electrode systems (*15*). In recent years Gauguin and coworkers have developed a similar method which they have named "potentiometry at constant current" (*2*, *5–7*). The experimental techniques described herein are identical in most respects with those of the aforementioned workers. A recent review by Furman covers the main points of their work which leans heavily on the theoretical derivation of polarization curves (*4*). Duyckaerts has also discussed the application of small currents to electrode systems (*3*). The study presented here, as an extension of current scanning polarography, represents a purely experimental approach and derives only from actual current-voltage curves (polarograms). No mathematical or theoretical treatment of these polarograms is necessary for titration purposes.

In conventional amperometry diffusion currents are measured at some voltage-insensitive portion of the polarographic wave—i.e., at some fixed voltage on the plateau. In the current input method, polarographic voltages are measured at a point on the polarographic wave which is relatively current-insensitive—i.e., near the foot of the wave. The use of small currents gives selectivity of electrode reaction. Selectivity is lost when the