Separation and Characterization of Petroleum Acids

Some Texas Petroleum Acids

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Operations involved in various methods of fractionation of acidic material from Texas petroleum are described. The necessity for use of a combination of constants as an aid in characterizing the various cuts obtained is pointed out and several schemes are given.

Phenol, *n*-valeric, *n*-butyric, dimethylmaleic, *n*-octanoic, and solid hexahydro-*p*toluic acids were isolated and identified.

WHEN a long-range program of research on petroleum acids was initiated in 1934, a survey showed that the only Texas petroleum material obtainable, including the boiling point range of C₆ to C₉ acids, consisted of alkali wash obtained in the refining of light burner oil at the Baytown Refinery of the Humble Oil and Refining Company. This material was obtained by washing a mixture of straight-run and cracking process products from Texas crudes. The offer of this company to furnish this material was gladly accepted, even though it was realized that the cracking process material would greatly complicate the mixture. It was felt from the first that physical methods should be employed much more extensively than in the past in the study of petroleum acids, and the success of such methods can be followed more readily on a complex mixture than on a simpler mixture consisting largely of members of a single homologous series.

Separation of types as well as of individuals among petroleum acids has become practically standardized in procedure involving the following steps:

1. Alkali neutralization of the acidic material

2. Liberation of acids from the sodium salt solution

3. More or less elaborate fractionation of the acids obtained 4. Esterification of the acids leaving phenols and most ter-

4. Esterification of the acids, leaving phenols and most tertiary acids unchanged but partially dissolved in the ester layer

5. Careful fractionation of the resulting esters by distillation 6. Saponification of each ester cut, followed by fractional distillation of the regenerated acids

7. Attempted isolation or identification of individual acids by formation of solid derivatives, various salts, amides, or degradation reactions

While under favorable conditions much has been accomplished considering the complexity of the raw material concerned, the use of other physical methods in addition to fractional distillation is clearly indicated, since separation by differences in vapor pressure alone would not be expected to succeed even when both the acids and their esters are fractionated. The authors developed and tried a number of methods, such as fractional esterification and saponification, fractional countercurrent neutralization and liberation, and fractional silver salt formation, but soon found that the development of these methods must go hand in hand with fast but reliable means of characterizing the various fractions, since these methods are not based on vapor pressure, neutral equivalent, density, or any other property alone; and therefore, no one of these can describe the fraction adequately. The combination and alternation of a number of different methods of fractionation lead soon either to an excessive number of small fractions or to recombinations that undo the separation effect of a previous step.

Characterizing Petroleum Acids

Since no one constant can then be relied upon in recombinations, a study of various combinations of constants was made and tried on known compounds and mixtures, as well as on fractions obtained here and in work reported from other laboratories. Of the many schemes that have been proposed for characterizing petroleum hydrocarbon fractions, a number yield about equally satisfactory results. The authors have, however, found the following schemes most useful.

Plot of
$$\frac{n^2 - 1}{n^2 + 2}$$
 vs. d_4^{20}

When the proper data for various types of acids and for saturated hydrocarbons are plotted as indicated, a fairly satisfactory separation of acid types is obtained except in the case of unsaturated and naphthenic acids, which, as might be expected, overlap. The authors used this scheme in much of the preliminary work. A plot of n - 1 vs. d_4^{20} has the advantage of simplicity in calculation and appears to yield roughly as satisfactory results.

$$\frac{n_{\rm D}-1}{\rm molecular \ weight} \ vs. \ d$$

Another scheme that seems to separate the various types of acids most satisfactorily but at the expense of simplicity is shown in Figure 1. It seems generally to yield a separate line for each different series and molecular weight.

$$n_{
m D} imes {
m d}_4^{20}$$

For fast routine work the authors have abandoned all of the more elaborate schemes for the simple purely empirical prod-





uct of $n_{\rm D}^{20} \times d_4^{20}$. Calculation of this value for a large number of reported aliphatic, unsaturated, and naphthenic acids, phenols, and hydrocarbons with from 5 to 10 carbon atoms was undertaken. When the constants were reported at temperatures other than $20^{\circ} \pm 2^{\circ}$ C., the 20° values were calculated, although in most cases the separation into acid type is so good that errors due to use of temperatures other than 20° do not shift the compound from one group to another.

