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IMPURITIES IN PETROLEUM

Occurrence, Analysis, Significance
to Refiners

PETROLEUM REFINING
AP-42 Section 9.1
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the Staff of Petrolite Corporation Laboratories
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PETRECO

A Division of Petrolite Corporation

1390 East Burnett Street, Long Beach, California • 3202 South Wayside Drive, Houston, Texas

PART I

THE NATURE OF IMPURITIES IN PETROLEUM

FOREWORD

Impurities commonly found in refinery charging stocks have reduced yields and degraded products throughout the history of petroleum refining. There has in the recent past been an increasing pressure to obtain maximum yields and premium products, which has spawned a great variety of new processes, especially of the catalytic variety. These in turn have been more sensitive to the impurities and have therefore magnified their deleterious effects.

Part I of this manual presents the most recent evaluations of such effects as developed by published information as well as Petreco's experience. It is a descriptive summary of the nature of the impurities and how they affect refining operations.

In order to evaluate the results of any remedial steps which are taken to combat the adverse effects of the impurities, it is necessary to make accurate analyses of the products involved. Part II of this manual presents a series of selected analytical methods which have for the most part been thoroughly tested in Petreco laboratories. It is designed to give operative details of methods applicable to the evaluation of processes designed for the removal of the impurities of most concern to the refiner.

Part III is not in the manual but represents our ambition to serve the petroleum industry wherever our highly specialized techniques are most applicable. Our background of more than four decades of wide experience in solving treating problems in both the production and refining phases of petroleum operations is your assurance of the reliability and integrity of our organization.

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GENERAL CHARACTER

Impurities in petroleum, or crude oil, as it is more generally and descriptively known, may as a first generalization be considered to be all constituents which have elements other than hydrogen and carbon in their molecular structure. Such materials may be classed as impurities from the refiner's standpoint because, to a greater or lesser degree, they produce adverse effects during the refining process, such as by producing corrosive conditions in the refining equipment, or by adversely affecting the quality of the products. In the early days of comparatively mild refining conditions, the processor was concerned primarily with two types of impurities, water and sulfur. The water, or brine as it is often termed because of its high saline content, represents the general class of impurities which are best characterized as being of the "oleophobic" type. In crudes as received by the refinery, these may be designated as follows:

| OLEOPHOBIC IMPURITIES | GENERAL RANGE |
|-----------------------|---------------|
| Salts | 10—1000 ptb* |
| Water | 0.1—2% |
| Sediment | 1—500 ptb* |

*ptb = pounds per thousand barrels of oil

These oleophobic constituents are inherently insoluble in crude oil, and are therefore present as a second phase, being carried as discrete particles by the oil.

Sulfur, on the other hand, represents a type of impurity which is soluble in crude oil, and may therefore be designated as of the "oleophilic" type. Typical constituents of this type may be listed as follows:

| OLEOPHILIC IMPURITIES | GENERAL RANGE |
|---|-------------------------|
| Sulfur Compounds | 0.1—5% as Sulfur |
| Organo-Metallic Compounds (Nickel, Vanadium, Iron, Arsenic, etc.) | 5—400 ppm. as the metal |
| Naphthenic Acids | .03—.4 vol. % |
| Nitrogen Compounds | .05—15 vol. % |
| Non-Acidic Oxygen Compounds (Resins, Cresols, etc.) | 0—2% as oxygen |

The industry quickly learned to dehydrate crude oils to satisfactorily low water contents, and experimented with various types of steels to reduce the corrosive effects of sulfur compounds on the refining equipment. Actual removal of the sulfur compounds was out of the question, since the sulfur atoms are combined into large molecules of hydrocarbons, so that in some cases probably half of the crude oil has sulfur as an integral part of its molecular structure. However, as thermal cracking and then catalytic cracking processes were introduced, the refiner found that some of the impurities, such as the residual salts associated with the small amount of brine left in the oil, had serious adverse effects on these newer refining techniques. It was only about a decade or so ago that it became generally

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recognized that the small inorganic salt contents of crude oil charging stocks placed serious limitations on the topping and thermal cracking processes of the refinery. It is now considered good practice to remove such salts to the lowest possible values that are economically justifiable in order to minimize their adverse effects on refining equipment and products.

In the catalytic cracking processes some types of impurities exhibit adverse effects on the distribution of the cracking products and on the catalyst itself. While only overhead products are charged to such catalytic crackers, small amounts of salts often appear in these charging stocks as a result of carryover from the residual material in the form of spray or foam, due either to excessive charging rates to the fractionators or to fouling of the trays with solids, such as sediment and ammonium chloride. Consequently a thorough desalting of the original crude is often further justified by the improved results obtainable in the catalytic cracking process. However, still other crude oil constituents can also have a pronounced influence on the cracking reactions, and of these the most important are such materials as nitrogen bases and other organic compounds, especially of an organo-metallic nature carrying relatively minute proportions of metals, such as vanadium, nickel, and copper. Arsenic compounds also have recently been shown to be the cause of catalyst poisoning and deterioration, especially where platinum catalysts are concerned.

Catalytic charging stocks prepared by the propane deasphalting process can have appreciable quantities of salt left in them, often in the range of 2-10 ptb.

In order to understand more fully the nature of the impurities referred to, a somewhat more detailed description is given below.

OLEOPHOBIC IMPURITIES

Water and Salts. The principal source of these impurities is the residual water droplets which are so small and so highly stabilized by emulsifying agents present in the oil that dehydration methods have failed to remove them by the customary procedures. Water itself is of course a highly undesirable oleophobic impurity, but refiners generally limit the amount of water which may be present in crude oils brought to the refinery to a value of less than about 2%, and usually less than 0.5%, depending upon the nature of the crude. These particular values for the maximum water contents are dictated, not by the amounts which the refinery would prefer to have, which is no water at all, but rather by the difficulties of commercially reducing water contents in crude oils to lower values by even the best dehydration methods. The oil field waters which are produced with crude oils vary widely in the composition and amount of salts which they carry in solution, but their concentration is generally greater than that of sea water, and they are therefore termed "brines." In order to indicate the amount of salts carried by even minute amounts of brines in the oil, some typical salt analyses are presented in Table 1. There is a great variation in the concentration of salts in these brines, the concentrations being characteristic of the particular oil field and zone from which they are derived. The total salt content of the oil, therefore, depends not only upon the amount

of water present, but also upon the concentration of salts in that water, so that different samples of the same oil will differ in salt and sediment contents, depending on the effectiveness of prior dehydration and sedimentation operations. On the other hand, the brine concentration in any one crude oil source usually remains quite constant, so that the amount of salt will vary proportionately with the quantity of brine it contains. There are very few instances where solid salt crystals are found to be present in crude oil, unless there has been opportunity for evaporation of water to permit such crystallization. The heavier oils are more difficult to dehydrate and usually have higher water contents when they arrive at the refinery. On the other hand some of the light crudes, as in Michigan, carry only small amounts of water, but in this case the water is heavily loaded with salts.

The presence of even small amounts of residual water in crude oil can lead to other refinery problems. For example, some of this water will gradually settle out in the refinery storage tanks in the form of a "sludge," producing an accumulation of "tank bottoms" with a continually rising level. Due to their high oil content, these bottoms cannot simply be drawn off into the water disposal system, and when the level rises to the suction line of the still charge pump, large amounts of water and salt are fed into the still, seriously upsetting its operation. Provisions need therefore to be made for taking care of such situations, as by a desalting procedure that is capable of handling such sludging conditions.

It will be noted that the Wyoming oils have very low chloride contents, but additional analyses show that they are comparatively high in sulfates. It is therefore of considerable importance to the refiner to determine not only the amount, but also the composition of the salts which are present in his charging stocks. In analyzing crude oils for salts, refiners have generally been content merely to ascertain the amount of chlorides present, since these substances are considered to be primarily responsible for the corrosive atmosphere produced as a result of their hydrolysis. However, it has been found that chlorides vary greatly in the degree of hydrolysis produced upon distillation, and of the salts commonly present in crude oils, they are in the following order of diminishing hydrolysis; iron and aluminum, magnesium, calcium, and sodium. In addition, the nature of the crude oil itself, as well as the non-chloride constituents of the brine, profoundly affect this hydrolytic decomposition. It can be readily seen that a chloride determination alone is not adequate for a reliable appraisal of the effects of salts on the refinery operations. Methods must therefore be provided for determining not only the distribution of the chloride salts, but of non-chloride constituents such as sulfates and bicarbonates, as well. While chlorides are the source of the hydrochloric acid evolved during distillation of the crude oil, non-chloride constituents contribute to scaling and plugging of the equipment, and must therefore also be considered as objectionable and kept to the lowest value possible. For example, some of the Wyoming crude oils previously referred to may have twice as many sulfates as chlorides and about half of the total salts as calcium and magnesium rather than sodium, whereas in California fields sodium represents about 80% of the total salts present.

TABLE 1
TYPICAL CRUDE OIL ANALYSES

| Area | Field | Gravity °API | Water % | Chlorides as NaCl, ptb. | Sediment ptb. | Acidity as NaOH, ptb. |
|-----------------------------|------------------|-----------------|------------|----------------------------|------------------|--------------------------|
| UNITED STATES FIELDS | | | | | | |
| Arkansas | Sour Schuler | 33.3 | .4 | 138.0 | | 20 |
| | Sweet Schuler | 37.6 | .2 | 105.0 | | 26 |
| California | Elk Hills | 22.6 | .3 | 54.0 | | 259 |
| | Huntington Beach | 22.8 | .7 | 65.0 | | 185 |
| | Kettleman | 32.1 | .1 | 12.6 | | 71 |
| | L. A. Basin | 22.5 | .7 | 78.8 | 144.0 | 342 |
| | Santa Maria | 15.3 | 1.3 | 123.0 | 16.6 | 357 |
| | Signal Hill | 25.7 | .2 | 53.3 | | 131 |
| | Ventura | 28.9 | .5 | 64.1 | | 97 |
| Wilmington | | 22.3 | .4 | 52.0 | 88.5 | 306 |
| | Illinois | 36.9 | .1 | 50.4 | 60.8 | 34 |
| Kansas | Kansas | 36.3 | .3 | 73.5 | 188.0 | 56 |
| | West Kansas | 37.5 | .15 | 66.0 | 74.5 | 36 |
| Kentucky | East Kentucky | 37.1 | .2 | 52.0 | 70.0 | 20 |
| Louisiana | Ecutta | 20.5 | .2 | 55.0 | 63.0 | |
| | Lake Labrador | 34.1 | .4 | 146.0 | 43.0 | 59 |
| | Magnolia | 28.4 | .1 | 32.2 | | 19 |
| | N. Louisiana | 22.2 | .9 | 170.0 | 56.0 | 296 |
| Michigan | Buckeye | 38.9 | .2 | 243.0 | 20.2 | 10 |
| | Kent Co. | 40.8 | .2 | 138.0 | 5.0 | 15 |
| | West Branch | 32.3 | .1 | 141.0 | | 36 |
| Mississippi | Baxterville | 16.4 | 1.8 | 337.5 | 20.6 | |
| | Boiton | 40.4 | .46 | 246.0 | 16.1 | 217 |
| Montana | Poplar | 40.2 | .1 | 15.0 | 67.9 | |
| New Mexico | Four Corners | 36.8 | .2 | 13.7 | 46.4 | |
| North Dakota | Beaver Lodge | 41.9 | .5 | 40.0 | 44.1 | |
| Oklahoma | Stroud | 20.7 | 1.6 | 1137.0 | 7.1 | 57 |
| | Duncan | 29.4 | .35 | 164.0 | 12.0 | 46 |
| Pennsylvania | Corning | 40.2 | .3 | 158.0 | 29.4 | 177 |
| | Pennsylvania | 43.6 | .05 | 3.6 | 29.4 | |
| Texas | Cayuga | 27.8 | .4 | 187.0 | 12.1 | 170 |
| | Duggan-Slaughter | 31.8 | .05 | 191.0 | 3.2 | 26 |
| | East Texas | 37.9 | .2 | 44.0 | 19.3 | 57 |
| | Hawkins | 26.1 | .12 | 56.0 | 72.8 | |
| | Hockley | 29.9 | .3 | 317.5 | 333.9 | |
| | Moore Co. | 36.8 | .2 | 209.0 | 160.0 | 42 |
| | Panhandle | 41.4 | .2 | 137.5 | | |
| West Texas | 33.7 | .15 | 69.0 | | | |
| Wyoming | Bonanza | 35.7 | .1 | 1.3 | | 30 |
| | Garland | 20.2 | .5 | 1.6 | 91.0 | 51 |
| | Hamilton Dome | 18.4 | .3 | 5.0 | | 130 |

| Area | Field | Gravity °API | Water % | Chlorides as NaCl, ptb. | Sediment ptb. | Acidity as NaOH, ptb. |
|-----------------------|--------------------|-----------------|------------|----------------------------|------------------|--------------------------|
| FOREIGN FIELDS | | | | | | |
| Arabia | Kuwait | 32.0 | .55 | 175.0 | | |
| | Kuwait | 24.9 | 2.8 | 162.5 | 29.4 | |
| | Wafra | 23.0 | .1 | 52.5 | 77.7 | |
| Argentina | Barrancas | 30.7 | .6 | 175.0 | 5.1 | |
| | Bahrain Island | 31.4 | .55 | 10.2 | | 18 |
| Canada | Fosterton (Sask.) | 21.1 | 1.0 | 25.0 | | |
| | Gull Lake | 22.4 | .6 | 23.8 | 93.1 | 28 |
| | Redwater | 34.3 | .4 | 31.3 | 10.5 | 42 |
| | Stettler (Alberta) | 29.7 | .5 | 148.0 | | |
| Columbia | | 20.6 | .4 | 43.8 | 12.6 | |
| | Egypt | | | | | |
| Egypt | Belayim | 22.8 | .10 | 153.0 | | 72 |
| | Feiran | 24.7 | 4.8 | 960.0 | | 187 |
| Germany | Hemmelte | 30.1 | .4 | 325.0 | | |
| Indonesia | Sumatra | 35.1 | .28 | 11.8 | 2.2 | |
| Mexico | Ebano | 11.4 | .7 | 50.4 | 26.0 | 301 |
| | El Plan | 21.7 | .5 | 292.0 | | 610 |
| Russia | Buguruslan | 28.5 | 1.1 | 300.0 | 32.0 | 27 |
| | Ishimbay | 27.0 | .7 | 436.0 | 14.0 | 28 |
| | Nebetdac | 32.3 | 1.6 | 155.0 | 92.0 | 86 |
| | Syzran | 25.9 | 1.3 | 484.0 | 45.0 | 18 |
| Trinidad | | 23.1 | .25 | 56.0 | | 640 |
| | Turkey | | | | | |
| Turkey | Garzan | 26.6 | .1 | 13.7 | | 22 |
| | Ramandag | 20.9 | .1 | 25.0 | | 52 |
| Venezuela | Lagunillas | 18.7 | 1.4 | 20.0 | | 336 |
| | Mara | 29.3 | .18 | 20.7 | | 19 |
| | Meray | 18.5 | .9 | 51.0 | | |
| | Quiriquiri | 16.5 | 1.3 | 41.0 | | 1440 |
| | San Joaquin | 41.3 | .38 | 11.2 | | |
| | Temblador | 21.1 | .8 | 94.5 | 15.1 | 71 |
| | Tia Juana | 14.8 | .08 | 25.5 | 12.0 | |

From these considerations it is readily evident that processing of crude oils can introduce enormous amounts of salts into the refinery equipment over comparatively short periods of operation. At present the value of the analysis of a crude charging stock for chlorides is generally appreciated by the refiner, and has to a large extent become a routine determination. However, the usual routine test methods do not provide a complete picture of the potential corrosivity and other detrimental characteristics of the crude, and must be supplemented by other tests to obtain better information for an accurate appraisal. For example, the sulfates occurring in a crude oil, especially if a portion should be present as micro-crystals of gypsum, cannot always be accurately determined by the extraction methods ordinarily employed for chlorides. Furthermore, the organic acidity in the crude has an important bearing on the degree of hydrolysis of the salts, and so also has the alkalinity of the brine particles themselves.

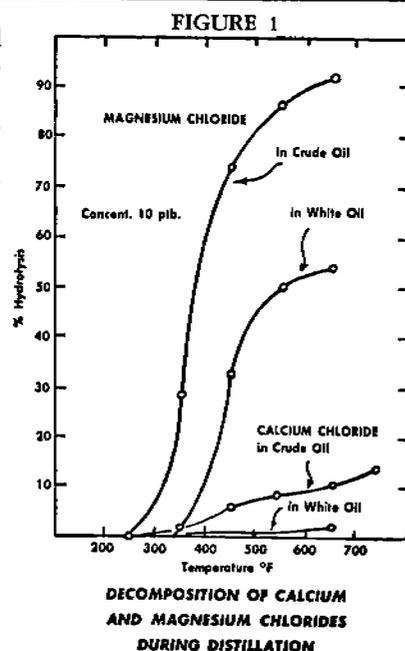
Methods of analysis of crude oils for salts and an evaluation of hydrochloric acid evolution during topping operations have previously been made available to the refinery analytical staffs in prior manuals and publications (1), (2). Some results on the distillation of various crude oils in the laboratory are shown in Table 2. The liquid temperatures

TABLE 2

HYDROCHLORIC ACID AND HYDROGEN SULFIDE EVOLUTION FROM CRUDE OILS

| AREA | FIELD | Chlorides as NaCl pib. | HCl evol. as NaCl pib. | H ₂ S evolution pib. | Mercaptan evolution pib. |
|------------|-------------------|------------------------|------------------------|---------------------------------|--------------------------|
| California | Wilmington | 198.0 | 6.0 | 15.8 | 2.0 |
| | L. A. Basin | 52.0 | 6.1 | 1.3 | 8.7 |
| | Kettleman | 12.6 | 3.2 | .5 | 2.0 |
| | Santa Maria | 88.0 | 6.8 | | |
| Texas | Cayuga | 187.0 | 10.8 | 2.4 | 1.1 |
| | Borger | 132.0 | 17.5 | 236.0 | 88.0 |
| | Moore County | 209.0 | 12.0 | 306.0 | 31.2 |
| | Hutchinson County | 261.0 | 31.7 | 208.0 | 14.1 |
| | Van | 15.1 | 2.7 | .5 | .2 |
| | East Texas | 44.0 | 2.6 | 1.8 | nil. |
| | Duggan-Slaughter | 191.0 | 64.0 | 53.5 | 249.0 |
| Michigan | West Branch | 25.0 | 20.3 | 19.2 | 144.0 |
| | Buckeye | 243.0 | 23.6 | 5.8 | 52.1 |
| | Midland | 69.0 | 11.9 | 24.5 | 27.4 |
| Louisiana | Rodessa | 144.0 | 20.2 | 16.8 | 3.1 |
| | Ville Platte | 95.0 | 2.4 | 2.0 | .2 |
| Illinois | Magnolia | 32.2 | 9.8 | 60.5 | |
| | | 270.0 | 30.5 | 12.2 | 39.0 |
| Kansas | | 35.4 | 3.8 | 3.7 | 8.2 |
| | | 72.1 | 15.7 | 36.2 | 32.2 |
| Arkansas | West Kansas | 45.5 | 15.7 | 8.5 | 17.9 |
| | Schuler | 105.0 | 18.1 | 36.7 | 28.6 |
| | Jones Sand | 60.3 | 6.8 | 2.1 | .7 |
| | Morgan Lime | 69.2 | 15.5 | 40.3 | 47.8 |
| Oklahoma | Stroud | 68.6 | 29.6 | .8 | .7 |
| Canada | Turner Valley | 26.3 | 8.1 | 37.6 | 101.0 |
| | Turner Valley | 45.2 | 16.8 | 42.4 | 142.5 |
| Bahrain | | 10.2 | 1.4 | 3.6 | 4.3 |
| Venezuela | Temblador | 94.5 | 7.3 | 0.5 | nil. |

in the still were carried to 650°F., and the hydrochloric acid and hydrogen sulfide collected in receivers and measured. It can be seen that some oils are much more susceptible to the evolution of hydrochloric acid than others having about the same total chloride content, indicating that there are other factors besides the chloride concentration which affect the hydrolysis of those salts. It is commonly assumed that the hydrochloric acid evolved in distillation is formed principally as a result of the hydrolysis of the magnesium chloride present, and that the calcium and sodium salts do not contribute to the evolution. Actually, this is true only in pure oil systems, such as when a mixture of magnesium, calcium, and sodium chlorides, made up as a brine, is incorporated in a pure oil (such as white oil) and subjected to the distillation procedure. The difference in the behavior of those salts in pure oil



as compared with crude oil systems is shown in Fig. 1. In the pure oil system, magnesium chloride is hydrolyzed to the extent of about 50%, and calcium chloride only about 2%. Sodium chloride shows virtually no decomposition under these conditions. However, in crude oils the evolution can be much higher, as indicated in the upper curves of the graph, which were obtained by the use of a synthetic brine mixture with a salt-free Mid-continent crude oil. The curves show that the chloride decomposition in crude oil begins at about 250°F. and proceeds rapidly thereafter. In the case of calcium chloride, the distillation was carried to 750°F. and it will be noted that there was no diminution in the rate beyond the 650°F. point. Various acidic materials in the crude oil, such as naphthenic acids, will promote the evolution of hydrochloric acid from the salts under distillation conditions, as will also any acidity in the water droplets themselves. Many of the Mid-continent and Texas brines have comparatively low pH values, and the evolution is therefore high for a given chloride content. On the other hand the California brines are predominantly on the alkaline side, and therefore have an inhibiting effect on the acid evolution. Consequently it is impossible to predict, from a simple chloride determination on the crude oil, the extent of the hydrochloric acid evolution to be expected during dis-

TABLE 3

EFFECT OF SALT CONCENTRATION ON HCl EVOLUTION

| CRUDE SOURCE | Acidity as NaOH pib. | Water % | Chlorides as NaCl pib. | HCl evolved as NaCl pib. | Hydrolysis % |
|------------------------------------|----------------------|---------|------------------------|--------------------------|--------------|
| <i>West Texas (41.1° API)</i> | | | | | |
| Raw Crude | 69.7 | .20 | 142.9 | 14.6 | 10.2 |
| Partially desalted | 14.9 | .50 | 14.2 | 5.5 | 38.7 |
| Further desalted | 14.9 | .23 | 3.9 | 3.9 | 100.0 |
| " " | 12.5 | .12 | 1.8 | 1.7 | 94.5 |
| " " | 3.8 | .03 | 1.3 | 1.5 | 100.0 |
| " " | 6.0 | .11 | 0.5 | 0.5 | 100.0 |
| <i>Hockley (Texas) 30.0° API</i> | | | | | |
| Raw Crude | 70.0 | .36 | 315.0 | 35.3 | 11.2 |
| Partially desalted | 26.5 | .38 | 12.8 | 7.3 | 57.0 |
| Further desalted | 28.0 | .40 | 5.0 | 4.0 | 80.0 |
| " " | 21.4 | .02 | 2.9 | 2.3 | 79.4 |
| " " | 27.5 | .05 | 2.6 | 2.5 | 96.2 |
| <i>Kansas 36.3° API</i> | | | | | |
| Raw Crude | 34.4 | .09 | 12.9 | 9.9 | 76.7 |
| Partially desalted | 38.4 | .45 | 3.4 | 3.3 | 97.1 |
| Further desalted | 39.9 | .65 | 2.2 | 2.0 | 90.9 |
| <i>Redwater (Canada) 34.7° API</i> | | | | | |
| Raw Crude | 32.2 | .04 | 46.8 | 22.3 | 47.6 |
| Partially desalted | 32.2 | .80 | 14.5 | 13.2 | 91.0 |
| Further desalted | 15.0 | .04 | 6.8 | 5.0 | 73.5 |
| " " | 30.0 | .94 | 5.7 | 5.0 | 87.6 |
| " " | 23.5 | .43 | 4.5 | 3.9 | 86.7 |

tillation. It may be noted that there is a general tendency for the degree of hydrolysis to increase with a decrease in the total salt content. This effect has been reported (3) and the results of experimental work on various crude oils which had been water-washed in various degrees to produce the desired lower salt contents are shown in Table 3. The results of these and other

HYDROCHLORIC ACID EVOLUTION FROM VARIOUS
CRUDE OILS DURING DISTILLATION

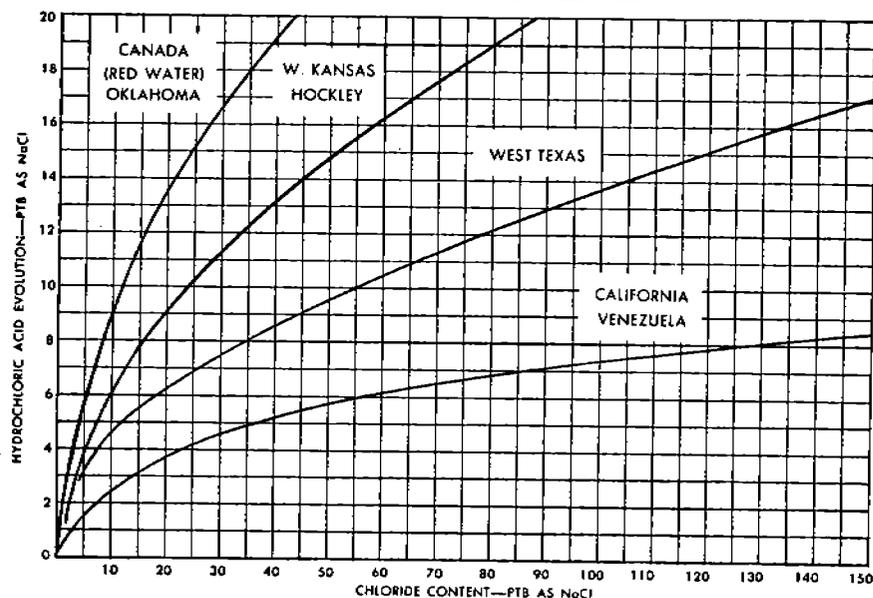


FIGURE 2

tests for hydrochloric acid evolution from a great variety of crudes are shown in the graph of Fig. 2. It is evident that the source of the crude and its brine content have an important bearing on the amount of hydrochloric acid evolved for a given salt content during the distillation process. In general, the Mid-continent types of crudes and those from similar geologic formations produce the higher evolutions, while the Californian and Venezuelan types give the lower results. As in other crude oil properties, there are of course individual exceptions to such a generalization and this must be kept in mind in interpreting the curves. At the lower salt values the curves tend to converge, probably indicating that the oil components, rather than the brine, exert a predominating influence on the decomposition.

In the region of very low salt contents (i.e. 3 or 4 ptb or less) the curves are steepest, indicating a more rapid drop-off in decomposition than at the higher values, and it appears necessary to remove the salt to this extent in order to reduce the adverse effects of hydrochloric acid evolution to negligible values.

Some of the laboratory tests indicated that the presence of even small amounts of iron compounds, such as are frequently found in crude oil, had an accelerating effect on the chloride evolution, possibly by catalytic action.

The undesirable effects arising from the presence of salts in crude charging stocks can be classified into four principal categories:

- (1) Salt deposits in exchangers and furnaces.
- (2) Evolution of corrosive hydrochloric acid.
- (3) Contamination of residual products.
- (4) Secondary effects on various petroleum fractions.

Deposition of salts in exchangers and furnaces results in shortened still runs and a corresponding loss in production, as well as increasing costs resulting from the shut-down and clean-out operations. The deposits tend to cause hot spots in the tubes and limit the temperatures considerably below those possible with salt-free crudes. The salts are therefore responsible, not only for increased maintenance costs, but also for decreased throughputs and lowered production of overhead products.

The evolution of hydrochloric acid is due to the hydrolytic decomposition of chlorides, principally sodium, calcium, and magnesium chlorides during the distillation operation. This hydrochloric acid is extremely corrosive and makes it necessary to inject ammonia into the overhead lines to minimize the corrosion damage. However, the ammonium chloride formed as a result of the neutralization reaction is itself still quite corrosive, and also tends to plug up condensers and columns in the run-down system. It is therefore highly desirable to prevent the evolution of hydrochloric acid altogether by a thorough desalting operation whenever it is at all possible to do so. The experience of refiners indicates that the corrosion due to sulfur is much decreased when the salt has been removed from the oil. It has been postulated that the hydrogen sulfide and hydrochloric acid enter into a cyclic reaction with the metals in the furnace tubes and fractionating equipment, whereby the iron sulfide, which is normally a thin and tightly adhering film, is loosened by decomposition as a result of reaction with the hydrochloric acid, thereby giving an opportunity for further formation of iron sulfide. Such a process obviously would greatly aggravate the corrosive action of hydrogen sulfide, and therefore make it highly desirable to remove as much of the chlorides as possible before subjecting the oil to distillation. Oils vary greatly in the amount of hydrogen sulfide evolved, as can be seen from Table 2, and this must also be taken into account in making an attempt to evaluate the potential corrosivity of a crude oil.

The contamination of residual products such as asphalt, fuel oils, etc., by inorganic salts is due to the fact that these salts remain almost entirely in the distillation residuums. Such residual salts, in fuel oil for example, tend to clog burners and also to deposit a slag on furnace tubes and brickwork of boiler installations. When appreciable amounts are left in asphalt, the properties of this material are adversely affected, such as by giving a positive Oliensis test in products used for roofing, etc., and by interfering with emulsion stability in the case of emulsified asphalts used for road building and similar purposes. Salts and solids in heavy fuel oils are also responsible for air pollution where these oils are burned under boilers.

Refiners report that there are various secondary effects resulting from the desalting operations which are of definitely beneficial character in both the topping and cracking operations, but in which the part played

by the salts is obscure. For example, there is some evidence that the presence of salt has some deleterious effects on the overhead products formed during the distillation or cracking operations, so that an improvement in quality is found when the crude is desalted. Among such reported improvements are (a) a decrease in doctor treating requirements of the gasoline produced, (b) superior color in gasoline and kerosine fractions, and (c) an increase in the lead susceptibility of the gasoline produced. The degree to which such improvements are evidenced in the products seems to depend primarily upon the amount and the nature of the salts present during the distillation or cracking operations. Some of the effects may be attributed to the mechanical entrainment of salts during the fractionation procedure, and others to a change in distribution of the types of products formed. In addition to the effects here reported, there is also evidence to indicate that the presence of salts exerts a catalytic effect on the corrosion produced by sulfur compounds, thereby compounding this type of corrosivity. It has also been demonstrated that the coke formed in still tubes that have processed salty crudes is of very hard and flinty nature and very difficult to drill out, as contrasted with the coke from salt-free oils which is comparatively soft and easy to remove. In those cases where residual oils are reduced to coke, the presence of residual salts will of course contaminate that product and contribute to the deterioration of the tubes and walls of boilers in which the coke is used as fuel. When used for the manufacture of electrode carbon, the cokes must have an especially low salt contamination.

All of these considerations are compelling reasons for a thorough desalting of all crude oils to be processed in a refinery, and indeed many companies now make it a rule to reduce the salt content of any crude processed to much lower values than was formerly considered to be economically justifiable. Whereas a few years ago residual salts of 10-20 ptb. were considered satisfactorily low by most refineries, many now aim at 5 ptb. or less and some insist on less than 1-2 ptb. Fortunately, advances in desalting techniques have made it possible to attain such high removal efficiencies.

Sediment. Another class of oleophobic materials comprises finely divided solids, which may be dispersed in the oil or carried in suspension in the brine droplets. Such solids may have their origin in the oil sands themselves, occurring as finely divided particles of siliceous matter, such as silt, etc., or they may be entrained drilling mud, etc., used in drilling the well or in its rehabilitation, or still further they may be iron rust, scale, and such type of material, picked up by the oil during the course of its passage through pipelines, tanks, valves, etc. Material of this nature is of course highly undesirable when present in crude oil, since it contributes to the plugging of pipe stills, to the erosion of equipment, and to a contamination of residual products.

COLOR PLATE

Showing photomicrographs of sediment on following page.

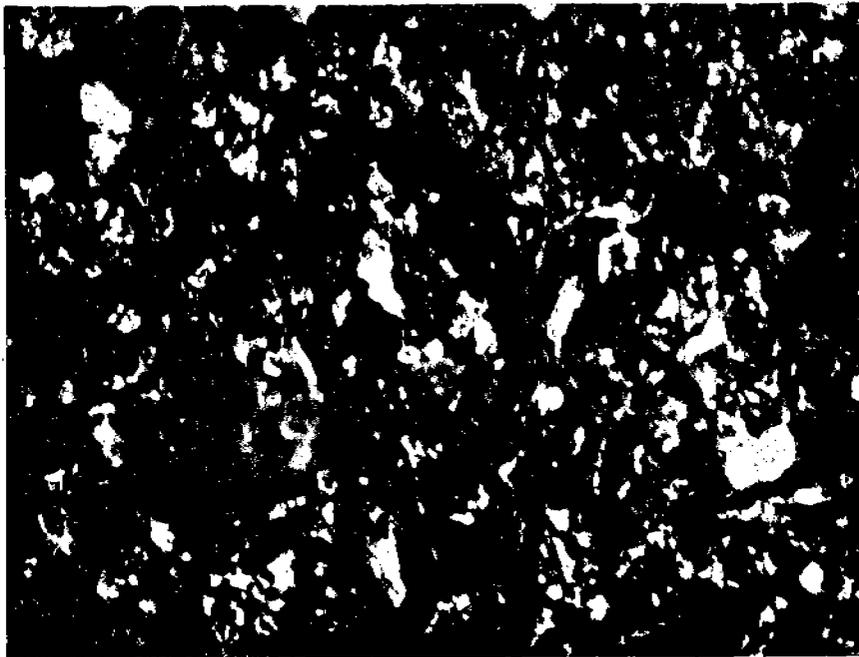
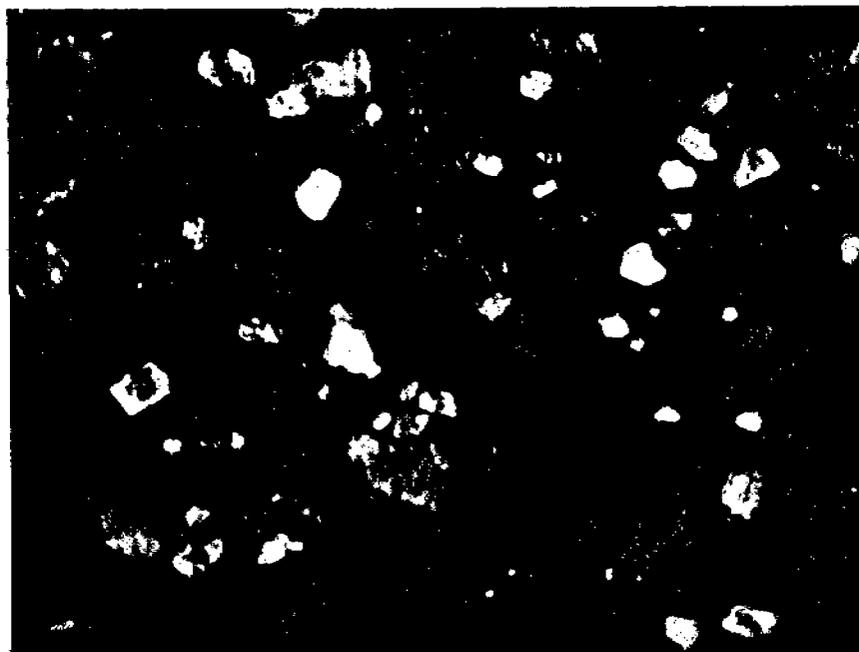


Figure 3 ▲

Figure 4 ▼



Consumers are becoming increasingly critical of these deleterious effects, and refiners are correspondingly finding it desirable to reduce these foreign materials to a minimum by appropriate desalting and other sediment removal processing methods.

The erosive character of suspended sediment in crude oil has recently been shown by Phelan (4) in its effect on hydraulic rodless pump operation, where a sediment removal process has developed dramatic savings by greatly increasing the service life of these pumps.

Table 1 shows some values of sediment contents of various crude oils. Most of these were obtained by the methods given in this manual, using a special centrifuging procedure. The figures shown are for the dried solids which usually contain some volatile matter of organic or carbonate character, so that the ignited weight (ash) will be about one-half, or sometimes a little less, of these values.

PHOTOMICROGRAPHS OF SEDIMENT

The nature of the sediment often found in crude oils is shown in the typical photomicrograph of Fig. 3. The material shown was filtered from a crude oil charging stock, and the great variety of particles present is readily apparent. Identifiable are particles of iron oxide (dark), quartz (translucent), mica, and feldspar. It is not surprising that this type of material can be a serious contaminant in asphalt and fuel oils, for example. Such sediment can to a large degree be removed by special processes such as described by Phelan, cited above, and to a considerable extent also by utilizing a highly efficient desalting process. What can be accomplished by such a desalting procedure is shown in Fig. 4, representing the sediment remaining in the crude of Fig. 3 after an electrical desalting operation. The electric desalting process appears to be particularly effective in this sediment-removing feature. The two photomicrographs are not only qualitatively but also quantitatively comparative, the concentration of sediment in the raw oil being 128 ppm, vs. 18 ppm in the desalted oil.

OLEOPHILIC IMPURITIES

The classification of these materials as impurities is quite arbitrary, since they are an innate part of crude oil itself, and is justified only in the sense that they have adverse effects on the refining operations, or produce unfavorable distribution of the refining yields.

Sulfur. Sulfur compounds have been recognized since the early days of refining as being undesirable constituents, but attempts to remove them by extraction, without also removing a large part of the oil itself, have not been successful. There are now catalytic processes available for the desulfurization of gasoline and even heavier fractions, but nothing of this nature is as yet commercially applicable to the crude oil itself. Consequently, the sulfur constituents are tolerated and the refining operations adjusted to minimize their deleterious effects. The sulfur of the crude appears in the products from gasoline down to the residuum, and numerous methods are used to reduce the sulfur content of the distillates or convert it to less noxious forms. These methods include acid treating, caustic washing, solutizer processes, doctor treating and various other types of sweetening processes, as well as catalytic desulfurization procedures. They are all well known to the refiner and each has its place for particular stocks and specifications requirements. The nature of the sulfur compounds present in crude oil has been the subject of a great deal of research activity, and the results are readily available in the literature. Consequently no ad-

TABLE 4

SULFUR AND NITROGEN CONTENTS OF CRUDE OILS

Selected from Representative Fields

| FIELD AND CRUDE | GRAVITY | SULFUR | NITROGEN |
|--------------------------|---------|--------|----------|
| | *API | % | % |
| Arkansas-Schuler | 33.2 | 1.54 | .063 |
| California-Elk Hills | 23.1 | .69 | .46 |
| California-Midway-Sunset | 20.3 | .88 | .58 |
| California-Santa Maria | 16.0 | 5.06 | .63 |
| California-Wilmington | 25.6 | 1.24 | .58 |
| Colorado-Rangely | 35.2 | .73 | .063 |
| Illinois-Louden | 38.8 | .26 | .094 |
| Kansas-Kraft Prusa | 43.0 | .27 | .17 |
| Louisiana-Delta Farms | 33.8 | .22 | .055 |
| Michigan-Deep River | 34.2 | .60 | .12 |
| Mississippi-Baxterville | 15.0 | 3.07 | .19 |
| Mississippi-Brookhaven | 26.6 | .86 | .066 |
| Montana-Cut Bank | 46.5 | .38 | .018 |
| New Mexico-Langlie | 34.8 | 1.35 | .066 |
| Oklahoma-Burbank | 35.8 | .21 | .05 |
| Oklahoma-Velma | 28.2 | .81 | .27 |
| Texas-East Texas | 37.8 | .36 | .085 |
| Texas-Hastings | 31.3 | .24 | .034 |
| Texas-Hawkins | 25.7 | 2.45 | .13 |
| Texas-Seeligson | 40.9 | .10 | .004 |
| Texas-Wasson | 34.2 | 1.90 | .10 |
| Wyoming-Elk Basin | 31.5 | 1.72 | .14 |
| Wyoming-Oregon Basin | 22.0 | 3.27 | .35 |
| Foreign-Iraq | 36.0 | 1.36 | .14 |
| Foreign-Iraq | 36.6 | 1.93 | .094 |
| Bitumens, Natural | | | |
| California-Edna | 4.3 | 3.20 | 1.23 |
| Utah-Vernal | 8.6 | .50 | 1.18 |
| Canada-Athabaska | 13.0 | 5.15 | .43 |

ditional discussion of these substances will be given here. An indication of typical sulfur contents of crudes from various sources is given in Table 4, which shows the great variability in the sulfur concentrations among the different oils.

Naphthenic Acids. Practically all crude oils contain organic acidic materials to a greater or lesser degree. These have been termed naphthenic acids because they are carboxylic derivatives of the naphthenes, which form a large proportion of the constituents of crude oils. However, the naphthene hydrocarbons are predominantly cyclohexane derivatives, while most of the experimental evidence to date indicates that the naphthenic acids are mostly of the cyclopentyl structure, the carboxyl group being in a side chain. The higher acids probably have bicyclic nuclei. A more appropriate nomenclature would be simply to term these materials "petrolic acids." They are generally of the acid strength of the long-chain aliphatic acids such as stearic acids, but vary in molecular weight to approximately the same extent as the hydrocarbons themselves. These materials can be highly corrosive at high temperatures, but their principal effect on the refining processes is in creating emulsions during the treatment of lube oil fractions with caustic soda. Their presence in the kerosine, diesel oil and gas oil fractions imparts to these products objectionable odors, which can put them at a disadvantage commercially. The insoluble calcium and magnesium soaps formed, when distillates containing naphthenic acids, as such or in their neutralized form as sodium naphthenates are washed with hard waters, tend to cause hazes in the oils that not only mar their appearance, but are the cause of other customer difficulties, such as the plugging of screens and burner tips in furnaces and stoves. These factors alone often make it desirable to remove the acids from certain oil streams.

It has been found that the acids in the lower boiling range have important commercial applications, so that it is often economically desirable to recover them for that reason. They find wide application in industry as carriers for paint driers in the form of manganese and other naphthenate soaps, and they are also used in the manufacture of mildew-proofing compounds, such as zinc and copper naphthenates, etc. During wartime they are in especially great demand for use as gelling agents for fire bombs. One of the deterrents to the wider use of naphthenic acids in industry has been that the crude acids are black in color, contain considerable quantities of non-acidic oils and have objectionable odors. However, considerable attention in recent years has been paid to adequate refining of these acids, and light colored products having little extraneous material are now readily available. The corrosive nature of these acids, especially at high temperatures, makes it necessary to utilize highly resistant materials for their processing.