The compiled data show that aliphatic acids have products ranging from 1.280 to 1.350 with most values between 1.300 and 1.310, the naphthenic acids range from 1.390 to 1.470 with most values between 1.410 and 1.440, while phenols have n d products above 1.500 and hydrocarbon values below 1.300 and usually below 1.280.

The only exception for acids containing the cyclopentyl group-the typical naphthenic acids-was 1,2,3-trimethylcyclopentane carboxylic acid, reported by Noyes and Burke (7). Its constants as reported yield a product of only 1.313, which would list it with the typical aliphatic acids. The abnormally low reported density of 0.9008 led the authors to repeat their synthesis. (Correspondence with Professors Noyes and Burke shows that the original notes are not available, but they suspect that their density should have been 0.9908 instead of 0.9008.) The following constants were found on an acid finally purified by repeated treatments with potassium permanganate followed in each case by refractionation and determination of the constants which finally remained unchanged: boiling point, 745 mm., 244°; d4²⁰, 0.9948; n_{D}^{20} , 1.4597; M_{D} , found 42.98; calculated 43.13; n·d 1.4573.

TABLE I. ACID CUTS

Fraction	Boiling Point, 35 Mm. ° C.	Approximate Volume <i>Liters</i>	n_{D}^{20} of Fraction	Acids %	n ²⁰ of Acids
1	100-110	3.8	1,4751	10,80	1.5279
$\overline{2}$	110-120	9.5	1,4807	15.40	1,5275
3	120-130	45.4	1,4903	20.30	1.5258
4	130-140	34.1	1,4949	24.10	1.5230
5	140 - 150	26.5	1.5008	33.80	1.5159
6	150 - 160	34.1	1.5003	37.00	1.5095
7	160-170	26.5	1.4965	42.60	1.4935
8	170-180	11.35	1.4872	43.40	1.4795
9	180-190	7.6	1.4852	54.30	1.4765
10	190 - 200	1.9	1.4825	60.20	1,4753
Residue		15.2			

As in the case of all other simple schemes tried, the singly unsaturated acids are placed with the naphthenic acids. The authors at present recombine fractions on the basis of $n \cdot d$, boiling point, and neutral equivalent.

Experimental

After a careful examination of various types of Texas acidic material available, one of the writers (Schutze) liberated the acids from 20 barrels of concentrated alkali wash from light burner oil as obtained at the Baytown Refinery of the Humble Oil and Refining Company. Three barrels of crude acids were obtained. This material was then distilled at the University of Texas Laboratory through a battery of twelve 2-liter Claisen flasks. The difficulty due to water in this material was best overcome by blowing air or natural gas through each charge as it was heated up until practically all of the moisture had been driven off. The acids were then distilled at water-pump vacuum to yield three cuts of 200 cc. each and a residue of about 1 liter from each charge of 1600 cc. This operation yielded 75.0 liters of material boiling at 110° to 135° C.; 75 liters boiling at 135° to 160° ; and 75 liters boiling at 160° to 180° , all at 25 mm. The three cuts were then separately fractionated at 35 mm. from a 57-liter steel still with a 275 imes15 cm. unpacked column. Fractions were collected at 10° intervals to yield the cuts shown in Table I.

The high index of refraction of the first seven cuts indicates

that they are predominantly phenolic in nature. In spite of this fact cut 3 with the largest volume was selected for detailed study because its boiling point range was the one desired.

Separation of Strong Organic Acids from Weak Acids, Phenols, and Hydrocarbons

Since large-size efficient fractionating apparatus was not available, it was decided to forego the advantage of "amplified distillation" or "carrier liquid" effect and to separate strong from weak acids before proceeding with separation_by distillation.

TABLE II.	SEPARATION	BY SC	DIUM CARB	ONATE TREATM	ENT

Fraction	n_{D}^{20}	Volume Cc.
A1 A2 A3 A4 A5 A6	$1.4478 \\ 1.4515 \\ 1.4638 \\ 1.4868 \\ 1.5035 \\ 1.5000$	$120 \\ 95 \\ 72 \\ 54 \\ 55 \\ 49$

Steam-distillation of the sodium salts to remove material formed by hydrolysis and nonacidic compounds proved effective but required an excessive amount of steam and time, so only 7.5 liters (2 gallons) were treated in this manner.