Removal of naphthenic acids from the lighter petroleum fractions is usually not difficult and provides an additional source of revenue to the refiner. Caution must however be exercised that no alkaline materials are left in the treated oil because their presence can have serious adverse effects on the subsequent use of the distillates. For example, even minute quantities of alkalis left behind in stove oil can corrode brass fittings and burners to the extent that serious trouble can be encountered in such use. The presence of sodium naphthenates also has an adverse effect on the inhibitors that are often added to various distillates. In addition, such

residual alkalis are poisonous to catalysts, and it is therefore essential to use highly efficient separation methods in the caustic washing steps.

It is generally not feasible to remove the naphthenic acids from crude oils directly, because of the serious emulsion difficulties encountered when an attempt is made to wash these oils with caustic soda. In some instances such washing can be successfully accomplished under carefully controlled conditions. As has been noted previously, one of the chief difficulties with the presence of naphthenic acids is in the formation of emulsions during the caustic treatment of lube oil fractions. In the processing of some oils that have high naphthenic acid contents the device of adding caustic to the crude oil before distillation is often employed to avoid these subsequent emulsions. The naphthenic acids react with the caustic to form soaps which are not distilled and therefore remain in the residuum. This effectively avoids the carry-over of acids into the lube oil fractions, but at the same time develops ash-forming constituents in the heavy fuel oil or asphalt products that are made from the residuums. Since these ash-formers are highly undesirable it is sometimes necessary to remove them by an acid wash to produce a satisfactory product. Such acid treatment of residual oils is commercially practiced and avoids the product degradation which would otherwise occur when it is necessary to treat crude oils with caustic before distillation.

The heavy naphthenic acids present in the lube oil fractions tend to form sodium soaps that are oil-soluble and therefore difficult to remove. Special techniques are required and great care must be exercised to avoid the formation of stable emulsions which greatly hamper the lube oil purification processes.

A general idea of the concentration in which naphthenic acids are found in various crude oils is shown by the figures in the appropriate column of Table 1, page 4. It can be seen that crude oils vary greatly in the amount of naphthenic acids present and in general, the more paraffinic the oil the less acidic material is present. The Californian and Venezuelan oils have especially high acid contents, although the variation even in these groups is considerable. It is probable that naphthenic acids will find increasing outlets in industry for specific uses, or as intermediates not competitive with animal and vegetable acids, and that their recovery from petroleum products will become of greater importance and magnitude in the future.

TABLE 5
PROTOTYPES OF NITROGEN COMPOUNDS IN PETROLEUM DISTILLATES

| Prototype | pKb | Structure |
|--------------------|------|---|
| Non-basic: Pyrrole | 13.6 |  |
| Indole | 14 |  |
| Carbazole | 15 |  |
| Basic: i-Quinoline | 8.9 |  |
| Pyridine | 8.8 |  |

Note: The actual compounds occurring in petroleum often have one or more hydrocarbon groups on side chains.

Nitrogen. The presence of nitrogen in crude oils has been known for at least fifty years but it is only rather recently that the nature of the nitrogen compounds has been at all well defined. Much of the pioneer work on these materials has been done by Bailey (5) and by Lochte (6) at the University of Texas.

The prototypes of nitrogen compounds present in crude oils are shown in Table 5. They divide themselves primarily into two groups, the basic and the non-basic. The non-basic are of the carbazole, indole and pyrrole types, and occur relatively in that order of decreasing concentration (7). The basic compounds are primarily of quinoline structure and, as can be judged from their dissociation constants, the strength of these bases is such that they can be virtually quantitatively removed from the oil by acid extraction. Obviously the non-basic materials are not affected by such acid treatment, but are reported to be removable by solvent extraction methods, such as by the furfural processes.

The magnitude of the nitrogen content of various types of petroleum oils is given in Table 4, obtained in the investigations of Ball, Whisman, and Wenger (8), who found a rough correlation between the nitrogen content and the carbon residue values. These results show that the nitrogen content varies greatly with the source of the oil and, as in the case of sulfur, the greatest concentrations are found in the California petroleums. The amount of nitrogen compounds present in the crude oils listed may at first seem disarmingly small, but it must be remembered that the values represent nitrogen only, and that the compounds in which it occurs will be many times as great in weight and volume. On the basis of an average molecular weight of the nitrogen compounds of about 300, which appears to be a reasonable value for the bases in the lighter distillates, the nitrogen values of the table must be multiplied by about 20 in order to convert them to percentages of actual nitrogen-containing compounds in the oil. This puts their concentration in the range of 1% for the lowest and 13% for the higher oils from California.

Differentiation between basic and non-basic nitrogen compounds has been made by analytical methods described by Deal et al., (9). These investigators have shown that the ratio of basic nitrogen to total nitrogen in some California, West Texas, and Middle East crudes is approximately 0.25 to 0.30. Similar results have been obtained by Richter et al (10) on a greater variety of crudes, and they have arrived at similar ratio figures. Their results are shown in the upper portion of Table 6.

The lower portion of the table contains some figures on the nitrogen contents of distillates. These of course are much lower than the corresponding crude oil values and are therefore expressed in parts per million. It is immediately apparent that the cracked materials contain vastly greater amounts of nitrogen than the straight run streams, which is of course a result of the cracking of the heavy nitrogen compounds which otherwise remain in the residuums. The cracking procedure also tends to convert most of the nitrogen in the crude to the basic form, although this varies considerably with the particular stock processed. The cracked distillates are therefore potentially highly poisonous to catalytic cracking catalysts, even when derived from crudes of originally low nitrogen content.

The distribution of the total nitrogen content among the various crude oil fractions is shown by the graph of Fig. 5. This indicates that there is a fairly uniform increase in nitrogen concentration as the molecular weight of the fraction increases. For the crudes shown, the concentration of nitro-

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PART I

THE NATURE OF IMPURITIES IN PETROLEUM

FOREWORD

Impurities commonly found in refinery charging stocks have reduced yields and degraded products throughout the history of petroleum refining. There has in the recent past been an increasing pressure to obtain maximum yields and premium products, which has spawned a great variety of new processes, especially of the catalytic variety. These in turn have been more sensitive to the impurities and have therefore magnified their deleterious effects.

Part I of this manual presents the most recent evaluations of such effects as developed by published information as well as Petreco's experience. It is a descriptive summary of the nature of the impurities and how they affect refining operations.

In order to evaluate the results of any remedial steps which are taken to combat the adverse effects of the impurities, it is necessary to make accurate analyses of the products involved. Part II of this manual presents a series of selected analytical methods which have for the most part been thoroughly tested in Petreco laboratories. It is designed to give operative details of methods applicable to the evaluation of processes designed for the removal of the impurities of most concern to the refiner.

Part III is not in the manual but represents our ambition to serve the petroleum industry wherever our highly specialized techniques are most applicable. Our background of more than four decades of wide experience in solving treating problems in both the production and refining phases of petroleum operations is your assurance of the reliability and integrity of our organization.

PETRECO—A Division of Petrolite Corporation

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PART II

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GENERAL CHARACTER

Impurities in petroleum, or crude oil, as it is more generally and descriptively known, may as a first generalization be considered to be all constituents which have elements other than hydrogen and carbon in their molecular structure. Such materials may be classed as impurities from the refiner's standpoint because, to a greater or lesser degree, they produce adverse effects during the refining process, such as by producing corrosive conditions in the refining equipment, or by adversely affecting the quality of the products. In the early days of comparatively mild refining conditions, the processor was concerned primarily with two types of impurities, water and sulfur. The water, or brine as it is often termed because of its high saline content, represents the general class of impurities which are best characterized as being of the "oleophobic" type. In crudes as received by the refinery, these may be designated as follows:

| OLEOPHOBIC IMPURITIES | GENERAL RANGE |
|-----------------------|---------------|
| Salts | 10—1000 pth* |
| Water | 0.1—2% |
| Sediment | 1—500 pth* |

*pth = pounds per thousand barrels of oil

These oleophobic constituents are inherently insoluble in crude oil, and are therefore present as a second phase, being carried as discrete particles by the oil.

Sulfur, on the other hand, represents a type of impurity which is soluble in crude oil, and may therefore be designated as of the "oleophilic" type. Typical constituents of this type may be listed as follows:

| OLEOPHILIC IMPURITIES | GENERAL RANGE |
|---|-------------------------|
| Sulfur Compounds | 0.1—5% as Sulfur |
| Organo-Metallic Compounds (Nickel, Vanadium, Iron, Arsenic, etc.) | 5—400 ppm. as the metal |
| Naphthenic Acids | .03—.4 vol. % |
| Nitrogen Compounds | .05—15 vol. % |
| Non-Acidic Oxygen Compounds (Resins, Cresols, etc.) | 0—2% as oxygen |

The industry quickly learned to dehydrate crude oils to satisfactorily low water contents, and experimented with various types of steels to reduce the corrosive effects of sulfur compounds on the refining equipment. Actual removal of the sulfur compounds was out of the question, since the sulfur atoms are combined into large molecules of hydrocarbons, so that in some cases probably half of the crude oil has sulfur as an integral part of its molecular structure. However, as thermal cracking and then catalytic cracking processes were introduced, the refiner found that some of the impurities, such as the residual salts associated with the small amount of brine left in the oil, had serious adverse effects on these newer refining techniques. It was only about a decade or so ago that it became generally

Reference # 6

PETRECO MANUAL

IMPURITIES IN PETROLEUM

Occurrence, Analysis, Significance
to Refiners

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the Staff of Petrolite Corporation Laboratories
and Published by*

PETRECO

A Division of Petrolite Corporation

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FOREWORD

Impurities commonly found in refinery charging stocks have reduced yields and degraded products throughout the history of petroleum refining. There has in the recent past been an increasing pressure to obtain maximum yields and premium products, which has spawned a great variety of new processes, especially of the catalytic variety. These in turn have been more sensitive to the impurities and have therefore magnified their deleterious effects.

Part I of this manual presents the most recent evaluations of such effects as developed by published information as well as Petreco's experience. It is a descriptive summary of the nature of the impurities and how they affect refining operations.

In order to evaluate the results of any remedial steps which are taken to combat the adverse effects of the impurities, it is necessary to make accurate analyses of the products involved. Part II of this manual presents a series of selected analytical methods which have for the most part been thoroughly tested in Petreco laboratories. It is designed to give operative details of methods applicable to the evaluation of processes designed for the removal of the impurities of most concern to the refiner.

Part III is not in the manual but represents our ambition to serve the petroleum industry wherever our highly specialized techniques are most applicable. Our background of more than four decades of wide experience in solving treating problems in both the production and refining phases of petroleum operations is your assurance of the reliability and integrity of our organization.

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THE NATURE OF IMPURITIES IN PETROLEUM

GENERAL CHARACTER

Impurities in petroleum, or crude oil, as it is more generally and descriptively known, may as a first generalization be considered to be all constituents which have elements other than hydrogen and carbon in their molecular structure. Such materials may be classed as impurities from the refiner's standpoint because, to a greater or lesser degree, they produce adverse effects during the refining process, such as by producing corrosive conditions in the refining equipment, or by adversely affecting the quality of the products. In the early days of comparatively mild refining conditions, the processor was concerned primarily with two types of impurities, water and sulfur. The water, or brine as it is often termed because of its high saline content, represents the general class of impurities which are best characterized as being of the "oleophobic" type. In crudes as received by the refinery, these may be designated as follows:

| OLEOPHOBIC IMPURITIES | GENERAL RANGE |
|---|---------------|
| Salts | 10—1000 ptb* |
| Water | 0.1—2% |
| Sediment | 1—500 ptb* |
| *ptb = pounds per thousand barrels of oil | |

These oleophobic constituents are inherently insoluble in crude oil, and are therefore present as a second phase, being carried as discrete particles by the oil.

Sulfur, on the other hand, represents a type of impurity which is soluble in crude oil, and may therefore be designated as of the "oleophilic" type. Typical constituents of this type may be listed as follows:

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| Naphthenic Acids | .03—.4 vol. % |
| Nitrogen Compounds | .05—15 vol. % |
| Non-Acidic Oxygen Compounds (Resins, Cresols, etc.) | 0—2% as oxygen |

The industry quickly learned to dehydrate crude oils to satisfactorily low water contents, and experimented with various types of steels to reduce the corrosive effects of sulfur compounds on the refining equipment. Actual removal of the sulfur compounds was out of the question, since the sulfur atoms are combined into large molecules of hydrocarbons, so that in some cases probably half of the crude oil has sulfur as an integral part of its molecular structure. However, as thermal cracking and then catalytic cracking processes were introduced, the refiner found that some of the impurities, such as the residual salts associated with the small amount of brine left in the oil, had serious adverse effects on these newer refining techniques. It was only about a decade or so ago that it became generally

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recognized that the small inorganic salt contents of crude oil charging stocks placed serious limitations on the topping and thermal cracking processes of the refinery. It is now considered good practice to remove such salts to the lowest possible values that are economically justifiable in order to minimize their adverse effects on refining equipment and products.

In the catalytic cracking processes some types of impurities exhibit adverse effects on the distribution of the cracking products and on the catalyst itself. While only overhead products are charged to such catalytic crackers, small amounts of salts often appear in these charging stocks as a result of carryover from the residual material in the form of spray or foam, due either to excessive charging rates to the fractionators or to fouling of the trays with solids, such as sediment and ammonium chloride. Consequently a thorough desalting of the original crude is often further justified by the improved results obtainable in the catalytic cracking process. However, still other crude oil constituents can also have a pronounced influence on the cracking reactions, and of these the most important are such materials as nitrogen bases and other organic compounds, especially of an organometallic nature carrying relatively minute proportions of metals, such as vanadium, nickel, and copper. Arsenic compounds also have recently been shown to be the cause of catalyst poisoning and deterioration, especially where platinum catalysts are concerned.

Catalytic charging stocks prepared by the propane deasphalting process can have appreciable quantities of salt left in them, often in the range of 2-10 ptb.

In order to understand more fully the nature of the impurities referred to, a somewhat more detailed description is given below.

OLEOPHOBIC IMPURITIES

Water and Salts. The principal source of these impurities is the residual water droplets which are so small and so highly stabilized by emulsifying agents present in the oil that dehydration methods have failed to remove them by the customary procedures. Water itself is of course a highly undesirable oleophobic impurity, but refiners generally limit the amount of water which may be present in crude oils brought to the refinery to a value of less than about 2%, and usually less than 0.5%, depending upon the nature of the crude. These particular values for the maximum water contents are dictated, not by the amounts which the refinery would prefer to have, which is no water at all, but rather by the difficulties of commercially reducing water contents in crude oils to lower values by even the best dehydration methods. The oil field waters which are produced with crude oils vary widely in the composition and amount of salts which they carry in solution, but their concentration is generally greater than that of sea water, and they are therefore termed "brines." In order to indicate the amount of salts carried by even minute amounts of brines in the oil, some typical salt analyses are presented in Table 1. There is a great variation in the concentration of salts in these brines, the concentrations being characteristic of the particular oil field and zone from which they are derived. The total salt content of the oil, therefore, depends not only upon the amount

of water present, but also upon the concentration of salts in that water, so that different samples of the same oil will differ in salt and sediment contents, depending on the effectiveness of prior dehydration and sedimentation operations. On the other hand, the brine concentration in any one crude oil source usually remains quite constant, so that the amount of salt will vary proportionately with the quantity of brine it contains. There are very few instances where solid salt crystals are found to be present in crude oil, unless there has been opportunity for evaporation of water to permit such crystallization. The heavier oils are more difficult to dehydrate and usually have higher water contents when they arrive at the refinery. On the other hand some of the light crudes, as in Michigan, carry only small amounts of water, but in this case the water is heavily loaded with salts.

The presence of even small amounts of residual water in crude oil can lead to other refinery problems. For example, some of this water will gradually settle out in the refinery storage tanks in the form of a "sludge," producing an accumulation of "tank bottoms" with a continually rising level. Due to their high oil content, these bottoms cannot simply be drawn off into the water disposal system, and when the level rises to the suction line of the still charge pump, large amounts of water and salt are fed into the still, seriously upsetting its operation. Provisions need therefore to be made for taking care of such situations, as by a desalting procedure that is capable of handling such sludging conditions.

It will be noted that the Wyoming oils have very low chloride contents, but additional analyses show that they are comparatively high in sulfates. It is therefore of considerable importance to the refiner to determine not only the amount, but also the composition of the salts which are present in his charging stocks. In analyzing crude oils for salts, refiners have generally been content merely to ascertain the amount of chlorides present, since these substances are considered to be primarily responsible for the corrosive atmosphere produced as a result of their hydrolysis. However, it has been found that chlorides vary greatly in the degree of hydrolysis produced upon distillation, and of the salts commonly present in crude oils, they are in the following order of diminishing hydrolysis; iron and aluminum, magnesium, calcium, and sodium. In addition, the nature of the crude oil itself, as well as the non-chloride constituents of the brine, profoundly affect this hydrolytic decomposition. It can be readily seen that a chloride determination alone is not adequate for a reliable appraisal of the effects of salts on the refinery operations. Methods must therefore be provided for determining not only the distribution of the chloride salts, but of non-chloride constituents such as sulfates and bicarbonates, as well. While chlorides are the source of the hydrochloric acid evolved during distillation of the crude oil, non-chloride constituents contribute to scaling and plugging of the equipment, and must therefore also be considered as objectionable and kept to the lowest value possible. For example, some of the Wyoming crude oils previously referred to may have twice as many sulfates as chlorides and about half of the total salts as calcium and magnesium rather than sodium, whereas in California fields sodium represents about 80% of the total salts present.

TABLE 1
TYPICAL CRUDE OIL ANALYSES

| Area | Field | Gravity °API | Water % | Chlorides as NaCl, ptb. | Sediment ptb. | Acidity as NaOH, ptb. |
|-----------------------------|------------------|-----------------|------------|----------------------------|------------------|--------------------------|
| UNITED STATES FIELDS | | | | | | |
| Arkansas | Sour Schuler | 33.3 | .4 | 138.0 | | 20 |
| | Sweet Schuler | 37.6 | .2 | 105.0 | | 26 |
| California | Elk Hills | 22.6 | .3 | 54.0 | | 259 |
| | Huntington Beach | 22.8 | .7 | 65.0 | | 185 |
| | Kettleman | 32.1 | .1 | 12.6 | | 71 |
| | L. A. Basin | 22.5 | .7 | 78.8 | 144.0 | 342 |
| | Santa Maria | 15.3 | 1.3 | 123.0 | 16.6 | 357 |
| | Signal Hill | 25.7 | .2 | 53.3 | | 131 |
| | Ventura | 28.9 | .5 | 64.1 | | 97 |
| Wilmington | | 22.3 | .4 | 52.0 | 88.5 | 306 |
| | | | | | | |
| Illinois | Illinois | 36.9 | .1 | 50.4 | 60.8 | 34 |
| Kansas | Kansas | 36.3 | .3 | 73.5 | 108.0 | 56 |
| | West Kansas | 37.5 | .15 | 66.0 | 74.5 | 36 |
| Kentucky | East Kentucky | 37.1 | .2 | 52.0 | 70.0 | 20 |
| Louisiana | Eucutta | 20.5 | .2 | 55.0 | 63.0 | |
| | Lake Labrador | 34.1 | .4 | 146.0 | 43.0 | 59 |
| | Magnolia | 38.4 | .1 | 32.2 | | 19 |
| | N. Louisiana | 22.2 | .9 | 170.0 | 56.0 | 296 |
| Michigan | Buckeye | 38.9 | .2 | 243.0 | 20.2 | 10 |
| | Kent Co. | 40.8 | .2 | 138.0 | 5.0 | 15 |
| | West Branch | 32.3 | .1 | 141.0 | | 36 |
| Mississippi | Baxterville | 16.4 | 1.8 | 337.5 | 20.6 | |
| | Bolton | 40.4 | .46 | 246.0 | 16.1 | 217 |
| Montana | Poplar | 40.2 | .1 | 15.0 | 67.9 | |
| New Mexico | Four Corners | 36.8 | .2 | 13.7 | 46.4 | |
| North Dakota | Beaver Lodge | 41.9 | .5 | 40.0 | 44.1 | |
| Oklahoma | Stroud | 20.7 | 1.6 | 1137.0 | 7.1 | 57 |
| | Duncan | 29.4 | .35 | 164.0 | 12.0 | 46 |
| Pennsylvania | Corning | 40.2 | .3 | 158.0 | 29.4 | 177 |
| | Pennsylvania | 43.6 | .05 | 3.6 | 29.4 | |
| Texas | Cayuga | 27.8 | .4 | 187.0 | 12.1 | 170 |
| | Duggan-Slaughter | 31.8 | .05 | 191.0 | 3.2 | 26 |
| | East Texas | 37.9 | .2 | 44.0 | 19.3 | 57 |
| | Hawkins | 26.1 | .12 | 56.0 | 72.8 | |
| | Hockley | 29.9 | .3 | 317.5 | 333.9 | |
| | Moore Co. | 36.8 | .2 | 209.0 | 160.0 | 42 |
| | Panhandle | 41.4 | .2 | 137.5 | | |
| West Texas | 33.7 | .15 | 69.0 | | | |
| Wyoming | Bonanza | 35.7 | .1 | 1.3 | | 30 |
| | Garland | 20.2 | .5 | 1.6 | 91.0 | 51 |
| | Hamilton Dome | 18.4 | .3 | 5.0 | | 130 |

| Area | Field | Gravity °API | Water % | Chlorides as NaCl, ptb. | Sediment ptb. | Acidity as NaOH, ptb. |
|-----------------------|--------------------|-----------------|------------|----------------------------|------------------|--------------------------|
| FOREIGN FIELDS | | | | | | |
| Arabia | Kuwait | 32.0 | .55 | 175.0 | | |
| | Kuwait | 24.9 | 2.8 | 162.5 | 29.4 | |
| | Wafra | 23.0 | .1 | 52.5 | 77.7 | |
| Argentina | Barrancas | 30.7 | .6 | 175.0 | 5.1 | |
| Bahrain Island | | 31.4 | .55 | 10.2 | | 18 |
| Canada | Fosterton (Sask.) | 21.1 | 1.0 | 25.0 | | |
| | Gull Lake | 22.4 | .6 | 23.8 | 93.1 | 28 |
| | Redwater | 34.3 | .4 | 31.3 | 10.5 | 42 |
| | Stettler (Alberta) | 29.7 | .5 | 148.0 | | |
| Columbia | | 20.6 | .4 | 43.8 | 12.6 | |
| Egypt | Belayim | 22.8 | .10 | 153.0 | | 72 |
| | Feiran | 24.7 | 4.8 | 960.0 | | 187 |
| Germany | Hemmelte | 30.1 | .4 | 325.0 | | |
| Indonesia | Sumatra | 35.1 | .28 | 11.8 | 2.2 | |
| Mexico | Ebano | 11.4 | .7 | 50.4 | 26.0 | 301 |
| | El Plan | 21.7 | .5 | 292.0 | | 610 |
| Russia | Buguruslan | 28.5 | 1.1 | 300.0 | 32.0 | 27 |
| | Ishimbay | 27.0 | .7 | 436.0 | 14.0 | 28 |
| | Nebetdac | 32.3 | 1.6 | 155.0 | 92.0 | 86 |
| | Syzran | 25.9 | 1.3 | 484.0 | 45.0 | 18 |
| Trinidad | | 23.1 | .25 | 56.0 | | 640 |
| Turkey | Garzan | 26.6 | .1 | 13.7 | | 22 |
| | Ramandag | 20.9 | .1 | 25.0 | | 52 |
| Venezuela | Lagunillas | 18.7 | 1.4 | 20.0 | | 336 |
| | Mara | 29.3 | .18 | 20.7 | | 19 |
| | Merey | 18.5 | .9 | 51.0 | | |
| | Quiriquiri | 16.5 | 1.3 | 41.0 | | 1440 |
| | San Joaquín | 41.3 | .38 | 11.2 | | |
| | Temblador | 21.1 | .8 | 94.5 | 15.1 | 71 |
| | Tía Juana | 14.8 | .08 | 25.5 | 12.0 | |