The remainder of the acids were treated with successive 6liter aliquots of 1 N potassium hydroxide. In this and in all subsequent fractional neutralization batch operations, prolonged and vigorous stirring with motor stirrer was employed to assure equilibrium neutralization. Each batch of potassium salts was then steam-distilled to remove hydrocarbons and other material carried down with the salt solution.

The strong organic acid fractions of the extracted acids were dissolved in an equal volume of petroleum ether and fractionally neutralized with 0.5 N sodium carbonate. Each alkali cut was acidified with sulfuric acid and saturated with sodium chloride to lower the solubility of any dissolved acids. The aqueous layers were extracted with several small batches of petroleum ether, since it has been found throughout this work that sodium salt solutions are much better solvents than water for phenols and hydrocarbons and further that hydrocarbons and phenols dissolve considerable amounts of sodium salts, so that double treatment as described above is always needed in concentrated solutions.

The degree of separation obtained with the sodium carbonate treatment just described is best shown by Table II.

While these 6 cuts represent only a small portion of the acidic material, the last two cuts obviously represent phenolic compounds which are being studied in a separate project, so no more fractions were obtained at this time.

Cut	$n_{\rm D}^{20}$	Boiling Point, 760 Mm. ° C.	Neutralization Equivalent	Density, 20/20	n∙d
1 2 3 4 5 6 7 8 9 10 11 12 14	$\begin{array}{c} 1.4100\\ 1.4358\\ 1.4444\\ 1.4520\\ 1.4490\\ 1.4395\\ 1.4309\\ 1.4309\\ 1.4293\\ 1.4319\\ 1.4419\\ 1.4419\\ 1.4478\\ 1.4520\\ 1.4561\end{array}$	$161 \\ 167 \\ 173 \\ 176 \\ 178 \\ 181 \\ 182 \\ 184 \\ 185 \\ 184 \\ 185 \\ 188 \\ 191 \\ 194 \\ 196 \\ 199 \\ 190 \\ 100 $	$\begin{array}{c} 99.80\\ 131.5\\ 143.3\\ 153.3\\ 147.0\\ 133.2\\ 126.0\\ 119.0\\ 118.6\\ 118.3\\ 131.8\\ 138.6\\ 143.3\\ 148.0\\ \end{array}$	0.9654 0.9806 0.9848 0.9889 0.9867 0.9809 0.9778 0.9776 0.9766 0.9764 0.9787 0.9879 	$\begin{array}{c} 1.360\\ 1.408\\ 1.423\\ 1.435\\ 1.430\\ 1.412\\ 1.405\\ 1.395\\ 1.395\\ 1.400\\ 1.425\\ \dots\\ \dots\end{array}$
15 16 17 18 Posiduo	1.4539 1.4515 1.4539 1.4635	202 203 207 213	140.0 134.0 129.9 139.2	$1.0179 \\ 1.0317 \\ 1.0490$	$1.450 \\ 1.500 \\ 1.535$
Residue					

Repetition of this procedure on the various nonphenolic fractions yielded a total of 365 cc. of strong organic acids from which, by similar operations, a 188-cc. fraction of the strongest acids was selected for more detailed study. This batch was next carefully fractionated into 10-cc. cuts. Some constants are presented in Table III. During the fractionation it was observed that a solid separated in the condenser, especially from cuts 9 through 16. The solid obtained when cut 13 was cooled was recrystallized twice from petroleum ether; it now melted at 95.5° and boiled at 220° at 760 mm. Reprecipitation by adding hydrochloric acid to its solution in alkali, and resublimation did not change the compound. Since 3.6-dimethyl phthalic acid was suspected, it was treated with resorcinol and sulfuric acid and then neutralized to yield a dichroic solution, green by reflected and red by transmitted light. An analysis gave C, 57.12, and H, 4.58; calculated for $C_6H_6O_3$: C, 57.14, and H, 4.77 per cent. Since the compound was not changed by sublimation while the phthalic acid would yield the anhydride, dimethylmaleic acid anhydride with a reported melting point of 96° and boiling point of 223° appeared the most probable compound. This anhydride was synthesized according to Rach (3) and its melting and mixed melting point showed the acidic material to have been dimethylmaleic anhydride. This compound has since been isolated also from straight-



SEPARATION THROUGH SILVER SALTS. Cadmium, silver, and lead salts have been used in separating petroleum acids but the usual technique of fractional precipitation of the silver salts by adding silver nitrate with very thorough stirring to a solution of ammonium salts did not yield pure organic salts. Through experiments on known mixtures of isovaleric and *n*-caproic acids the following technique was developed and found very satisfactory.

The silver salts are fractionally precipitated in the usual manner and each cut is then dissolved in ammonium hydroxide. Normal nitric acid is added from a buret with a long tip extending to the bottom of the vessel, while the solution is stirred very vigorously by a motor stirrer until a fraction of silver salts of the desired size has been precipitated. After filtering off this fraction another is precipitated and this fractionation is continued until a slight excess of nitric acid has been added. The use of a long tip leading deep into the solution is made necessary by the fact that some of the silver salts tend to form a highly hydrophobic floating layer. As would be expected, only the least soluble salt can be obtained in a state of purity in one set of operations. This method will hereafter be termed the silver salt method.

When this technique was applied to 2 cc. of cut 5, Table III, the silver content (determined very easily by ignition of microsamples above and then in an electric crucible furnace) indicated that no pure salt resulted from one fractionation.

When the acids from the first fractions were liberated from the silver salts by mixing with an excess of phosphoric acid which had been dehydrated by heating to 180° at a pressure of 20 mm. and the organic acids then distilled off at water-pump vacuum with a capillary of sufficient capacity to help sweep the vapors out of the flask into the receiver, a main cut of dry colorless acids was readily obtained. This method of liberation will be referred to hereafter as the phosphoric acid method. ISOLATION OF *n*-VALERIC ACID. Analysis of the *o*-phenylene-

ISOLATION OF *n*-VALERIC ACID. Analysis of the *o*-phenylenediamine as well as the *p*-nitrobenzyl bromide derivatives showed that the heart cut of acid mentioned above was not pure enough to obtain a pure derivative, but a repetition of the silver salt method yielded a main fraction that gave an *o*-phenylenediamine derivative melting at 153°. Six recrystallizations failed to raise this melting point. A mixed melting point with a sample of derivative of known *n*-valeric acid also melted at 153°. Analyses for nitrogen: calculated for $C_{11}H_{14}N_2$, 16.08 per cent; found, 16.15 per cent. The analogous derivative of isovaleric acid melts at 189°. The presence of *n*-valeric acid is then definitely established.

ISOLATION OF PHENOL. When the final filtrate from the silver salt treatment was further acidified with hydrochloric acid and steam-distilled to recover the acids from soluble silver salts, the solution turned red and a yellow solid separated from the distillate. A melting and mixed melting point of 45° as well as analysis of the silver salt showed this to be *o*-nitrophenol. While the yield was less than 0.5 gram, the result is interesting because phenol has often been reported as missing in petroleum acids. ISOLATION OF *n*-BUTTRIC ACID. Cut 1, Table III, was next

ISOLATION OF *n*-BUTTRIC ACID. Cut 1, Table 111, was next fractionated by the silver salt method and this treatment repeated on the heart cut to yield 1.03 grams of acids recovered by the phosphoric acid technique. This fraction yielded an *o*phenylenediamine derivative melting at 157.5°. The mixed melting point with a sample of derivative of known *n*-butyric acid melted at 158° while the known derivative melted at 158.5°. Analyses for nitrogen: calculated for $C_{10}H_{12}N_2$, 17.50 per cent; found, 17.50 per cent. The corresponding derivative of isobutyric acid melts at 234-235°.