From these considerations it is readily evident that processing of crude oils can introduce enormous amounts of salts into the refinery equipment over comparatively short periods of operation. At present the value of the analysis of a crude charging stock for chlorides is generally appreciated by the refiner, and has to a large extent become a routine determination. However, the usual routine test methods do not provide a complete picture of the potential corrosivity and other detrimental characteristics of the crude, and must be supplemented by other tests to obtain better information for an accurate appraisal. For example, the sulfates occurring in a crude oil, especially if a portion should be present as micro-crystals of gypsum, cannot always be accurately determined by the extraction methods ordinarily employed for chlorides. Furthermore, the organic acidity in the crude has an important bearing on the degree of hydrolysis of the salts, and so also has the alkalinity of the brine particles themselves.

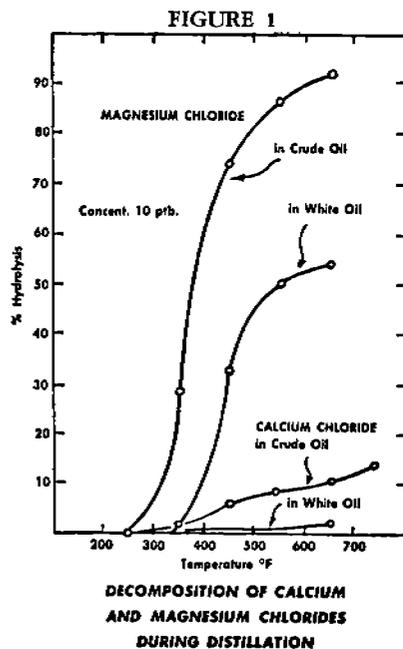
Methods of analysis of crude oils for salts and an evaluation of hydrochloric acid evolution during topping operations have previously been made available to the refinery analytical staffs in prior manuals and publications (1), (2). Some results on the distillation of various crude oils in the laboratory are shown in Table 2. The liquid temperatures

TABLE 2

HYDROCHLORIC ACID AND HYDROGEN SULFIDE EVOLUTION FROM CRUDE OILS

| AREA | FIELD | Chlorides as NaCl ptb. | HCl evol. as NaCl ptb. | H ₂ S evolution ptb. | Mercaptan evolution ptb. |
|------------|-------------------|------------------------|------------------------|---------------------------------|--------------------------|
| California | Wilmington | 198.0 | 6.0 | 15.8 | 2.0 |
| | L. A. Basin | 52.0 | 6.1 | 1.3 | 8.7 |
| | Kettleman | 12.6 | 3.2 | .5 | 2.0 |
| | Santa Maria | 88.0 | 6.8 | | |
| Texas | Cayuga | 187.0 | 10.8 | 2.4 | 1.1 |
| | Borger | 132.0 | 17.5 | 236.0 | 88.0 |
| | Moore County | 209.0 | 12.0 | 306.0 | 31.2 |
| | Hutchinson County | 261.0 | 31.7 | 208.0 | 14.1 |
| | Van | 15.1 | 2.7 | .5 | .2 |
| | East Texas | 44.0 | 2.6 | 1.8 | nil. |
| | Duggan-Slaughter | 191.0 | 64.0 | 53.5 | 249.0 |
| Michigan | West Branch | 25.0 | 20.3 | 19.2 | 144.0 |
| | Buckeye | 243.0 | 23.6 | 5.8 | 52.1 |
| | Midland | 69.0 | 11.9 | 24.5 | 27.4 |
| Louisiana | Rodessa | 144.0 | 20.2 | 16.8 | 3.1 |
| | Ville Platte | 95.0 | 2.4 | 2.0 | .2 |
| Illinois | Magnolia | 32.2 | 9.8 | 60.5 | |
| | | 270.0 | 30.5 | 12.2 | 39.0 |
| Kansas | | 35.4 | 3.8 | 3.7 | 8.2 |
| | | 72.1 | 15.7 | 36.2 | 32.2 |
| Arkansas | West Kansas | 45.5 | 15.7 | 8.5 | 17.9 |
| | Schuler | 105.0 | 18.1 | 36.7 | 28.6 |
| | Jones Sand | 60.3 | 6.8 | 2.1 | .7 |
| | Morgan Lime | 69.2 | 15.5 | 40.3 | 47.8 |
| Oklahoma | Stroud | 68.6 | 29.6 | .8 | .7 |
| Canada | Turner Valley | 26.3 | 8.1 | 37.6 | 101.0 |
| | Turner Valley | 45.2 | 16.8 | 42.4 | 142.5 |
| Bahrain | | 10.2 | 1.4 | 3.6 | 4.3 |
| Venezuela | Temblador | 94.5 | 7.3 | 0.5 | nil. |

in the still were carried to 650°F., and the hydrochloric acid and hydrogen sulfide collected in receivers and measured. It can be seen that some oils are much more susceptible to the evolution of hydrochloric acid than others having about the same total chloride content, indicating that there are other factors besides the chloride concentration which affect the hydrolysis of those salts. It is commonly assumed that the hydrochloric acid evolved in distillation is formed principally as a result of the hydrolysis of the magnesium chloride present, and that the calcium and sodium salts do not contribute to the evolution. Actually, this is true only in pure oil systems, such as when a mixture of magnesium, calcium, and sodium chlorides, made up as a brine, is incorporated in a pure oil (such as white oil) and subjected to the distillation procedure. The difference in the behavior of those salts in pure oil



as compared with crude oil systems is shown in Fig. 1. In the pure oil system, magnesium chloride is hydrolyzed to the extent of about 50%, and calcium chloride only about 2%. Sodium chloride shows virtually no decomposition under these conditions. However, in crude oils the evolution can be much higher, as indicated in the upper curves of the graph, which were obtained by the use of a synthetic brine mixture with a salt-free Mid-continent crude oil. The curves show that the chloride decomposition in crude oil begins at about 250°F. and proceeds rapidly thereafter. In the case of calcium chloride, the distillation was carried to 750°F. and it will be noted that there was no diminution in the rate beyond the 650°F. point. Various acidic materials in the crude oil, such as naphthenic acids, will promote the evolution of hydrochloric acid from the salts under distillation conditions, as will also any acidity in the water droplets themselves. Many of the Mid-continent and Texas brines have comparatively low pH values, and the evolution is therefore high for a given chloride content. On the other hand the California brines are predominantly on the alkaline side, and therefore have an inhibiting effect on the acid evolution. Consequently it is impossible to predict, from a simple chloride determination on the crude oil, the extent of the hydrochloric acid evolution to be expected during dis-

TABLE 3

EFFECT OF SALT CONCENTRATION ON HCl EVOLUTION

| CRUDE SOURCE | Acidity as NaOH ptb. | Water % | Chlorides as NaCl ptb. | HCl evolved as NaCl ptb. | Hydrolysis % |
|------------------------------------|----------------------|---------|------------------------|--------------------------|--------------|
| <i>West Texas (41.1° API)</i> | | | | | |
| Raw Crude | 69.7 | .20 | 142.9 | 14.6 | 10.2 |
| Partially desalted | 14.9 | .50 | 14.2 | 5.5 | 38.7 |
| Further desalted | 14.9 | .23 | 3.9 | 3.9 | 100.0 |
| " " | 12.5 | .12 | 1.8 | 1.7 | 94.3 |
| " " | 3.8 | .03 | 1.3 | 1.5 | 100.0 |
| " " | 6.0 | .11 | 0.5 | 0.5 | 100.0 |
| <i>Hockley (Texas) 30.0° API</i> | | | | | |
| Raw Crude | 70.0 | .36 | 315.0 | 35.3 | 11.2 |
| Partially desalted | 26.5 | .38 | 12.8 | 7.3 | 57.0 |
| Further desalted | 28.0 | .40 | 5.0 | 4.0 | 80.0 |
| " " | 21.4 | .02 | 2.9 | 2.3 | 79.4 |
| " " | 27.5 | .05 | 2.6 | 2.5 | 96.2 |
| <i>Kansas 36.3° API</i> | | | | | |
| Raw Crude | 34.4 | .09 | 12.9 | 9.9 | 76.7 |
| Partially desalted | 38.4 | .45 | 3.4 | 3.3 | 97.1 |
| Further desalted | 39.9 | .65 | 2.2 | 2.0 | 90.9 |
| <i>Redwater (Canada) 34.7° API</i> | | | | | |
| Raw Crude | 32.2 | .04 | 46.8 | 22.3 | 47.6 |
| Partially desalted | 32.2 | .80 | 14.5 | 13.2 | 91.0 |
| Further desalted | 15.0 | .04 | 6.8 | 5.0 | 73.5 |
| " " | 30.0 | .94 | 5.7 | 5.0 | 87.6 |
| " " | 23.5 | .43 | 4.5 | 3.9 | 86.7 |

tillation. It may be noted that there is a general tendency for the degree of hydrolysis to increase with a decrease in the total salt content. This effect has been reported (3) and the results of experimental work on various crude oils which had been water-washed in various degrees to produce the desired lower salt contents are shown in Table 3. The results of these and other

HYDROCHLORIC ACID EVOLUTION FROM VARIOUS
CRUDE OILS DURING DISTILLATION

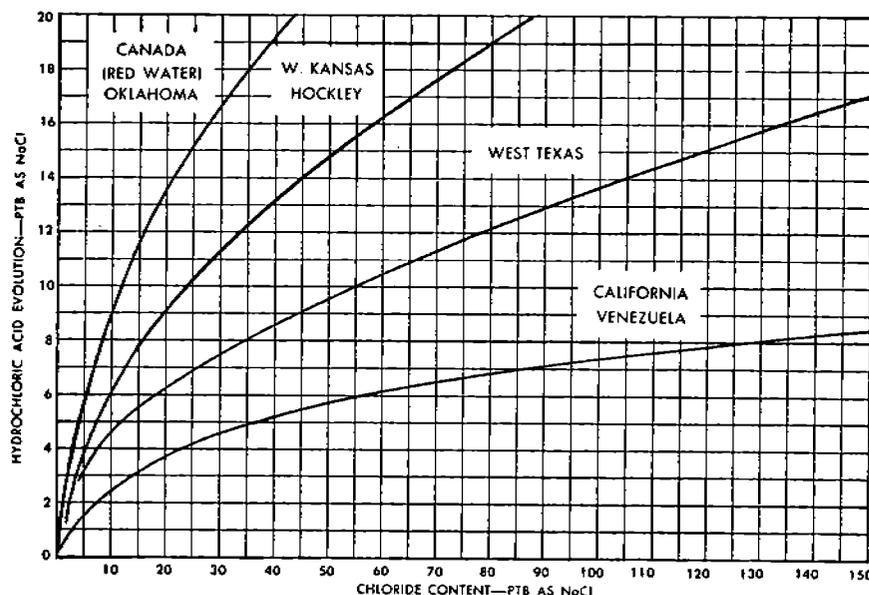


FIGURE 2

tests for hydrochloric acid evolution from a great variety of crudes are shown in the graph of Fig. 2. It is evident that the source of the crude and its brine content have an important bearing on the amount of hydrochloric acid evolved for a given salt content during the distillation process. In general, the Mid-continent types of crudes and those from similar geologic formations produce the higher evolutions, while the Californian and Venezuelan types give the lower results. As in other crude oil properties, there are of course individual exceptions to such a generalization and this must be kept in mind in interpreting the curves. At the lower salt values the curves tend to converge, probably indicating that the oil components, rather than the brine, exert a predominating influence on the decomposition.

In the region of very low salt contents (i.e. 3 or 4 ptb or less) the curves are steepest, indicating a more rapid drop-off in decomposition than at the higher values, and it appears necessary to remove the salt to this extent in order to reduce the adverse effects of hydrochloric acid evolution to negligible values.

Some of the laboratory tests indicated that the presence of even small amounts of iron compounds, such as are frequently found in crude oil, had an accelerating effect on the chloride evolution, possibly by catalytic action.

The undesirable effects arising from the presence of salts in crude charging stocks can be classified into four principal categories:

- (1) Salt deposits in exchangers and furnaces.
- (2) Evolution of corrosive hydrochloric acid.
- (3) Contamination of residual products.
- (4) Secondary effects on various petroleum fractions.

Deposition of salts in exchangers and furnaces results in shortened still runs and a corresponding loss in production, as well as increasing costs resulting from the shut-down and clean-out operations. The deposits tend to cause hot spots in the tubes and limit the temperatures considerably below those possible with salt-free crudes. The salts are therefore responsible, not only for increased maintenance costs, but also for decreased throughputs and lowered production of overhead products.

The evolution of hydrochloric acid is due to the hydrolytic decomposition of chlorides, principally sodium, calcium, and magnesium chlorides during the distillation operation. This hydrochloric acid is extremely corrosive and makes it necessary to inject ammonia into the overhead lines to minimize the corrosion damage. However, the ammonium chloride formed as a result of the neutralization reaction is itself still quite corrosive, and also tends to plug up condensers and columns in the run-down system. It is therefore highly desirable to prevent the evolution of hydrochloric acid altogether by a thorough desalting operation whenever it is at all possible to do so. The experience of refiners indicates that the corrosion due to sulfur is much decreased when the salt has been removed from the oil. It has been postulated that the hydrogen sulfide and hydrochloric acid enter into a cyclic reaction with the metals in the furnace tubes and fractionating equipment, whereby the iron sulfide, which is normally a thin and tightly adhering film, is loosened by decomposition as a result of reaction with the hydrochloric acid, thereby giving an opportunity for further formation of iron sulfide. Such a process obviously would greatly aggravate the corrosive action of hydrogen sulfide, and therefore make it highly desirable to remove as much of the chlorides as possible before subjecting the oil to distillation. Oils vary greatly in the amount of hydrogen sulfide evolved, as can be seen from Table 2, and this must also be taken into account in making an attempt to evaluate the potential corrosivity of a crude oil.

The contamination of residual products such as asphalt, fuel oils, etc., by inorganic salts is due to the fact that these salts remain almost entirely in the distillation residuums. Such residual salts, in fuel oil for example, tend to clog burners and also to deposit a slag on furnace tubes and brickwork of boiler installations. When appreciable amounts are left in asphalt, the properties of this material are adversely affected, such as by giving a positive Oliensis test in products used for roofing, etc., and by interfering with emulsion stability in the case of emulsified asphalts used for road building and similar purposes. Salts and solids in heavy fuel oils are also responsible for air pollution where these oils are burned under boilers.

Refiners report that there are various secondary effects resulting from the desalting operations which are of definitely beneficial character in both the topping and cracking operations, but in which the part played

by the salts is obscure. For example, there is some evidence that the presence of salt has some deleterious effects on the overhead products formed during the distillation or cracking operations, so that an improvement in quality is found when the crude is desalted. Among such reported improvements are (a) a decrease in doctor treating requirements of the gasoline produced, (b) superior color in gasoline and kerosine fractions, and (c) an increase in the lead susceptibility of the gasoline produced. The degree to which such improvements are evidenced in the products seems to depend primarily upon the amount and the nature of the salts present during the distillation or cracking operations. Some of the effects may be attributed to the mechanical entrainment of salts during the fractionation procedure, and others to a change in distribution of the types of products formed. In addition to the effects here reported, there is also evidence to indicate that the presence of salts exerts a catalytic effect on the corrosion produced by sulfur compounds, thereby compounding this type of corrosivity. It has also been demonstrated that the coke formed in still tubes that have processed salty crudes is of very hard and flinty nature and very difficult to drill out, as contrasted with the coke from salt-free oils which is comparatively soft and easy to remove. In those cases where residual oils are reduced to coke, the presence of residual salts will of course contaminate that product and contribute to the deterioration of the tubes and walls of boilers in which the coke is used as fuel. When used for the manufacture of electrode carbon, the cokes must have an especially low salt contamination.

All of these considerations are compelling reasons for a thorough desalting of all crude oils to be processed in a refinery, and indeed many companies now make it a rule to reduce the salt content of any crude processed to much lower values than was formerly considered to be economically justifiable. Whereas a few years ago residual salts of 10-20 ptb. were considered satisfactorily low by most refineries, many now aim at 5 ptb. or less and some insist on less than 1-2 ptb. Fortunately, advances in desalting techniques have made it possible to attain such high removal efficiencies.

Sediment. Another class of oleophobic materials comprises finely divided solids, which may be dispersed in the oil or carried in suspension in the brine droplets. Such solids may have their origin in the oil sands themselves, occurring as finely divided particles of siliceous matter, such as silt, etc., or they may be entrained drilling mud, etc., used in drilling the well or in its rehabilitation, or still further they may be iron rust, scale, and such type of material, picked up by the oil during the course of its passage through pipelines, tanks, valves, etc. Material of this nature is of course highly undesirable when present in crude oil, since it contributes to the plugging of pipe stills, to the erosion of equipment, and to a contamination of residual products.

COLOR PLATE

Showing photomicrographs of sediment on following page.

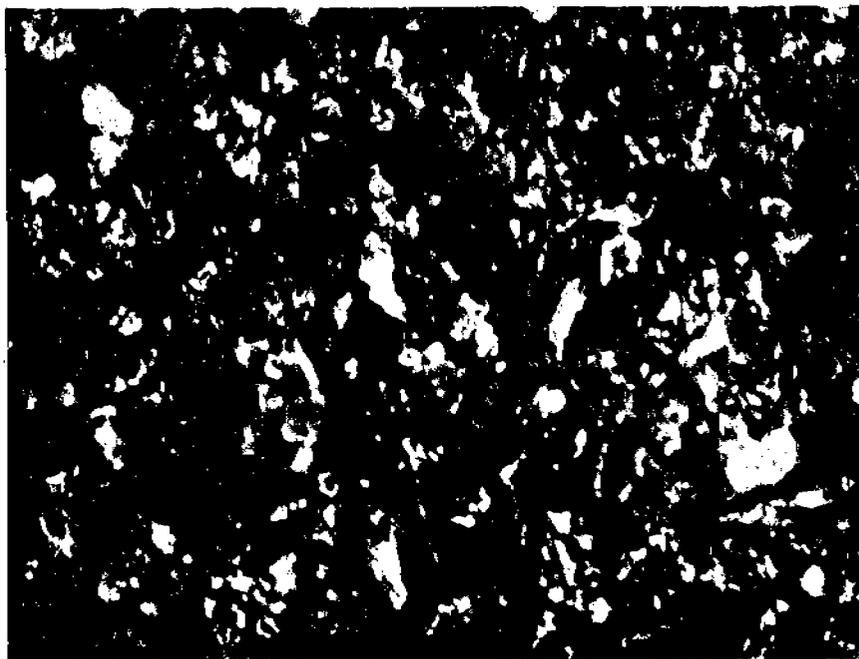
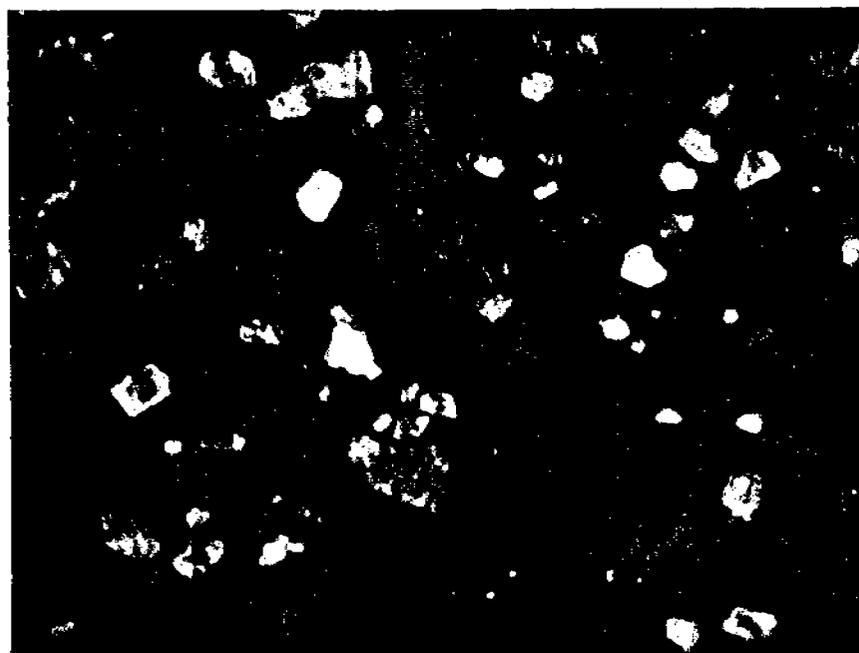


Figure 3 ▲

Figure 4 ▼



Consumers are becoming increasingly critical of these deleterious effects, and refiners are correspondingly finding it desirable to reduce these foreign materials to a minimum by appropriate desalting and other sediment removal processing methods.

The erosive character of suspended sediment in crude oil has recently been shown by Phelan (4) in its effect on hydraulic rodless pump operation, where a sediment removal process has developed dramatic savings by greatly increasing the service life of these pumps.

Table 1 shows some values of sediment contents of various crude oils. Most of these were obtained by the methods given in this manual, using a special centrifuging procedure. The figures shown are for the dried solids which usually contain some volatile matter of organic or carbonate character, so that the ignited weight (ash) will be about one-half, or sometimes a little less, of these values.

PHOTOMICROGRAPHS OF SEDIMENT

The nature of the sediment often found in crude oils is shown in the typical photomicrograph of Fig. 3. The material shown was filtered from a crude oil charging stock, and the great variety of particles present is readily apparent. Identifiable are particles of iron oxide (dark), quartz (translucent), mica, and feldspar. It is not surprising that this type of material can be a serious contaminant in asphalt and fuel oils, for example. Such sediment can to a large degree be removed by special processes such as described by Phelan, cited above, and to a considerable extent also by utilizing a highly efficient desalting process. What can be accomplished by such a desalting procedure is shown in Fig. 4, representing the sediment remaining in the crude of Fig. 3 after an electrical desalting operation. The electric desalting process appears to be particularly effective in this sediment-removing feature. The two photomicrographs are not only qualitatively but also quantitatively comparative, the concentration of sediment in the raw oil being 128 ppm, vs. 18 ppm in the desalted oil.

OLEOPHILIC IMPURITIES

The classification of these materials as impurities is quite arbitrary, since they are an innate part of crude oil itself, and is justified only in the sense that they have adverse effects on the refining operations, or produce unfavorable distribution of the refining yields.

Sulfur. Sulfur compounds have been recognized since the early days of refining as being undesirable constituents, but attempts to remove them by extraction, without also removing a large part of the oil itself, have not been successful. There are now catalytic processes available for the desulfurization of gasoline and even heavier fractions, but nothing of this nature is as yet commercially applicable to the crude oil itself. Consequently, the sulfur constituents are tolerated and the refining operations adjusted to minimize their deleterious effects. The sulfur of the crude appears in the products from gasoline down to the residuum, and numerous methods are used to reduce the sulfur content of the distillates or convert it to less noxious forms. These methods include acid treating, caustic washing, solutizer processes, doctor treating and various other types of sweetening processes, as well as catalytic desulfurization procedures. They are all well known to the refiner and each has its place for particular stocks and specifications requirements. The nature of the sulfur compounds present in crude oil has been the subject of a great deal of research activity, and the results are readily available in the literature. Consequently no ad-

TABLE 4

SULFUR AND NITROGEN CONTENTS OF CRUDE OILS

Selected from Representative Fields

| FIELD AND CRUDE | GRAVITY | SULFUR | NITROGEN |
|--------------------------|---------|--------|----------|
| | *API | % | % |
| Arkansas-Schuler | 33.2 | 1.54 | .063 |
| California-Elk Hills | 23.1 | .69 | .46 |
| California-Midway-Sunset | 20.3 | .88 | .58 |
| California-Santa Maria | 16.0 | 5.06 | .63 |
| California-Wilmington | 25.6 | 1.24 | .58 |
| Colorado-Rangely | 35.2 | .73 | .063 |
| Illinois-Louden | 38.0 | .26 | .094 |
| Kansas-Kraft Prusa | 43.0 | .27 | .17 |
| Louisiana-Delta Farms | 33.8 | .22 | .055 |
| Michigan-Deep River | 34.2 | .60 | .12 |
| Mississippi-Baxterville | 15.0 | 3.07 | .19 |
| Mississippi-Brookhaven | 26.6 | .86 | .066 |
| Montana-Cut Bank | 46.5 | .38 | .018 |
| New Mexico-Langlie | 34.8 | 1.35 | .066 |
| Oklahoma-Burbank | 35.8 | .21 | .05 |
| Oklahoma-Verma | 28.2 | .81 | .27 |
| Texas-East Texas | 37.8 | .36 | .085 |
| Texas-Hastings | 31.3 | .24 | .034 |
| Texas-Hawkins | 25.7 | 2.45 | .13 |
| Texas-Seeligson | 40.9 | .10 | .004 |
| Texas-Wasson | 34.2 | 1.90 | .10 |
| Wyoming-Elk Basin | 31.5 | 1.72 | .14 |
| Wyoming-Oregon Basin | 22.0 | 3.27 | .35 |
| Foreign-Iran | 36.0 | 1.36 | .14 |
| Iraq | 36.6 | 1.93 | .094 |
| Bitumens, Natural | | | |
| California-Edna | 4.3 | 3.20 | 1.23 |
| Utah-Vernal | 8.6 | .50 | 1.18 |
| Canada-Athabaska | 13.0 | 5.15 | .43 |

ditional discussion of these substances will be given here. An indication of typical sulfur contents of crudes from various sources is given in Table 4, which shows the great variability in the sulfur concentrations among the different oils.

Naphthenic Acids. Practically all crude oils contain organic acidic materials to a greater or lesser degree. These have been termed naphthenic acids because they are carboxylic derivatives of the naphthenes, which form a large proportion of the constituents of crude oils. However, the naphthene hydrocarbons are predominantly cyclohexane derivatives, while most of the experimental evidence to date indicates that the naphthenic acids are mostly of the cyclopentyl structure, the carboxyl group being in a side chain. The higher acids probably have bicyclic nuclei. A more appropriate nomenclature would be simply to term these materials "petrolic acids." They are generally of the acid strength of the long-chain aliphatic acids such as stearic acids, but vary in molecular weight to approximately the same extent as the hydrocarbons themselves. These materials can be highly corrosive at high temperatures, but their principal effect on the refining processes is in creating emulsions during the treatment of lube oil fractions with caustic soda. Their presence in the kerosine, diesel oil and gas oil fractions imparts to these products objectionable odors, which can put them at a disadvantage commercially. The insoluble calcium and magnesium soaps formed, when distillates containing naphthenic acids, as such or in their neutralized form as sodium naphthenates are washed with hard waters, tend to cause hazes in the oils that not only mar their appearance, but are the cause of other customer difficulties, such as the plugging of screens and burner tips in furnaces and stoves. These factors alone often make it desirable to remove the acids from certain oil streams.

It has been found that the acids in the lower boiling range have important commercial applications, so that it is often economically desirable to recover them for that reason. They find wide application in industry as carriers for paint driers in the form of manganese and other naphthenate soaps, and they are also used in the manufacture of mildew-proofing compounds, such as zinc and copper naphthenates, etc. During wartime they are in especially great demand for use as gelling agents for fire bombs. One of the deterrents to the wider use of naphthenic acids in industry has been that the crude acids are black in color, contain considerable quantities of non-acidic oils and have objectionable odors. However, considerable attention in recent years has been paid to adequate refining of these acids, and light colored products having little extraneous material are now readily available. The corrosive nature of these acids, especially at high temperatures, makes it necessary to utilize highly resistant materials for their processing.

Removal of naphthenic acids from the lighter petroleum fractions is usually not difficult and provides an additional source of revenue to the refiner. Caution must however be exercised that no alkaline materials are left in the treated oil because their presence can have serious adverse effects on the subsequent use of the distillates. For example, even minute quantities of alkalis left behind in stove oil can corrode brass fittings and burners to the extent that serious trouble can be encountered in such use. The presence of sodium naphthenates also has an adverse effect on the inhibitors that are often added to various distillates. In addition, such

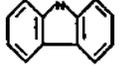
residual alkalis are poisonous to catalysts, and it is therefore essential to use highly efficient separation methods in the caustic washing steps.

It is generally not feasible to remove the naphthenic acids from crude oils directly, because of the serious emulsion difficulties encountered when an attempt is made to wash these oils with caustic soda. In some instances such washing can be successfully accomplished under carefully controlled conditions. As has been noted previously, one of the chief difficulties with the presence of naphthenic acids is in the formation of emulsions during the caustic treatment of lube oil fractions. In the processing of some oils that have high naphthenic acid contents the device of adding caustic to the crude oil before distillation is often employed to avoid these subsequent emulsions. The naphthenic acids react with the caustic to form soaps which are not distilled and therefore remain in the residuum. This effectively avoids the carry-over of acids into the lube oil fractions, but at the same time develops ash-forming constituents in the heavy fuel oil or asphalt products that are made from the residuums. Since these ash-formers are highly undesirable it is sometimes necessary to remove them by an acid wash to produce a satisfactory product. Such acid treatment of residual oils is commercially practiced and avoids the product degradation which would otherwise occur when it is necessary to treat crude oils with caustic before distillation.

The heavy naphthenic acids present in the lube oil fractions tend to form sodium soaps that are oil-soluble and therefore difficult to remove. Special techniques are required and great care must be exercised to avoid the formation of stable emulsions which greatly hamper the lube oil purification processes.

A general idea of the concentration in which naphthenic acids are found in various crude oils is shown by the figures in the appropriate column of Table 1, page 4. It can be seen that crude oils vary greatly in the amount of naphthenic acids present and in general, the more paraffinic the oil the less acidic material is present. The Californian and Venezuelan oils have especially high acid contents, although the variation even in these groups is considerable. It is probable that naphthenic acids will find increasing outlets in industry for specific uses, or as intermediates not competitive with animal and vegetable acids, and that their recovery from petroleum products will become of greater importance and magnitude in the future.

TABLE 5
PROTOTYPES OF NITROGEN COMPOUNDS IN PETROLEUM DISTILLATES

| Prototype | pKb | Structure |
|--------------------|------|---|
| Non-basic: Pyrrole | 13.6 |  |
| Indole | 14 |  |
| Carbazole | 15 |  |
| Basic: 1-Quinoline | 8.9 |  |
| Pyridine | 8.8 |  |

Note: The actual compounds occurring in petroleum often have one or more hydrocarbon groups on side chains.

Nitrogen. The presence of nitrogen in crude oils has been known for at least fifty years but it is only rather recently that the nature of the nitrogen compounds has been at all well defined. Much of the pioneer work on these materials has been done by Bailey (5) and by Lochte (6) at the University of Texas.

The prototypes of nitrogen compounds present in crude oils are shown in Table 5. They divide themselves primarily into two groups, the basic and the non-basic. The non-basic are of the carbazole, indole and pyrrole types, and occur relatively in that order of decreasing concentration (7). The basic compounds are primarily of quinoline structure and, as can be judged from their dissociation constants, the strength of these bases is such that they can be virtually quantitatively removed from the oil by acid extraction. Obviously the non-basic materials are not affected by such acid treatment, but are reported to be removable by solvent extraction methods, such as by the furfural processes.

The magnitude of the nitrogen content of various types of petroleum oils is given in Table 4, obtained in the investigations of Ball, Whisman, and Wenger (8), who found a rough correlation between the nitrogen content and the carbon residue values. These results show that the nitrogen content varies greatly with the source of the oil and, as in the case of sulfur, the greatest concentrations are found in the California petroleums. The amount of nitrogen compounds present in the crude oils listed may at first seem disarmingly small, but it must be remembered that the values represent nitrogen only, and that the compounds in which it occurs will be many times as great in weight and volume. On the basis of an average molecular weight of the nitrogen compounds of about 300, which appears to be a reasonable value for the bases in the lighter distillates, the nitrogen values of the table must be multiplied by about 20 in order to convert them to percentages of actual nitrogen-containing compounds in the oil. This puts their concentration in the range of 1% for the lowest and 13% for the higher oils from California.

Differentiation between basic and non-basic nitrogen compounds has been made by analytical methods described by Deal et al., (9). These investigators have shown that the ratio of basic nitrogen to total nitrogen in some California, West Texas, and Middle East crudes is approximately 0.25 to 0.30. Similar results have been obtained by Richter et al (10) on a greater variety of crudes, and they have arrived at similar ratio figures. Their results are shown in the upper portion of Table 6.

The lower portion of the table contains some figures on the nitrogen contents of distillates. These of course are much lower than the corresponding crude oil values and are therefore expressed in parts per million. It is immediately apparent that the cracked materials contain vastly greater amounts of nitrogen than the straight run streams, which is of course a result of the cracking of the heavy nitrogen compounds which otherwise remain in the residuums. The cracking procedure also tends to convert most of the nitrogen in the crude to the basic form, although this varies considerably with the particular stock processed. The cracked distillates are therefore potentially highly poisonous to catalytic cracking catalysts, even when derived from crudes of originally low nitrogen content.

The distribution of the total nitrogen content among the various crude oil fractions is shown by the graph of Fig. 5. This indicates that there is a fairly uniform increase in nitrogen concentration as the molecular weight of the fraction increases. For the crudes shown, the concentration of nitro-

TABLE 6
NITROGEN CONTENTS OF CRUDE OILS AND FRACTIONS

| CRUDE OIL | NITROGEN CONTENT | | RATIO B/T |
|---------------------------------|------------------|---------|-----------|
| | BASIC % | TOTAL % | |
| Jackson | .01 | .04 | .25 |
| Mirando | .01 | .04 | .25 |
| Scurry County | .02 | .06 | .33 |
| East Texas | .02 | .08 | .25 |
| West Texas | .03 | .11 | .27 |
| Kansas | .04 | .12 | .33 |
| Midcontinent Mix | .025 | .10 | .25 |
| Santa Maria Valley | .19 | .66 | .29 |
| Kettleman Hills | .14 | .41 | .34 |
| Wilmington | .14 | .50 | .28 |
| Ventura | .13 | .42 | .31 |
| Tibu | .033 | .13 | .25 |
| Guico Guario | .02 | .08 | .25 |
| Kuwait | .03 | .12 | .25 |
| Wilmington Residuum | .34 | 1.13 | .30 |
| Asphaltene fraction | .69 | 2.33 | .30 |
| Pentane Sol. fraction | .26 | .87 | .30 |
| Kuwait Residuum | .09 | .35 | .26 |
| Asphaltene fraction | .24 | .91 | .26 |
| Pentane Sol. fraction | .08 | .28 | .29 |
| (Expressed in ppm) | | | |
| DISTILLATES | | | |
| California Naphtha | 3.7 | 7.3 | .51 |
| Penn. S. R. Gasoline | 3.2 | 15.0 | .47 |
| Michigan S. R. Gasoline | 2.0 | 5.0 | .40 |
| Kuwait Naphtha | | 3.1 | |
| Wyoming Naphtha | 1.8 | 4.6 | .39 |
| Calif. cracked naphtha | 171 | 184 | .93 |
| Calif. thermal cracked | 224 | 234 | .96 |
| Calif. (Sta. Maria) toker dist. | 62 | 130 | .48 |
| Calif. thermal No. 2 fuel | 22 | 56 | .39 |
| Wyoming cat. No. 2 fuel | 61 | 210 | .29 |
| Midcont. thermal No. 2 fuel | 161 | 224 | .72 |

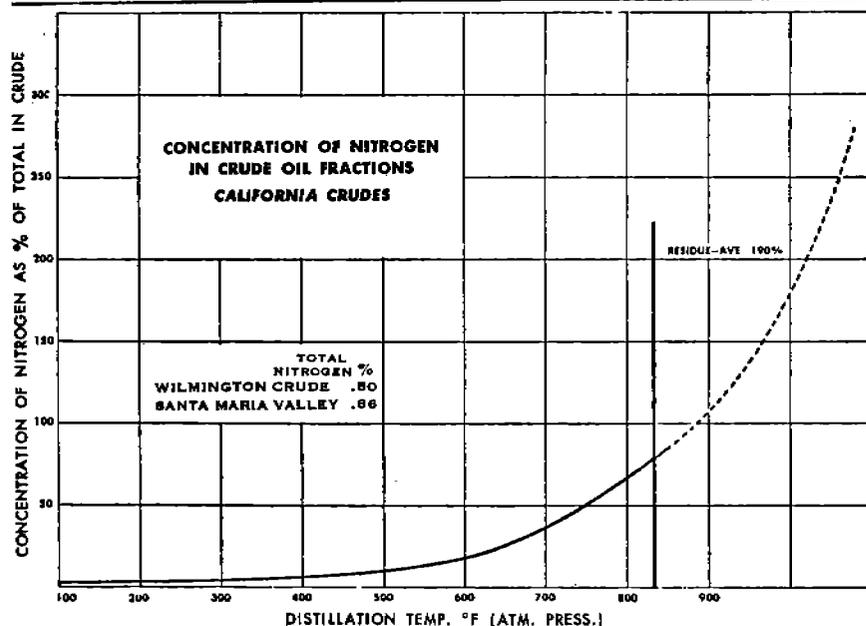


FIGURE 5

gen in the residue above 830°F. is about double that of its concentration in the original crude.

The presence of nitrogen compounds in crude oils has not received much attention from the refinery operation standpoint until rather recently. The recovery of basic nitrogen from distillates, while entirely feasible from a technical standpoint, was not attractive commercially because of the lack of adequate outlet for such bases. As in the case of naphthenic acids, the crude nitrogen bases are black, and contain considerable proportions of non-basic oily material. However, even after being refined these bases have not been found to be as suitable for chemical purposes as those derived from coal tar. Little attention was therefore given these materials until it became evident that they had adverse effects on the distribution of products and general performance of catalytic cracking processes.

When gas oil charging stocks containing appreciable amounts of nitrogen bases are treated with sulfuric acid, practically all of these bases can be removed and the stock thus greatly improved from the standpoint of gasoline yields and enhanced catalyst performance because of reduced carbon lay-down.

Pilot tests on numerous gas oil charging stocks with nitrogen base contents of about 1% (corresponding to about .05% expressed as Nitrogen) have shown that when 90-95% of the bases are removed, improvement in efficiency of the catalytic cracking operation can be obtained in a number of ways. Table 7 is a summary of the results, showing that if the cracking operation is unchanged, increased yields and lower carbon lay-downs are achieved. If the conversion is held constant, the carbon deposition is greatly reduced, and if the operation is carried to the same carbon values, much greater yields are obtainable. The marked economies to be realized, and the possibility of increasing the gasoline production from existing equipment by a nitrogen base removal operation on such stocks, can be readily appreciated from the figures in the table.

TABLE 7
EFFECT OF NITROGEN BASE REMOVAL ON
CATALYTIC CONVERSION OF GAS OILS

| COMPARISON BASIS | Original Stocks Containing Approximately 1% of Nitrogen Bases (as such) Treated With Acid for a Removal of About 90% | | |
|----------------------|---|---------------------------|----------------------------|
| | CONVERSION INCREASE % | GASOLINE YIELD INCREASE % | CARBON LAY-DOWN DECREASE % |
| Same operation | 15 | 20 | 12 |
| Same conversion | 0 | 5 | 30 |
| Same Carbon Lay-down | 24 | 14 | 0 |

The experiments showed that oils from California and Mid-continent sources exhibited similar beneficial results if they had about the same nitrogen base contents, and that the favorable effects are roughly proportional to the amount of bases removed from the oil by the acid treatment.

It should also be noted that if the nitrogen bases are removed from the gas oil by treatment with sulfuric acid, about 30% of the gas oil will be removed in the sludge phase in the case of the California stocks. While the bases as well as the non-basic nitrogen compounds can be removed by solvent extraction methods, as with furfural, something like 30% of the oil is thereby retained in the extract phase, and such solvent treatments are therefore not suited for an efficient process where only the removal of nitrogen bases is desired.