Since the lower fractions so far studied seemed to be free of naphthenic acids, it was decided to examine fraction 6, Table I. Separation into strong and weak acids by fractional neutralization with potassium hydroxide soon led to very stable emulsions which were finally broken by saturation with carbon dioxide gas. This decreased the yield per cut but eliminated the long settling periods. Finally 3200 cc. of acidic material with $n \cdot d$ values less than 1.48 were selected for further study and were distilled through a 150-cm. (5-foot) marble-filled column with 10 to 1 or higher reflux ratio at 5-mm. pressure. This procedure was repeated four times with combination of similar cuts as indicated by density and refractive index.

Out of 16 cuts of 200 cc. each finally obtained, fractions 5, 6, and 7 were selected for detailed study. The constants of these and neighboring cuts are shown in Table IV.

	Boilin	ng Point	m 27	127		Neutralization
Fraction	5 Mm.	760 Mm.	ⁿ D	u ₄	$n \cdot d$	Equivalent
	° C.	° C.				
4	94-95	236	1.4507	0.9555	1.390	176
5	95-98	240	1.4466	0.9499	1.373	164
6	98	243	1.4445	0.9455	1.365	159
7	98 - 103	245	1.4452	0.9450	1.365	159
8	103 - 105	248	1.4461	0.9450	1.367	161

TABLE IV. CONSTANTS OF FRACTIONS

The results obtained on cuts 5, 6, and 7 with a combination of fractional distillation and the rotary extraction column have already been reported. Figure 5 of the previous paper (9) is reproduced as Figure 2 to facilitate discussion of further results obtained on this material. $n \cdot d$ products for the 19 cuts indicate that Fraction E IV 3 is probably largely phenolic, that 4 and 5 represent mixtures, that 6 to 11 appear to be almost purely aliphatic, and 12 to 14 mixtures of types, while cuts E IV 15 and 16 and E III 15 to 17 seem to be naphthenic mixed with a new type of acid with abnormally high $n \cdot d$ values combined with high K_a value or solubility.

To check these predictions an exploratory study of this series of cuts was undertaken.

Study of Extraction Fractions E IV 1 to 16 and E III 15 to 17

FRACTIONS E IV 1 TO 4. Since the extraction should have concentrated the very weak acids in the first few cuts and since the density and index of refraction were high, it was expected that the first four cuts would be high in phenols. The total volume was only 16 cc. Qualitative tests for sulfur were positive for only 1 and 2. Three cubic centimeters of methyl esters were obtained when the combined fractions 1 to 4 were refluxed with an excess of methanol-hydrochloric acid mixture. The unesteri-fiable portion was too weakly acidic to permit silver salt fractionation of possible tertiary acids present in this essentially phenolic mixture; neither could crystalline picrates of phenols be isolated.

FRACTION E IV 5. Esterification, followed by fractionation FRACTION E 1V 3. Exterincation, followed by fractionation of the unesterified 25 per cent of material through a 90 cm. (3-foot) \times 10 mm. column with rotating steel band as filling (6) showed that this portion still contained large amounts of phenolic material. The esters were not studied further, since they were

material. The esters were not studied further, since they were similar to those obtained from subsequent cuts. FRACTIONS E IV 6 TO 8. The combined fractions were esteri-fied and the esters fractionated through a 150 \times 1.25 cm. (5 foot \times 0.5 inch) Widmer column with rotating steel band as filling to yield six 14-cc. fractions and a 20-cc. residue. Cuts 4, 5, and 6 of this series had d³₂ of 0.8682, 0.8683, 0.8683, and n^{33}_{23} of 1.4179, 1.4180, and 1.4181; but in spite of this apparent purity neither o-phenylenediamine derivatives nor amides of acids from cut 5 assumed a constant melting point after six or more recrystallizations. The material must still be a mixture. The constants indicated that aliphatic acids predominate here, but no further attempt was made to isolate individuals.

TABLE V. CONSTANTS OF FRACTION

	Fraction 1	Caprylic Acid (5)
M. p.	15-16	16
В. р. d ²⁰	237.4 0.9116	237.5
$n_{\rm D}^{20}$	1.4286	1.4272
n·d H 0%	1.304	1,300 11 19 calcd
Ċ, %	66.68	66.55 calea.