It is of considerable interest that a sulfuric acid treatment of a gas oil

for nitrogen base removal will be of additional benefit from other considerations. Such an acid wash not only removes the basic materials, but often also considerable proportions of the heavy metals that occur as organo-metallic compounds in the oils and that are known to have serious adverse effects on the catalytic cracking operation. These will be discussed more fully in the section on organo-metallics, below.

While dilute sulfuric acid will remove the basic materials from oils with the least loss of hydrocarbons to the sludge, it is usually more desirable to use spent alkylation acid for the purpose. The dilute acid is highly corrosive and requires expensive metals for the settling tanks, pumps, and pipe lines. The alkylation acid is not nearly so corrosive and furthermore is usually a cheap refining commodity. The stronger acid will also tend to remove most of the heavy resinous fractions that are carried over into the gas oil charging stocks, thus reducing the carbon lay-down tendencies from that source. On the other hand, the dilute acids seem to be somewhat more effective in the removal of metals, as will be subsequently discussed.

A series of carefully conducted pilot plant tests was made by Viland (11) who showed quantitatively the deleterious effects of the presence of basic nitrogen on the yields of catalytically cracked gas oil. His data also demonstrated that non-basic nitrogen had virtually no effect on the product qualities and yields.

It is generally considered that the poisoning of catalysts by nitrogen bases is what may be called "temporary," i.e., when the nitrogen compounds are removed the activity is again increased, although not entirely to the value it would have had, had the bases not been introduced at all. Investigations have shown that these bases are highly stable, even under the temperatures encountered in the catalytic cracking operations, and that the poisoning is due to the adsorption of the compounds in the active centers of the catalyst. The nitrogen compounds have been determined by Mills et al (12) to be in the following order of diminishing poisoning effects: quinaldine, quinoline, pyrrole, piperidine, decylamine, aniline. Ammonia apparently does not seriously reduce the catalytic activity.

TABLE 8
ANALYSIS OF ASH FROM OIL-SOLUBLE
CONSTITUENTS OF CRUDE OILS

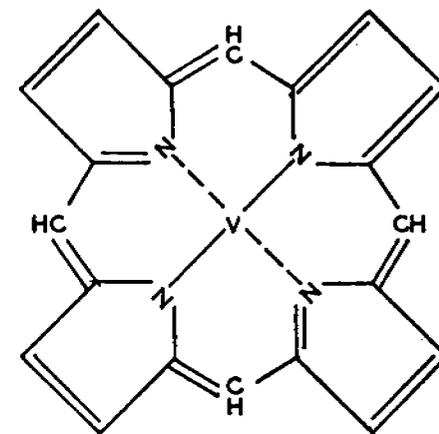
(On Water-Free and Sediment-Free Oils)

| | Ash, as Oxides ppm. | Chemical, Wt. % of Ash | | | | | | | |
|-------------------------|---------------------------|------------------------|-------------------|------------------|-------------------------------|--------------------------------|--------------------------------|-------|-----------------|
| | | NI ₂ O | Na ₂ O | SiO ₂ | V ₂ O ₅ | Fe ₂ O ₃ | Al ₂ O ₃ | CoO | SO ₂ |
| North Louisiana | 44 | 1.7 | 46.5 | | 4.3 | 3.3 | | 2.8 | 42.9 |
| Louisiana-Miss. | 11 | 0.1 | 61.7 | | 0.1 | 2.7 | 1.1 | 6.1 | 42.1 |
| Mississippi (Eucutta) | 319 | 2.4 | 16.3 | | 8.6 | 0.8 | | | 50.7 |
| Yates-Pecos | 22 | 15.1 | 4.1 | 11.7 | 63.3 | 0.7 | 12.1 | 1.1 | 16.4 |
| West Texas | 66 | 3.3 | 33.1 | 7.0 | 23.0 | 1.9 | 2.4 | | 30.3 |
| East Texas | 36 | 3.1 | 46.1 | 4.9 | 6.0 | 2.0 | 7.0 | | 43.4 |
| Texas Coastal-Hvy. | 73 | 4.0 | 33.2 | | 2.3 | 1.5 | | | 55.2 |
| " Refugio-Lt. | 5 | 17.9 | 7.7 | 3.9 | 24.1 | 9.8 | 2.2 | | 10.0 |
| Illinois-Indiana | 75 | 2.3 | 28.6 | | 9.1 | 2.2 | | | 47.7 |
| Oklahoma-Kansas | 49 | 2.0 | 33.3 | 7.0 | 10.9 | 1.0 | 3.3 | 2.8 | 38.7 |
| Wyoming (Big Horn) | 44 | 10.4 | 3.0 | 4.3 | 64.9 | 2.6 | 3.2 | | 14.6 |
| Venezuela (Quiriquire) | 236 | 3.2 | 10.0 | | 23.7 | 1.2 | 2.1 | 33.2 | 31.5 |
| " (San Joaquin) | 5 | 3.6 | 29.5 | 16.9 | 11.7 | 12.8 | 3.5 | | 15.4 |
| " (Lagunillas) | 348 | 3.0 | 8.7 | 11.2 | 59.9 | 0.4 | 1.3 | | 0.2 |
| California (Sto. Maria) | 375 | 8.0 | | | 20.0 | | | | |

Organo-metallic Compounds. Of the organo-metallic compounds present in crude oils, those of principal interest to the refiner are the organic combinations with the heavy metals, nickel, vanadium, and copper, as well as those of iron and arsenic. An analysis of the ash of oil-soluble material from various crude oils has been made by Jones and Hardy (13) and some of their results are shown in Table 8. There is a great variation in the composition of these ashes among the different oils investigated. While sodium and sulfate are the predominating constituents, considerable quantities of vanadium are also seen to be present in many of the oils. The other elements are present in the following order of decreasing magnitude: iron, nickel, aluminum, silicon and calcium, in the crudes reported. The heavy metals are believed to be present in porphyrin-like compounds, and they are thought to be derived directly from the original plant and animal matter that was the source of the petroleum. The general structure of these porphyrins is shown in Fig. 6 in the form of a vanadium porphyrin prototype.

Jones and Hardy found that the vanadium compounds are particularly destructive of refractories when present in fuel oils or cokes used in boilers, and are therefore to be avoided as much as possible. The sodium compounds were found to cause superficial fusion on fire bricks, but unless the bricks were porous, the principal damage was from a tendency for spalling to take place.

It had formerly been considered that during distillation all of the compounds containing metals would remain in the residue, with the exception of those lost by entrainment. However, Woodle and Chandler (14) have recently shown that some of these organo-metallics are actually volatilized and thus carried over into the distillate fractions even in the absence of entrainment. It is therefore probable that these compounds exist in various boiling ranges, although by far the greater portion is associated with the heavy fractions of asphaltic character of the residuums. If the behavior of vanadium and nickel is representative of the other heavy metals, then about 5% of the total organo-metallics are in the boiling range of the overhead distillates.



PROTOTYPE OF METALLO-PORPHYRIN COMPOUNDS

FIGURE 6

As has been indicated above, the presence of metals such as vanadium in residual products, as fuel oil and coke, can have seriously damaging effect on the refractories of boilers. Their presence in overhead fractions, such as gas oils, has also been shown to have deleterious effects when these oils are used as charging stocks to catalytic cracking plants. The compounds of vanadium, nickel, and iron are especially offensive in this respect, as shown by Mills (15). The serious effects which the deposition of heavy metals upon the catalyst can have upon the yield of the desirable products is shown in Fig. 7. These are from the data given in the Mills reference and show how vanadium and iron impair the selectivity of a typical cracking catalyst. The curves show the large effect which relatively small amounts of these metals can have upon the gasoline yields, and demonstrate the need for keeping such impurities to a minimum in the charging stocks. This metal poisoning effect is of the "permanent" type, i.e., the lost catalyst activity is not regained when the metals are removed from the charging stock, so that the damage is permanent. It should be noted that the presence of the metals can be the result of entrainment during the fractionation process as well as of direct distillation of such compounds as vanadium in the form of their porphyrin complexes. Alkali metals also have well known adverse effects on the catalyst activity, and the best insurance against their presence in charging stocks is a thorough desalting of the crude oil from which they are derived. In this way entrainment of the alkalis is minimized. There is no evidence that the alkali metals can be carried over into the distillates by direct distillation, in the absence of entrainment.

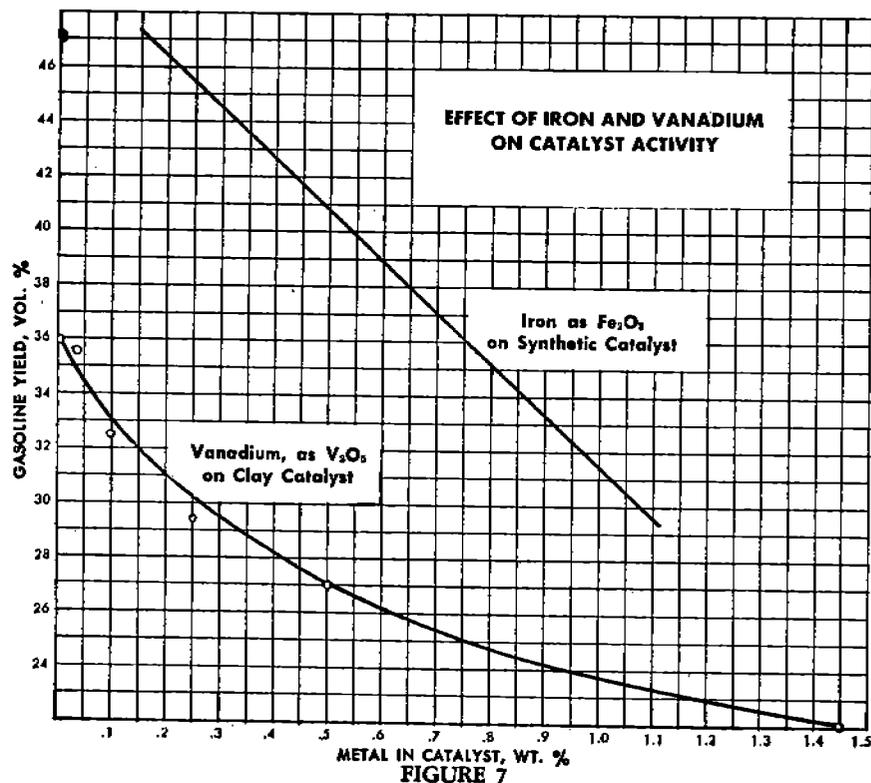


TABLE 9
REMOVAL OF METALS FROM GAS OIL
BY ACID EXTRACTION

| METAL | RAW STOCK PPM. | ACID-TREATED PPM. | REMOVAL % |
|----------|----------------|-------------------|-----------|
| Nickel | .56 | .22 | 61 |
| Vanadium | .33 | .15 | 55 |

It has been found that the treatment of gas oil charging stocks with a small amount of dilute sulfuric acid can cause appreciable reduction in the heavy metal content of the oil. Table 9 shows the results obtained when a California gas oil was thus treated. It would undoubtedly be possible to obtain greater percentage removals by changing the conditions of treatment with the acid to promote increased reaction. Since this acid treatment removes not only the heavy metals but nitrogen bases as well, such a pretreatment of gas oil stocks used as feeds to catalytic crackers can have important economic advantages. The use of strong acid, such as alkylation acid is not so conducive to the removal of these metals from gas oils, apparently because the weaker acid reacts more readily with the porphyrin-type compounds.

The effect of arsenic in the poisoning of platinum catalysts is so marked that its presence in concentrations of more than a few parts per billion can seriously interfere with the catalyst activity. This is of considerable importance to the refiner in view of the expanding use of platinum in refining operations. Laboratory tests have shown that, in the case of a crude oil containing about 40 ppb (parts per billion) of arsenic, a major portion of the arsenic was associated with the centrifugible matter in the oil (dispersed water and solids), and that a conventional desalting procedure would therefore be effective in the removal of most of the arsenic present. This has actually been confirmed by analysis of the oils from several commercial desalting plants, where for example a reduction in arsenic from 12 ppb to 0.6 ppb in the desalted oil was obtained. The naphtha produced in the refinery from these oils had corresponding arsenic values of 4.2 and less than 0.5 ppb. However, in another desalting plant the arsenic reduction was found to be rather small. This experience indicates that the arsenic is usually, but not always, associated with organic matter that has some interfacial activity which tends to make it concentrate at the oil-water or oil-solid interfaces. Because of its affinity for acids, there may also be some connection between the arsenic compounds and the nitrogen bases present in the oil.

Lead is often a serious contaminant in refinery distillates. The greatest source of this lead contamination is the tetraethyl lead used for octane improvement of gasoline. Because of rerunning procedures, etc. it seems to find its way into many of the distillates. Streams going to platinum-type catalytic reformers should contain well under 1 ppm of lead to avoid serious deactivation difficulties. As in the case of arsenic, considerable quantities of lead can often be removed from distillates by a simple acid-wash procedure.

Miscellaneous Oxygen Compounds. In addition to naphthenic acids, other hydrocarbon combinations with oxygen exist in crude oil. In asphalt

and in the heavy lube oil fractions such oxygen compounds occur as resins, but the compounds are so large and the structure so complicated that no definite knowledge as to their exact nature is as yet available. These resins are objectionable components of lube oils, and are generally removed by strong sulfuric acid treatment or by solvent extraction. As constituents of asphalt, the resins are usually considered desirable, as they contribute adhesive qualities and have desirable dispersion effects on the asphaltenes. The separation of these resins on an analytical basis is quite readily accomplished (16), and they are now also available in commercial quantities for numerous industrial applications.

In the over-head fractions, oxygen compounds, in addition to naphthenic acids, are often found in appreciable concentrations in the products from thermal and catalytic naphtha fractions, from which they are usually removed by caustic washing processes. They are composed principally of mono- or dimethylated phenols and cresols, the cresols predominating in the higher boiling fractions.

The cresol contents of naphthas from numerous commercial cracking operations were determined by Gallo et al (17) and their analytical reactions studied. An idea of the magnitude of the amounts of cresols carried in cracked naphthas is shown by a tabulation of some of these authors' results in Table 10. It is plainly evident that the cresols tend to concentrate in the heavier ends of the catalytic naphthas, and that the amounts involved are comparatively large in terms of pounds of material

TABLE 10
CRESYLIC ACID CONTENTS OF NAPHTHAS

| CRUDE SOURCE | CRACKING PROCESS | END POINT °F | ACIDS VOL. % |
|--------------|------------------|--------------|--------------|
| West Texas | Catalytic | 300 | .023 |
| | | 370 | .051 |
| | | 426 | .14 |
| | | 446 | .14 |
| Louisiana | " | 325 | .02 |
| | | 405 | .15 |
| Mixed Texas | " | 370 | .07 |
| | | 440 | .37 |
| | | 450 | .22 |
| | | Thermal | 275 |
| | " | 430 | .04 |

which can be produced per day from those stocks. It should also be noted that the sulfur compounds, principally in the form of thio-cresols, were in highest concentration in the end fractions (i.e., both in the low and the high ends) of the naphthas, being relatively sparse in the intermediate fractions. This furnishes a means for some separation by distillation, although much better results can be obtained by pH separation methods in the caustic extract treatment.

The cresols and the thio-cresols (also termed aromatic mercaptans) are objectionable constituents of naphthas and of the heavier distillates as well, because they increase the gum-forming characteristics and degrade the color

stability of these products. A wash with concentrated caustic soda is usually effective in removing these materials and thereby improving the distillate quality (18) (19).

Because of the increasing commercial demand for phenols and cresols, there is an additional economic justification for their removal from the gasoline streams, and since the gasoline is usually caustic scrubbed in order to reduce gums, the cresols are thereby concentrated in the alkaline extract. The latter will, of course, contain not only phenols and cresols, but also hydrogen sulfide, mercaptans, thio-cresols and other alkali-extractible materials that were originally present in the naphtha. As with other extracts from petroleum, the organic constituents of the caustic wash are of great variety, and thorough purification is required to obtain a reasonably good and commercially attractive cresolic material.

IMPURITY RESIDUES FROM CHEMICAL TREATMENTS

In order to make them suitable for marketing or for further refinery processing, many distillates require treatments with chemicals such as acids, caustic, doctor solutions, etc. In such cases the chemical refining agent is insoluble in the oil and the reacted impurities dissolve in the reagent and are carried away from the oil in the separation process. The separations are made by the conventional settling or centrifuging procedures or by the more modern electric precipitation processes. It is of course important for the purity of the product that virtually all of the reagent and reacted impurities be removed. If this can not be accomplished by settling or precipitation, a water-washing step of some sort is usually added. Even such wash-water must be virtually completely precipitated since otherwise any residue will form a haze and the product will be unsatisfactory for the market.

The residues from caustic treating processes often present serious problems to the refiner. Sodium is poisonous to catalytic cracking and reforming catalysts and promotes a color degradation if the products are used directly for the market. In the form of soaps it can cause fouling in burners and jets and corrosion in brass fittings. These soaps also have emulsification properties which can cause serious difficulties if the product is brought into contact with water, either by inadvertent mixing or simply by the collection of moisture on storage tank walls, roofs, etc. This is especially serious in the case of jet fuels where the safety of the plane's complement as well as the execution of its mission depend on the absence of foreign matter in the fuels. Similarly if the oil is to be shipped in tankers where contact with sea water is inevitable, the presence of soaps can cause a good portion of the fuel to become emulsified with water and therefore render it unfit for use. Sensitive tests are now prescribed for determining whether any such interfacially active residual material is present. One such test is called the "water reaction test" which is specified for jet fuels and described subsequently in the analytical section of this manual. In general, not more than a few parts per million of sodium can be tolerated in petroleum distillates. Similar considerations hold for sulfuric acid residues, which can cause corrosion and fouling of equipment, as well as product quality deterioration.

It is becoming increasingly important that the processes used for separation of chemical reagents from oils be carefully designed if the treated products are to meet the requirements of purity demanded by consumers as well as by modern catalytic processing methods.

**SELECTED
ANALYTICAL METHODS
FOR IMPURITIES
IN PETROLEUM**

SELECTED ANALYTICAL METHODS FOR IMPURITIES IN PETROLEUM

Because of the constantly increasing interest by refiners in the nature and amounts of impurities in their crude oil sources and refined products, it is desirable to have readily at hand analytical methods for the most important of these constituents, from the standpoint of the refiner's interests, and this is the objective of the following pages. Most of the analytical methods presented have been tested in the Petreco laboratories on crude oils and distillates, as well as on residual products. Some of the methods are original, others are conventional ones intended for light distillates, which have been modified to adapt them for use on such dark-colored products as crude oil and residuums. It is obviously impossible, in a manual of this type, to include manipulative details for complicated procedures such as spectroscopic test methods, and in such cases reference has simply been made to the literature wherein such methods have been described. It is believed that the present compilation will be generally useful to the refiner in his attempt to learn more about the products which he processes and to help him circumvent some of the problems which are encountered because of the presence of the many deleterious impurities in crude oil.

An attempt has also been made not only to provide manipulative details, but to include sufficient general information regarding the nature of the impurities and the interpretation of the analytical results to make the methods as helpful as possible.

SAMPLING

It is, of course, essential that the sample of oil to be analyzed be as representative as possible of the whole body of oil under consideration. To obtain a representative sample is especially difficult when the impurities to be studied are in the form of a suspension in the oil, such as water and sediment. These are subject to sedimentation which often results in stratification in tanks and even in small sample cans, making accurate sampling particularly difficult. The futility of conducting extensive laboratory tests on samples that do not represent the conditions to be investigated is of course obvious—perhaps too much so—and this initial step in the analytical procedure should be given most careful attention by the analyst. The reason for these special precautions in sampling will be evident when it is considered that the impurities, including water, usually comprise less than 0.5 volume-percent of the oil and that considerable portions may have settled to the bottom of the container in the form of an adherent sludge when the samples arrive at the laboratory.

Some sedimentation ("sludging") frequently occurs in these sample containers and thorough agitation of the contents by vigorous shaking or stirring methods is essential to insure proper sampling. For accuracy and convenience of measuring, it is desirable to withdraw samples from cans by means of pipettes, the lower portion of the tips of which have been cut off to expedite filling. Immediately after agitation of the sample, the tip of the pipette is lowered nearly to the bottom of the container and the sample taken as quickly as possible. In this manner, even oils with rapidly settling impurities may be accurately sampled. After the sample has drained from it, the pipette should be rinsed with whatever solvents are subsequently added so that all of the brine particles and solids which might wet the glass are recovered.

DETERMINATION OF WATER CONTENT OF OILS

It is usually desirable to determine the total suspended water content of the crude charging stocks and the methods are, of course, routine and standardized. The A.S.T.M. method for water-by-distillation (D95-40) is most often used, but for very low water contents can give appreciable percentage errors. These are generally in the direction of giving low results and may be due to slight losses of water vapor through the condenser or to the tendency of condensed water droplets to collect on the condenser tube. However, the method is usually sufficiently accurate for refinery purposes, and various refinements for obtaining greater accuracy need not be discussed here. The centrifuge method for water determination (D96-40) is not universally applicable to oils from all fields and should be used with considerable caution. Various local areas have modified the amounts and kinds of solvents used in order to take into account the character of the oils involved. It is in general desirable to add a demulsifying chemical to the oil-solvent system, and to make the tests at elevated temperatures (about 130°F.) in order to break the emulsion so that clean separation of the water will be obtained. Otherwise not all of the water particles may be precipitated by the centrifugal action, or the emulsion which is precipitated will contain variable amounts of oil, so that the actual water content can not be accurately estimated. The types of solvents and chemicals applicable to oils from various districts have been studied by the Petreco laboratories and the information is available to the industry upon request.

The centrifuge method has the advantage of being more expeditious than the water-by-distillation procedure, and in addition furnishes information regarding the presence of sand, clay, and other solid material which may be of concern to the refiner. If suitable solvents and chemicals are known to give accurate results, they are therefore to be preferred.

The determination of water actually dissolved in petroleum is ordinarily of no particular importance to the refiner and will not be described here. However, it can readily be determined by the well known Karl Fischer method, the adaptation of which to petroleum is described in the literature (20). The solubility of water in various hydrocarbons is of occasional interest, and a graph taken from the data of Griswold and Kasch (21) is shown in Fig. 8.

DETERMINATION OF CARRYOVER FROM CHEMICAL TREATING PROCESSES

In the treatment of distillates with acids and alkalis it is of course essential that the reagents together with the extracted or reacted impurities be finally removed as completely as possible from the oil, but commercial separation and settling methods vary greatly in their effectiveness in accomplishing this. The most direct measure of this effectiveness is simply to take a sample of the overhead oil and throw down the residual dispersed material by the usual centrifuge procedures. However, especially in the case of the lighter distillates, the permissible amount of reagent carried over is usually very small, that is, of the order of .01% or less, and the ordinary centrifuge methods, such as ASTM method D96-40, make no provision for measuring such small amounts.

Special 100-ml. centrifuge tubes with capillary tips are now available

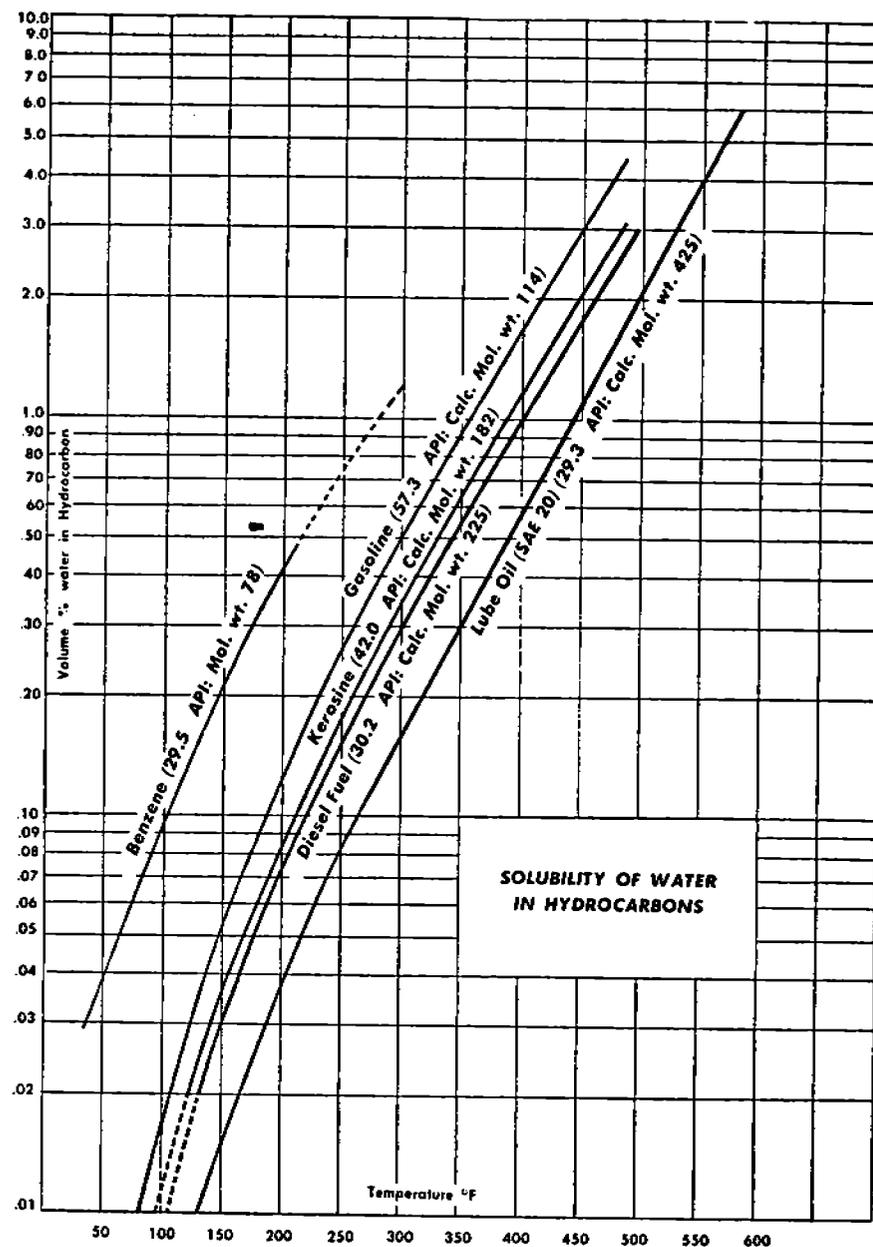


FIGURE 8

(22) which have graduations to .001 ml., thus permitting readings to .0005% on an undiluted sample.

With the lighter distillates, such as naphthas, kerosine, diesel oil, burning oil etc. which are often treated with caustic, either directly or as a final wash following an acid treating step, it usually suffices to centrifuge the sample directly without dilution for about 15 minutes or so in a conventional petroleum laboratory centrifuge. This is true also for oils which have been treated with dilute acids, as for example in the removal of arsenic, nitrogen bases etc. Care must always be taken to make certain that all of the dispersed material has been thoroughly centrifuged to the bottom of the tube and that none of it is hung up on the sloping sides, thus giving low results. If wall deposition does occur, the centrifuging period should be extended for a sufficiently long period to throw all material to the bottom.

In the treatment of the heavier distillates, such as lube oil stocks, with concentrated acids, the problem of deposition of the sludge on the walls of the tube can be very serious. It is usually not desirable to dilute the stock since this tends to alter the solvent character of the system, thereby either increasing or decreasing the amount of the dispersed phase. In such cases it is best to make the test at the treater operating temperature in a steam heated centrifuge in order to give a clean separation. The carryover of acid sludge in the treated distillates can be alternatively determined by acidimetry as described below.

Sludge Carryover Determination by Titration.

Place 50 ml. of the sour oil sample in a 100 ml. centrifuge tube and dilute to 75 or 100 ml. with a light solvent if necessary to reduce viscosity. Centrifuge for about 30 minutes and decant the oil from the precipitated sludge.

If the oil-soluble and sulfur dioxide acidities are desired, the decanted oil should be retained for titration before and after blowing with air to remove sulfur dioxide. If these determinations are not required, the oil may be discarded.

Add 5 to 10 ml. of acetone to the centrifuge tube to dissolve the separated sludge and dilute to about 50 ml. with isopropyl alcohol. Titrate the mixture directly in the centrifuge tube to the pink phenolphthalein endpoint with standard 0.1 N. caustic.

The results obtained can be used to calculate the acid carryover, which will of course not be affected by the amount of sludge which was hung up on the walls of the tube.

The weight of acid sludge carryover can be calculated as follows:

$$S_w = .098 AN$$

Where S_w = grams of 100% sulfuric acid in 100 ml. of oil
 A = the ml. of NaOH used to reach the end point
 and N = the normality of the NaOH titrating solution.

When lube oils are treated with about 10 pounds per barrel of 98% acid, the resulting sludge has a specific gravity of about 1.3 and an acid content about 65 weight percent. Assuming these values, the volume percent of the sulfuric acid sludge in the sample is as follows:

$$S_v = 82.7 AN$$

Where S_v = the volume percent of sludge in the sample.

DETERMINATION OF SALTS

The most common method for determining the salts present in crude oils is by extraction of samples with water in the presence of suitable solvents, and analysis of the aqueous extract. Many such methods have been proposed in the literature, and most of them have been tested in the Petreco laboratories. In general they are adequate for the oils for which they were developed, but they are not all universally applicable to oils from all fields. Care should therefore be taken in selecting a method suitable for the particular problem at hand.

The Petreco Centrifuge method, previously described in the literature (1), (2) and detailed below, has been used for many years on a great variety of crude oils and has been found to be reliable and accurate. It is therefore recommended for general use. The separatory funnel method given is that of Blair (23) and is similar in principle to those described by Horne and Christianson (24) and by Neilson, Hume, and Lincoln (25). It is important that this type of method be tested for the specific oil under consideration to make certain that the relatively mild agitation conditions produce adequate extraction of the salt from the oil.

In addition to the common extraction methods, procedures for the direct argentometric titration of chlorides in the oil phase have been proposed (26). Such methods have the disadvantage that the presence of mercaptans tends to interfere with the chloride determination, and this is particularly the case when the concentration of chlorides is low, such as in samples of desalted oil. In addition, this method can only determine the chloride content of the oil, in contrast to the extraction methods which lend themselves to the analysis of all of the water-extractible salts. However, in the absence of interfering substances, such methods are rapid and reasonably accurate and useful for routine testing. A method of this type developed by the Petreco laboratories will therefore be described.

Refiners are becoming increasingly interested in determining low salt contents (from 0.5 to 5 ptb.) in crude oils, and the usual methods are not adequate in this case. Furthermore, oil samples are encountered occasionally in which the chlorides can not be completely extracted by the ordinary laboratory procedures (due to temperature limitations, etc.), such as when solid salt crystals protected by high-melting wax films are present. Therefore a method of greater potency and sensitivity is required, and this can be found in the phosphoric acid distillation procedure also described below. It is somewhat more tedious than the others but has been found to be considerably more accurate and reliable for oils having difficultly-extractible salts or very low salt content.

Extraction Methods

PETRECO CENTRIFUGE METHOD

Requisites

Piston emulsifier. A standard 250 ml. graduated glass cylinder can be used for this purpose, the piston being made of a $1/8$ -inch brass rod to one end of which has been transversely affixed a brass disc about $1/16$ inch smaller in diameter than the interior of the cylinder. The other end is conveniently bent for a handle. A brass cylinder of similar dimensions is,

however, to be preferred to one made of glass, because it heats more rapidly and allows more complete transfer of the aqueous phase since the brass is not so easily wetted by the water.

The solvents *benzol* and *acetone* need not be of the C.P. grade, but should be water-white and, of course, free of chlorides.

A good *demulsifying agent*, such as "Destabilizer C," made for the purpose by the Tretolite Company, should be available when difficultly extractable oils are encountered.

A *wash-bottle type of pump*, made to fit the centrifuge tubes used, is convenient for removing the aqueous phase after the centrifuging step.

Standard 100 ml. oil testing *centrifuge tubes*.

Sampling

It is, of course, of prime importance that the sample used be representative of the oil under consideration. Since only 50 ml. of oil are required for this test, the sample can best be obtained with a 50 ml. pipette whose tip has been partially cut off to permit faster flow of the oil. After the sample container has been thoroughly shaken, the pipette is lowered to within one inch of the bottom and then filled to the mark. The sample is then transferred to the cylinder as described below.

Procedure

1. Measure 50 ml. of the oil sample, 50 ml. benzol, 25 ml. acetone, and 75 ml. distilled water into the 250 ml. emulsifier cylinder. The oil volume should be accurately measured, preferably with a pipette, which should be rinsed with the subsequently added solvents.
2. Heat to 120°F. in a water bath, and emulsify thoroughly with at least 25 hard strokes of the piston, avoiding the incorporation of air in the mixture to preclude loss of sample.
3. Transfer the contents of the cylinder to two 100 ml. centrifuge tubes, rinsing with small volumes of benzol and acetone. It is desirable to distribute the water phase in approximately equal portions in the tubes. Warm the tubes to 120°F., and note whether most of the water has separated into a clear layer. If not, add 1 drop of demulsifying chemical to each tube, and mix by gentle shaking.
4. Centrifuge for 10 minutes at 1500-1800 r.p.m., and then siphon or pipette off as much of the free water in the tubes as possible through a filter paper into the titrating vessel, taking care that no emulsion or sludge is removed from the tube.
5. Add an additional 10 ml. water to each tube, heat to 120°F., shake thoroughly, and again centrifuge.
6. Transfer the separated water completely to the filter previously used, and wash the filter with a little distilled water.
7. Analyze the extract for chlorides and other elements, as desired.

In general, this procedure gives essentially complete extraction of the water soluble salts in the oil, with a precision of about 0.5 ptb. Some of the heavier oils and residuums will sometimes leave a little unresolved emulsion in the second extraction, but this seldom contains an appreciable amount of salts.

SEPARATORY FUNNEL METHOD

A number of methods of this type have been described in the literature, (23), (24), (25). The following outline is taken from the Blair reference and is, in general, quite satisfactory. However, caution is necessary, and the applicability of any of the cited separatory funnel methods should first be tested on the type of oil it is desired to analyze, since modifications are sometimes necessary to obtain accurate results.

Procedure

Into a 750 or 1000 ml. separatory funnel, place 100 ml. of the crude oil, 100 ml. of xylene, and 4 ml. of a 5% xylene solution of suitable demulsifying agent such as the "Destabilizer C" available from the Tretolite Company. Shake for 30 seconds and add 100 ml. of boiling hot distilled water. Stopper the funnel and shake, releasing the pressure occasionally at first, for a total time of 5 minutes, then allow the mixture to settle, breaking up any loose emulsion which may collect at the interface by gentle agitation with a long stirring rod. Draw off the aqueous layer and analyze for salts as desired. If the chloride content of the oil is high, it may be desirable to use an aliquot of the water phase for the titration.

Analysis of the Aqueous Extracts

The methods employed for analysis of the aqueous extract will, of course, depend upon the purpose for which the extraction was made. From the standpoint of the refiner who is interested in the prevention of corrosion and plugging of his equipment and in improving the quality of his products, a knowledge of the concentration of certain mineral constituents of the crude oil is of paramount importance. These will in general include the chlorides, sulfides, sulfates, acidity, alkalinity, calcium, and magnesium. Sodium is generally determined only by difference. It is only by a thorough analysis for these substances that a comprehensive picture of the crude oil, so far as its potential corrosivity, effects on catalysts, and quality of product is concerned, can be obtained. Since the relative amounts of the various minerals in the brine accompanying a particular crude are fairly constant, it is necessary to make this analytical breakdown only occasionally. The determination of a single constituent such as the chlorides will subsequently be sufficient for practical purposes.

The constituents of particular interest to the refiner are the chlorides. This is due to the generally recognized fact that hydrolytic and pyrolytic decomposition of these salts generates the powerfully corrosive hydrochloric acid which must be kept to minimal values to prevent serious equipment deterioration during processing. It should be kept in mind that this acid is responsible not only for the direct corrosion effects on equipment but also indirectly for accelerated plugging and coking induced by such corrosion. A detailed method for the analysis of chlorides is described below.

In the case of some oils containing appreciable amounts of hydrogen sulfide the aqueous extract will contain sulfides, and since these interfere with the chloride determination they must first be removed, as described. However, it is sometimes desirable actually to determine the total sulfides thus present, and a procedure for this purpose is also provided.

The methods given below utilize the usual analytical techniques. However, the more rapid and sensitive methods employing spectrographic equipment, such as the flame photometer, can be used on the extracts where such equipment is available. No attempt has been made to describe these highly specialized methods. They are especially suitable where only traces of the sought materials are present.

Determination of Chlorides

The most common method for chlorides is the Mohr titration with silver nitrate to the red silver chromate endpoint. Since this titration must be carried out in a neutral solution, ions other than the halides may be precipitated, notably sulfur compounds and soaps which may have been extracted from the oil. Because titration in acid solution will avoid interference by nearly all of these substances except hydrogen sulfide, methods which permit titration under acid conditions are in general more desirable. These include the Volhard and electrometric methods. However, the extracts from the great majority of crudes tested have been found free of such interfering substances, so that the Mohr method is usually adequate, especially for comparative routine tests on the same oil.

Since the Mohr method depends upon the visual determinations of a color change for an endpoint, it has the inherent disadvantage of dependence upon lighting conditions, the operator's color discrimination, blunt endpoints, initial solution colors, etc., which are often serious for the systems under consideration. By proper arrangement, the electrometric method can be made nearly as rapid, and its use is recommended wherever the apparatus is available. It is used exclusively in the Petreco laboratories, but the Mohr method is described below because of its wide use where electrometric equipment is not readily available.

MOHR METHOD

In this method the chlorides are titrated with silver nitrate in a neutral solution in the presence of chromate; the endpoint is the red coloration produced by silver chromate, which is not formed until all the chlorides have been precipitated. Special attention should be given to proper blank determinations, since these corrections are relatively large, and vary with different operators.

Solutions Required

Silver nitrate, 1 ml. = 1 mg. NaCl. Dissolve 5.813 g. of dry, C.P. silver nitrate in distilled water and make up to 2 liters in a volumetric flask. Standardize it by the procedure below against weighed quantities of dried, C.P. sodium chloride, or a standard sodium chloride solution. If a good grade of silver nitrate is used, no adjustment of the solution is usually necessary.

Potassium chromate, C.P., 5% solution.

Sodium hydroxide and *nitric acid* solutions, 0.1 N.

Methyl red and *phenolphthalein* indicator solutions, 1%, in alcohol.

Procedure

1. Prepare a blank by adding about 0.1 g. chloride-free calcium carbonate to 100 ml. of the distilled water that is being used for the extractions, and titrating to the first reddish coloration of the solution by the procedure following. This blank is usually about 0.1 ml.

2. Place the extract, which should have a volume of 100-125 ml., in a 250 ml. casserole.

3. Add 1 drop of silver nitrate from the burette to the quiescent solution in the casserole. If the precipitate is white, proceed as directed in the next paragraph; if it is black or brown, the presence of sulfides is indicated, and these must first be removed before the chlorides can be titrated. The procedure for their removal is given subsequently.

4. Add 1 drop methyl red indicator; if a red color appears, add 0.1 N. sodium hydroxide drop by drop until the color is just changed to yellow.

5. Add 1 drop phenolphthalein indicator; if a red color appears, add 0.1 N. nitric acid drop by drop until the color is just discharged. The solution as finally adjusted must be neutral (yellow) to both indicators.

6. Add 1 ml. (approx.) of the chromate indicator solution with a medicine dropper.

7. Titrate with the silver nitrate solution to the same endpoint color used for the blank. Illumination with an ordinary electric lamp and the use of yellow goggles facilitate detection of the color change from yellow to red. When the endpoint has been reached the solution should be stirred for about 1 minute to be sure that the coloration is permanent.

8. If the endpoint has been overstepped, a measured quantity of standard sodium chloride solution may be added, and the endpoint obtained by further titration with silver nitrate, proper correction of the results being made for the amount of sodium chloride added.

ELECTROMETRIC METHOD

If a good potentiometer system is available, the electrometric titration method is by far the most satisfactory, since no delicate color distinctions are necessary. With a well designed set-up, the time required is little more than for a Mohr titration, and the results are much more dependable, especially for low chloride concentrations.

No attempt will be made to describe potentiometer circuits because there are now a number of accurate meters on the market and the arrangement of electrodes, etc., will need to be adapted for each. One of the most convenient types is the vacuum tube potentiometer used with the glass-electrode as a pH meter. These contain circuits so sensitive that small electrodes and compact set-ups are possible. The procedure and equipment described below were used with a Beckman pH meter and the readings taken in pH units. These can, of course, be converted directly to millivolts, but this is unnecessary except for comparison with other systems employing different meters or reference electrodes.

Requisites

A Beckman pH meter or its equivalent.

Silver electrode. This is conveniently made out of a 6-inch piece of No. 8 pure silver wire, threaded at the top end for meter connection and bent in the form of a U at the end which is immersed in the solution. This is stiff enough to be conveniently fitted with an insulating bushing for support, and can be easily cleaned. The electrode is "sensitized" by immersing the silver wire for a few seconds in concentrated hydrochloric acid, and then washing it thoroughly with distilled water.

A *reference electrode*. This can be made by converting a calomel cell to a mercurous sulfate cell. Mercurous sulfate is substituted for the calomel, and saturated potassium sulfate for potassium chloride. Such

cells are now also on the market.

A *mechanical stirrer*, preferably air-driven to avoid electrical interference. The stirrer should be thoroughly grounded electrically.

Burette. A 25 ml. burette graduated in 0.1 ml. divisions is most suitable.

Standard *silver nitrate* solution, as previously described.

12 N. *sulfuric acid* in a dropping bottle.

Procedure

1. Wash off and inspect the electrodes to make sure they are in good condition. Let a few drops of solution out of the mercurous sulfate cell if this has not been previously done on this day. The silver electrode should periodically be rejuvenated by scraping the silver wire, dipping in concentrated HCl for a few seconds and then thoroughly rinsing, in order to put it into sensitive operating condition.

2. Place the solution to be titrated, which should have a volume of about 100 ml., in a 150 ml. beaker, and add 0.5 ml. (about 10 drops) of 12 N. sulfuric acid per 100 ml. of solution. If for some reason the extract is strongly alkaline, add a few drops of methyl red indicator, neutralize with sulfuric acid, and then add the excess as described.

3. Lower the electrodes into the beaker so that they are immersed sufficiently to cover the silver wire coil and the sleeve of the reference cell.