FRACTIONS E IV 10 to 12. Fraction E IV 9 as a transition cut was not studied, but 10 to 12 were combined, esterified, purified, and fractionated by the 90-cm. (3-foot) rotary column. Only 7 per cent (8 cc.) by volume of acids did not esterify. Five of seven 15-cc. fractions of esters were similar and were combined and saponified, and the acids liberated and fractionated. The acids of the first seven of thirteen 5-cc. cuts resulting were now fractionally precipitated by the silver salt method to yield thirteen crops of silver salts. This process was repeated starting with the first four cuts, adding ammonium hydroxide and aliquots of dilute nitric acid to get two cuts, then adding the next two cuts and repeating the fractional precipitation until finally all acids were again in the form of thirteen cuts. The acids of the dried salts were then liberated in groups of three and four cuts by the phosphoric acid method in vacuum. The first three fractions of acids now crystallized readily on cooling and consisted of almost pure caprylic acid, as shown by the constants of Table V.

The p-phenylphenacyl esters of fraction 1 and of a known caprylic acid were prepared according to Drake and Bronitsky (2) and gave the results shown in Table VI.

TABLE VI. CONSTANTS

	Fraction 1	Known Caprylic Acid	Mixed M. P.
Acid	$\begin{smallmatrix}15-16\\66,6-67,3\end{smallmatrix}$	14.6-15.8	14.8-16.0
p-Phenylphenacyl ester		66.7-67.4	66.7-67.4

Further silver salt fractionation of the remaining cuts of the series yielded only caprylic acid with a few cubic centimeters of a mixture of other acidic material. About 15 cc. of a mixture from mixture of other acidic material. About 15 cc. of a mixture from which caprylic acid would not separate on cooling were now mixed with 100 cc. of a carefully purified mixture of neutral hydrocar-bons and subjected to fractionation by Bailey's "amplified dis-tillation" method (1). The acids extracted from the first four of eight cuts crystallized readily on cooling and proved to be pure caprylic acid and only the last cut of 8 cc. indicated by its con-stants that it was not practically purely aliphatic in nature. FRACTIONS E IV 13 TO 16. Esterification of the combined cuts E IV 13 to 16 yielded the usual small amount of unesterifiable material and a good yield of methyl esters. Three systematic fractionations through the rotary Widmer column resulted now in

fractionations through the rotary Widmer column resulted now in two fairly clear cut series of cuts with n_3^{cr} of 1.4179-1.4190 and 1.4285-1.4372, and d_4^{as} of 0.8788-0.8956 and 0.8983-0.9091. The first series is obviously aliphatic; the second contains acids with higher constants but not in high enough amount to warrant at-tempts to isolate individuals. Since cuts 15 and 16 should con-

tain larger amounts of these acids, they were studied next. FRACTIONS E IV 15 AND 16. Treatment of Fractions E IV 15 and 16 in exactly the same manner as 13 and 14 yielded a series of cuts with n_{19}^{19} , 1.4332-1.4430, and d_{29}^{29} , 0.9170-0.9284, which places all of these in the range of mixtures rich in esters with constants too high for aliphatic esters, but not yet purely naphthenic. If larger amounts had been available, further frac-tionation by extraction would probably have yielded acids rich

enough in naphthenics to permit isolation of individuals. FRACTIONS III 15 to 17. Fractions III 15 to 17 were combined and fractionally esterified by adding 0.83 equivalent of methanol containing 2 per cent dry hydrogen chloride and refluxing over-night. The cold mixture was extracted twice with 6 per cent sodium hydroxide and finally with water. The acids were liber-sted dired and distilled while the esters were saponified and ated, dried, and distilled while the esters were saponified, and fractionally esterified as before. This series of operations was repeated until four cuts of acids were obtained with properties shown in Table VII.

TABLE VII. PROPERTIES OF ACID CUTS

Cut	Volume Cc.	n 25 D	$d_{4}^{27.5}$	n-d	Neutralization Equivalent	Boiling Point, 760 Mm. ° C.
1 2 3 4	$15 \\ 12 \\ 22 \\ 26$	$1.4625 \\ 1.4583 \\ 1.4538 \\ 1.4523 \\ 1.4523$	$\begin{array}{c} 1.0051 \\ 0.9956 \\ 0.9878 \\ 0.9830 \end{array}$	$1.470 \\ 1.452 \\ 1.435 \\ 1.427$	$146.9 \\ 146.6 \\ 143.9 \\ 144.8$	$240 \\ 240 \\ 240.5 \\ 241.5$

The $n \cdot d$ values indicate that all these cuts are well in the naphthenic acid range, although the density for the first cut at least

chemic acid range, although the density for the first cut at least is too high for ordinary naphthenic acids of this boiling range. Cuts 3 and 4 were combined and fractionated through the small rotary column to yield eleven cuts of 4 cc. each with n_{1}^{sy} , 1.4505-1.4578; d_{2}^{sr} , 0.9788-0.9944; and $n \cdot d_{1}$, 1.420-1.450. The first six cuts were combined and fractionally precipitated by the silver salt method. The acids liberated from the silver salts had constants agracing vary elevely: so the first four suite very constants agreeing very closely; so the first four cuts were com-bined and converted to the acyl chlorides by thionyl chloride. constants agreeing very closely; so the first four cuts were com-bined and converted to the acyl chlorides by thionyl chloride. The chlorides were then converted to the amides by pouring them into concentrated ammonium hydroxide. The amides were recrystallized from water and then from a petroleum ether-alcohol mixture. During this process a remarkable rise in melt-ing point from 147° to 220° occurred during seven systematic recrystallizations. The only known 8-carbon atom amide melting as high as 220° appears to be that of solid *p*-hexahydrotoluic acid melting at 220-221°. Since only a few milligrams of the high-melting amide had been obtained, all of the cuts of the 3-4 series were recombined and converted to amides, which were then sys-tematically recrystallized to obtain larger amounts of the 220-221° amide. In this process another amide melting at 155-157° (prob-ably a meta isomer) and another melting at 151-152°, possibly a "cis" ortho isomer, appeared. While only 50 mg. of the 220-isomer were obtained, about 1 gram of each of the lower ones has been isolated but not yet in entirely pure form. Attempts to prepare *p*-hexahydrotoluic acid by hydrogenation of *p*-toluic acid over Raney nickel at 275° to 350° C. and up to 5000 pounds per square inch failed; so the acid was prepared from 1,4-dimethylcyclohexanol by converting it to the chloride and this by the Grignard reaction to the acid. The yield from alcohol to chloride was 60 per cent and from chloride to acid was 90 per cent. The resulting acidic material was converted to the acid chloride and to the amide as before. Six recrystallizations

alcohol to chloride was 60 per cent and from chloride to acid was 90 per cent. The resulting acidic material was converted to the acid chloride and to the amide as before. Six recrystallizations of the amide yielded 1 gram of the pure amide melting at 219– 220.8°. The isolated pure amide melted at 220–221° and the mixed melting point was 220–221°. Skraup and Binder (10) re-port 220–221°. Analysis for nitrogen: calculated for C₈H₁₈ON, 9.92 per cent; found, 10.03 per cent. As a further check of identity a few milligrams of each of the amides were hydrolyzed in a sealed tube with 25 per cent sodium hydroxide, and the liberated acids recrystallized twice from water. The isolated, swithetic, and mixed acids all melted at 108–109°

The isolated, synthetic, and mixed acids all melted at 108-109°, whereas Gutt (3) reports 110-111° on a pure acid.

Finally a micro-Dumas determination was run on one of the amide fractions melting at 155-157° to determine whether the mixture had the same composition as the isolated isomer. Nitro-gen determined was 10.10 per cent, while that calculated for amides of toluic acids is 9.92, so that the mixture is apparently one of the different isomers of toluic acid.

The naphthenic acids with unusually high $n \cdot d$ values turn out to be hexahydrotoluic acids, perhaps mixed with other cyclohexyl acids. While formerly naphthenic acids were thought to consist of cyclohexyl acids, the tendency in the last decade has been to assume that naphthenic acids are all cyclopentyl acids, since only very little indication of cyclohexyl acids had been obtained and none had been isolated. The amount of the pure solid isomer of p-hexahydrotoluic acid isolated herein is very small, but other isomers

appear to be present in larger amounts in this cut which boils below the boiling point of the pure acids, so that more may be present in somewhat higher boiling fractions. It should, of course, be remembered that the acids isolated were obtained from a mixture of straight-run and cracking process products, so that the cyclohexyl acids may have been formed during the cracking process.

Acknowledgment

The authors wish to thank the Humble Oil and Refining Company for donating the acids used and permitting them to isolate the crude acids at the refinery with their equipment. Thanks are also due Douglas Henson for cooperating in the early stages of this work.

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FROM theses submitted by Henry G. Schutze and Billie Shive in partial fulfillment of requirements for doctor of philosophy and master of arts degrees, respectively.

Determination of Sulfate by Tetrahydroxyquinone Method

Effect of Sodium Sulfite and Procedure for Its Elimination

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Sulfite, frequently used as a chemical deaerant in boiler water treatment, has some effect on the tetrahydroxyquinone method of sulfate determination, and a simple method has been established for its elimi-

IN PREVIOUS papers (1-7) describing the tetrahydroxyquinone method for sulfate and its modifications, the effects of certain ions have been discussed.

Since the appearance of the first paper, considerable research has been continually carried out to aid in the execution of this method.

The method has been found to be unaffected by silicate, tannin, magnesium, chloride, and calcium in concentrations occurring in natural and boiler waters (3, 4). Phosphate interfered if the titration was carried out at pH 8.3. An alternate method was devised for eliminating the effect of phosphate by adjusting the system to pH 4.0 before titration; by this method the tolerance of phosphate was raised above the normal excess soluble phosphate found in boiler waters (4). Aluminum, zinc, lead, copper, nickel, ferric and ferrous iron, etc., form insoluble compounds at pH 8.3 and should be filtered off before titration. The residual concentrations of these metals after filtration gave only slight interference, since their solubilities are very low (3-6).

Sodium sulfite, frequently used in boiler water treatment to remove oxygen, has been found to offer some interference and it is the purpose of this paper to define the extent of the interference and the simple method devised for its elimination.

Experimental

MATERIALS AND REAGENTS. Standard barium chloride solution: 1 cc. = 1 mg. of sulfate. Tetrahydroxyquinone indicator, manufactured by W. H. & L. D. Betz, Philadelphia, Penna., composed of disodium tetrahydroxyquinone dispersed in an organic medium. Standard sodium sulfate solutions, composed of 66 and 165 p. p. m. as sulfate. Ethyl alcohol, denation. A rough correlation was found to exist between sulfite present and sulfite titrated. Restrictions and suggestions for the tetrahydroxyquinone method are presented.

natured ethyl alcohol No. 30 or 3A, or isopropyl alcohol. Anhydrous sodium sulfite, c. p., Baker's.

In determining the effect of residual sulfite, a 25-cc. sample of known sulfate concentration was treated with a weighed amount of solid sodium sulfite and adjusted to pH 8.3. Twenty-five cubic centimeters of the alcohol were added and the system was titrated with standard barium chloride solution until the indicator changed from yellow to red. Because of the difficulty in maintaining sulfite in solution, solid sodium sulfite was added to the test system in preference to a solution of sodium sulfite. In each case the test system was treated with 5000 p. p. m. of manitol to help preserve the sulfite until the titration was complete.

TABLE I. EFFECT OF SULFITE ON SULFATE TITRATION BY TETRAHYDROXYQUINONE METHOD

Sulfate Present P. p. m.	Sulfate Found P. p. m.	Difference P. p. m.	Sulfite ^a Introduced P. p. m. SO ₄	Sulfite Titrated %
66	64	-2		
165	168	+3		
165	164	-1		
66	80	+14	18	77.7
66	110		55	80.0
66	140	+74	92	80.4
66	204	+138	168	82.1
165	182	+17	19	89.5
165	200	+35	39	89.7
165	232	+67	78	85.9
165	296	+131	157	83.4

^a Error in weighing and purity of sodium sulfite did not exceed 2 p. p. m. as SO4.

The results of these experiments, presented in Table I, show that residual sulfite offers some interference with the tetrahydroxyquinone method. Approximately 80 to 90 percent of the sulfite introduced into the system was titrated. The effect of the sulfite is also brought out in Figure 1, which shows it to be linear throughout the range investigated.