4. Connect the terminals (silver wire to the calomel and mercurous sulfate to the glass electrode posts of the pH meter) and start the stirrer.

5. Read the initial voltage. If the "pH" reading is less than about 2, sulfides are probably present, and they should first be removed, as subsequently described.

6. Add silver nitrate solution; 1 ml. increments may be used if the "pH" is in the vicinity of 3 or 4, but smaller additions should be made if the "pH" is higher, since the endpoint occurs at 5.6 or thereabouts.

7. Record the volume of solution used after each addition, allowing about 10 seconds for equilibrium to be reached, and record the corresponding meter readings. Between "pH" readings of 5 and 6, the readings for each tenth ml. should be taken.

8. Stop the titration when the increments produce relatively small "pH" changes (between "pH" 6 and 7), and plot the curve. Choose the titration volume at the inflection (which occurs at approximately "pH" 5.6) as the equivalence point.

9. Remove the electrodes from the solution, wash thoroughly, and store in distilled water.

10. By the same procedure determine the blank on the appropriate quantity of distilled water used in obtaining the sample (as in an extraction) and in its subsequent dilution, if any.

For routine chloride analyses it is usually sufficiently accurate to titrate directly to the "pH" value which has been established as the point of inflection with the particular electrode system and solution concentration at hand. In this way the titrations can be carried out nearly as expeditiously as with the Mohr method and with considerably greater accuracy.

When the chloride concentration in the extract is low, so that only 0.2 to 0.5 ml. of the silver nitrate solution is required for titration, inflections are likely to be ill-defined. This can be remedied by evaporating the extract to 15 ml. before titrating. For very low chloride values, 1 ptb. or less, in the oil, no inflections are usually obtainable, and titration to the established endpoint is then the only means of ascertaining the proper titration value.

REMOVAL OF SULFIDES

If sulfides are known to be present in the solution, or if they are detected by the dark color of the precipitate formed by the first drop of silver solution added or by the low initial reading of the pH meter, they must be removed before chlorides can be determined. The procedure follows:

Procedure

1. Add 1 ml. of 12 N. sulfuric acid to the solution, having a volume of about 100 ml., in a 150 ml. beaker.

2. Boil gently for 5 minutes; if large quantities of hydrogen sulfide are present, boil until moist lead acetate paper is only slightly discolored by the vapors. If necessary, add water to avoid excessive reduction of the volume of the solution.

3. Cool the solution, and add 1% potassium permanganate dropwise with stirring until the pink color persists for at least 5 seconds; then discharge the color with 1 drop of 1% oxalic acid. Titrate for chlorides by the selected method.

DETERMINATION OF SULFIDES

If the solution has been found to contain sulfides, they may be determined by titrating one portion of the sample with silver nitrate directly, and another after the sulfide removal procedure described above, the first giving the sulfides and chlorides together, and the second the chlorides only.

The Mohr method is not adaptable to this titration because the black sulfide color masks the endpoint, but the electrometric method can readily be used. Since the addition of acid to the solution before titration may cause some loss of hydrogen sulfide, it is preferable to add the solution directly to a measured excess of acidified silver nitrate and to modify the subsequent procedure slightly, as described below.

Procedure

1. Run standard silver nitrate solution from a burette into a 150 ml. beaker in an amount that is in excess of the expected chloride and sulfide content of the sample.

2. Add 1 ml. of 12 N. sulfuric acid and mix well.

3. Add to this solution a volume of the sample of the same size as used in the determination for chlorides, mix, and insert the electrodes.

4. Start the stirrer, connect the potentiometer, and note whether the "pH" reading is above 6. If it is not, insufficient silver solution has been added, and for accurate results a new sample should be taken and a larger quantity of silver used. If only approximate sulfide values are desired, silver nitrate may be added from the buret until the chloride inflection point has been determined.

5. If the presence of an excess of silver nitrate is indicated by the potentiometer reading ("pH" reading greater than 6), add a measured quantity of standard sodium chloride solution (1 ml. = 1 mg. NaCl) from a burette or pipette sufficient to bring the "pH" reading back to about 4 or 4.5. It is often convenient to add sodium chloride solution equal to the silver nitrate used in step 1 as the following titration then is directly equivalent to sulfides plus chlorides.

6. Titrate the excess chloride with silver nitrate as directed for the chloride determination.

7. Correct the total volume of silver nitrate for the equivalent of the standard chloride added, to obtain the net silver nitrate equivalent to chlorides plus sulfides.

DETERMINATION OF SULFATES

The amount of sulfates present in the oil may conveniently be determined by analysis of the extracts as obtained by the methods previously described, using standard barium sulfate precipitation procedures. However, oils have occasionally been encountered in which these extraction methods do not completely remove the sulfates from the oil, and it has been found desirable to make the extraction with a hydrochloric acid solution rather than with distilled water. In such a case, the extraction methods described above are simply modified by using 1 N. HCl solution instead of the distilled water.

Hydrochloric acid is more effective than water alone in extracting all sulfates, especially if any are present as solids such as gypsum crystals.

However, the extract may contain some suspended organic matter which can interfere with clean precipitation of barium sulfate unless special precautions are taken. Therefore, if the solution is turbid after filtration, the turbidity should be removed. This can be conveniently done by a clean-up with alumina, as shown in the following procedure.

Procedure

1. Filter the water sample through Whatman No. 42 or an equivalent paper.

2. If the filtrate is clear, omit steps 5, 6 and 7. If the filtrate contains suspended matter, or is turbid, proceed as follows.

3. A suitable sample is one of approximately 150 ml. containing 15 to 200 mg. of sulfate. If 150 ml. of the sample contains less than 10 mg. of sulfate, take a larger sample and evaporate to 150 ml. If it contains more than about 300 mg. of sulfate, take a smaller sample and dilute to 150 ml.

4. Add 3 drops of methyl red indicator (1% solution).

5. Add 5 ml. of 5% aluminum chloride solution.

6. Neutralize with conc. ammonia and add 1 ml. excess.

7. Filter and wash precipitate thoroughly with distilled water.

8. Neutralize filtrate with 6 N. HCl and add 2 ml. excess.

9. Heat the solution to boiling and add 10 ml. of 10% barium chloride solution dropwise with vigorous stirring.

10. Let stand overnight on a warm hotplate.

11. Filter through Whatman No. 42 filter paper or its equivalent and wash precipitate 5 times with hot distilled water.

12. Burn off filter paper slowly with a burner or an open electric heater in a weighed crucible and then ignite the ash at a moderate red heat.

13. Cool and weigh.

DETERMINATION OF OTHER MINERAL CONSTITUENTS

It is often desirable to determine the distribution of the various chloride and sulfate salts in a crude oil, especially when stocks from new sources are received. Since the chlorides of iron and aluminum are usually decomposed by hydrolysis under distillation conditions to form hydrochloric acid, the presence of appreciable amounts of such salts is obviously highly undesirable in a crude charging stock. However, their concentration in the brine particles carried by the oil is in general quite low, probably because the pH is usually high enough to preclude their presence in dissolved form.

The chlorides of calcium and magnesium are generally the prime sources of the hydrochloric acid evolved during the distillation process, and are therefore most commonly included in the analysis of the extracts.

The presence of alkaline or acid constituents in the extract also has an important bearing on the degree to which chlorides are hydrolyzed, and their determination is also desirable. The methods for determination of these various constituents are well standardized and can be found in any text book on analysis, see e.g. refs. (27), (28), (29).

It will in general be necessary to make separate extractions of the oil for chlorides, for sulfates, for alkalinity and acidity, and for the balance of the mineral constituents. If the total salt content is low, several extraction samples may need to be combined to obtain sufficient for adequate weighing or titrating purposes.

A quick method of ascertaining whether there are appreciable amounts of non-chloride salts present in the sample is simply to evaporate the extract to dryness and weigh it. If the total salts thus found are considerably greater than can be accounted for by the chloride determination it will usually be desirable to analyze for other constituents. It should be kept in mind that while hydrolyzable salts, like the chlorides, are particularly obnoxious, as indicated above, others such as sulfates and carbonates can also be detrimental in aggravating plugging difficulties due to their deposition on exchanger and furnace tube walls.

For convenience, brief summaries of the methods for the various constituents are listed below.

TOTAL EXTRACTIBLE SOLIDS

An estimate of the total extractible solids content of the oil can be obtained by evaporating the aqueous extract to dryness. Any suspended matter initially present in the extract should first be filtered off, washed, dried, and separately weighed. The evaporation is best carried out in a 100 ml. platinum dish, and the solids dried at 105°C. for one hour. After cooling in a desiccator, the dish must be weighed rapidly because the salts are often hygroscopic.

Due to the uncertain changes produced upon ignition of the salts, no attempt is made to burn off the traces of organic matter usually present. The salts can subsequently be redissolved and any of the other constituents determined.

IRON AND ALUMINUM

The oxides of iron and aluminum are determined together by this procedure. If it is desired to determine iron separately, the mixed iron and aluminum oxides, as obtained in step 7 of the following procedure, may be dissolved by fusion in a platinum crucible with previously fused potassium bisulfate and analyzed for iron by the electrometric dichromate titration subsequently described. If determination of iron alone is desired, the dichromate titration may be directly applied to the extract without removal of any other ions.

Procedure

1. To the neutral solution having a volume of 150 ml. in a 250 ml. beaker, add 5 ml. of concentrated hydrochloric acid.
2. Heat to boiling, add 3 ml. of saturated bromine solution, and boil for 5 minutes to remove the excess.
3. Add 3 drops of 1% methyl red indicator, then 1-1 ammonia slowly from a pipette with constant stirring until the indicator just changes to yellow. Not more than 2 drops of ammonia should be added in excess. (When much iron is present, the reddish precipitate may obscure the endpoint, but by allowing the precipitate to settle slightly, the indicator color is readily determined.)
4. Boil the solution gently for about 5 minutes, then set aside to settle.
5. When the precipitate is well settled, decant the clear liquid through a filter, and finally transfer the precipitate to the paper with the aid of hot 2% ammonium nitrate solution from a wash bottle. Collect the filtrate in a 400 ml. beaker.
6. Wash the precipitate 3 times with the ammonium nitrate solution, then ignite the filter at 950-1000°C. for 15 minutes.
7. Cool and weigh, and record the weight as iron and aluminum oxides.

IRON (ELECTROMETRIC DICHROMATE TITRATION)

It has been found most satisfactory to titrate the iron potentiometrically, using a platinum working electrode and either a glass or a calomel reference electrode. The reduction of the ferric iron with stannous chloride is carried out at a temperature of 75°C. because the reaction is not quantitative in the cold. In order to avoid excessive quantities of stannous chloride this reduction is accomplished with the electrodes immersed in the solution, the addition of stannous chloride being continued until the potential drops to a minimum. The solution is then titrated with a standard dichromate solution.

It is advisable before attempting this analysis on an unknown to prepare a solution of known iron content, using this for the sample. This enables the operator to ascertain the form of the titration curve and the location of the two inflections, or jumps, in E.M.F. corresponding to the point at which the excess stannous chloride has been consumed, and the point at which all of the ferrous iron has been converted to ferric iron. The difference in the titrations at these two points of inflection is, of course, the desired titration value for the iron content. The use of too much stannous chloride can do no harm excepting that it may make the first titration unduly large.

Solutions, such as aqueous extracts of crude oil, in which the presence of organic matter may be found to interfere with the operation of the electrodes, can be evaporated to dryness, charred thoroughly, and then taken up in hydrochloric acid and water as prescribed in Step 1.

Requisites

1. *Potentiometer, Titration Beaker, Air-Driven Stirrer, and Burette*, as described for electrometric chloride titration. The metal shield may be omitted from the titration beaker.
2. *Electrodes*. The working electrode consists of a piece of platinum foil or a spiral of platinum wire having an area of about 11/2 sq. inch. The reference electrode may be either a calomel electrode or a glass electrode. It is convenient to use the millivolt scale on the potentiometer with this electrode system, but if the pH scale is employed the platinum foil will be connected to the terminal post usually used for the glass electrode.
3. The *stannous chloride* reducing solution is prepared by dissolving 5 g. of the salt in a mixture of 15 ml. of water and 5 ml. concentrated hydrochloric acid. Iron-free tin is added and the solution kept nearly boiling until clear. Store in the presence of metallic tin.
4. The *standard dichromate solution* is prepared by dissolving in distilled water 2.452 g. of C.P. potassium dichromate, that has been dried at 110°C. for two hours, and diluting to one liter. It need not be standardized.

Procedure

1. To 50 ml. of the approximately neutral sample in a 150 ml. beaker, add 10 ml. of concentrated hydrochloric acid and 5 ml. of saturated bromine water. This will destroy any organic matter and oxidize the iron to the ferric state.
2. Boil the solution for 5 minutes to expel excess bromine.
3. Cool the solution to about 75°C., insert the platinum and calomel (or glass) electrodes. Add stannous chloride solution dropwise until the potential indicated by the potentiometer falls to a point below the plateau at which iron titrates. Dilute the reduced iron solution with 50 ml. of cold distilled water and titrate with standard potassium dichromate solution. By plotting the titration curves, the end points for tin and for iron can be readily determined. A blank should be run on the water and reagents, but usually this is negligible.

CALCIUM

Procedure

1. If the sample has not been treated for the precipitation of iron and aluminum, it is necessary to add sufficient ammonium chloride to prevent precipitation of the magnesium with the calcium. About 10 ml. of a saturated solution to 250 ml. of the sample in a 600 ml. beaker are sufficient for this purpose.
2. Add 3 drops of 1% methyl red indicator, and sufficient 6 N. HCl to make the solution slightly acid (about 0.5 ml. excess acid).
3. Add 25 ml. of a 4% ammonium oxalate solution and heat to boiling.
4. Slowly neutralize the solution to the yellow endpoint by adding dilute (1-10) ammonia with constant stirring.
5. Boil the solution for a few minutes, then set aside in a warm place for at least one-half hour.

6. Decant the clear liquid, transfer the precipitate to the filter with hot 0.1% ammonium oxalate solution, and wash it six times with that solution.

7. Ignite the precipitate at 1000°C. for one hour, cool, and weigh the calcium oxide.

MAGNESIUM

Since the magnesium can not be accurately determined without the prior removal of calcium, the method above must always precede this one.

Procedure

1. Slightly acidify the filtrate from the calcium determination (which should have a volume of about 400 ml. in a 600 ml. beaker), with hydrochloric acid, and add 10 ml. of a 25% di-ammonium phosphate solution.

2. Thoroughly cool the solution in running tap water, and add 100 ml. of concentrated ammonia slowly, with thorough stirring. If a mechanical stirrer is available, the solution can be stirred for about 30 minutes and is ready for filtering after one hour of further standing. Otherwise allow the solution to stand overnight.

3. Filter through a quantitative filter paper and wash the precipitate four times with cold dilute ammonia (1 to 4) containing 10% ammonium nitrate.

4. Ignite the precipitate at 1000°C. for one hour and weigh the magnesium pyrophosphate.

ALKALINITY

The presence of strong alkalinity in a crude oil sample is an indication that it has been treated with caustic soda, lime, or similar substances, since the naturally produced material does not contain such strongly alkaline constituents. However, bicarbonates are sometimes naturally present, and their determination is desirable since they tend to exert a mild inhibitory action on the hydrolysis of chloride salts. The aqueous extract may be titrated with acid to a pH of 4 (methyl orange endpoint) to obtain a quantitative measure of such constituents. Electrometric titrations are more accurate than those involving indicators, since the aqueous extract is not always entirely colorless to begin with. Furthermore, a knowledge of the pH of the extract provides an indication of the degree of acidity or alkalinity of the oil. A low pH is, of course, undesirable, since the presence of acid greatly promotes the hydrolysis of the chlorides.

The procedure for determination of alkalinity in the extract is well standardized, and can be found in detail in the references previously cited. In ordinary water analyses the alkalinity is commonly expressed as calcium carbonate, but for the purposes of crude oil evaluation it is more desirable to express it in terms of either sodium hydroxide or sodium chloride. The latter figure is especially useful for purposes of correlation with decomposition of the chlorides.

CALCULATIONS AND REPORTING OF RESULTS

The terms in which the results of the analysis of the several constituents of the sample will be reported are necessarily dictated by the use to which the data are to be put. Since these studies of the impurities in crude oil are primarily concerned with their effect upon refinery equipment and operation, the method of reporting suggested below is oriented with the view to best describing the system from that standpoint. Furthermore, a number of the constituents are inter-related, so that it is desirable to report them in terms that are directly additive, even though they are known actually to exist in another form in the system. Thus, for example, chlorides are first assigned to the alkaline earths, since if any chlorides are present at all, the alkaline earths will be hydrolyzed and give rise to hydrochloric acid evolution. Any sulfates and carbonates are subsequently assigned to the alkali metals, which again is contrary to the usual water analysis system.

When alkalis are to be determined by difference, it is obviously necessary to calculate the various constituents to the compounds that are actually present in the dried solids. This composition can, of course, not be rigorously established without a comprehensive analysis, so that the analyst must make his own estimates as well as he can from the nature of the sample and the analytical results. After these calculations have been made and the approximate alkali content determined, the compounds are reported as previously indicated, and the reader of the report must be apprised of the convention employed to avoid the appearance of inconsistencies in the results.

The following sections give the details of the reporting system here recommended. By several years' usage this has been found to be self-consistent and convenient as a picture of the crude oil systems under consideration.

In the following formulas it is assumed that all of the extract from the oil sample has been used in making the determination for the particular constituent. If aliquot portions are used, appropriate corrections must be made.

Chlorides and Sulfides

Chlorides or sulfides are generally computed in terms of their weight as sodium chloride or hydrogen sulfide, respectively, per unit volume of oil or water. In the case of extractions for salts in crude oil, these units are quite generally in terms of "pounds per thousand barrels" (ptb.).

If the total aqueous extract has been used in the titration, the formula for the calculation of sodium chloride as determined by the procedure described is:

$$S = \frac{350 AC}{V}$$

Where S = the chloride content as NaCl, in ptb.,

A = the net ml. of silver nitrate used,

C = its concentration in terms of grams of sodium chloride per liter,

V = the volume of the oil sample extracted, in ml.

Proper modifications must be made if an aliquot portion of the extract has been used in the titration.

When sulfide is to be determined, subtract the ml. of silver nitrate solution required to titrate the sample for chlorides, from the titration for chlorides plus sulfides, and insert in the preceding formula. This results in the value of hydrogen sulfide expressed as sodium chloride, ptb. To obtain results in terms of hydrogen sulfide, in ptb., use the formula:

$$H = \frac{102 AC}{V}$$

Where H = sulfide content as H₂S, in ptb.,
 A = ml. silver nitrate by procedure for chlorides plus sulfides, minus ml. by procedure for chlorides only,
 C = its concentration expressed as grams NaCl per liter,
 V = volume of oil sample extracted, in ml.
 (1 unit expressed as NaCl = 0.291 unit expressed as H₂S.)

Sulfates

$$S = \frac{213 P}{V}$$

Where S = sulfates as sodium sulfate, ptb.,
 P = weight of barium sulfate precipitate, mg.,
 V = volume of oil sample extracted, ml.
 To express results as calcium sulfate, replace the numerical coefficient by 204.

Total Extractible Solids

$$S = \frac{350 R}{V}$$

Where S = total solids, ptb.,
 R = weight of solids residue, in mg.,
 V = volume of oil sample extracted, ml.

Iron and Aluminum

These are reported as R₂O₃, ptb., using "R" in the formula for total solids to represent the weight of ignited combined oxides.

Iron (Electrometric Dichromate Titration)

$$I = \frac{1397 A}{V}$$

Where I = Iron expressed as Fe₂O₃, ptb.
 A = volume of 0.05 N. dichromate solutions used for titration, ml.,
 V = volume of oil sample extracted, ml.

If it is desired to express the result as elemental iron, or as the equivalent of hydrolyzable chlorides as NaCl, replace the numerical coefficient by one of the following to obtain results in ptb.:

| | | |
|----------------|-----|------|
| Compound | Fe | NaCl |
| Factor | 977 | 2046 |

Calcium

$$C = \frac{732 P}{V}$$

Where C = calcium expressed as sodium chloride, ptb.,
 P = weight of calcium oxide precipitate, mg.,
 V = volume of oil sample extracted, ml.

If it is desired to express the result in some compound of calcium, replace the numerical coefficient in the formula by one of the following to obtain results in ptb.:

| | | | | |
|----------------|-----|-------------------|------------------------------------|-------------------|
| Compound | CaO | CaCO ₃ | Ca(HCO ₃) ₂ | CaCl ₂ |
| Factor | 350 | 625 | 1011 | 693 |

Magnesium

$$M = \frac{367 P}{V}$$

Where M = magnesium expressed as sodium chloride, ptb.,
 P = weight of magnesium pyrophosphate precipitate, mg.,
 V = volume of oil sample extracted, ml.

If it is desired to express the result in some compound of magnesium, replace the numerical coefficient in the formula by one of the following to obtain results in ptb.:

| | | |
|----------------|-------|-------------------|
| Compound | MgO | MgCl ₂ |
| Factor | 126.8 | 300 |

Alkalinity

The alkalinity is given by the following formula:

$$A = \frac{1000 v NF}{V}$$

Where A = the alkalinity in ptb.,
 v = volume of acid used in titration, ml.,
 N = the normality of the acid,
 V = volume of the oil sample used in the extraction,
 F = the factor given in the table below.

| | | | | | | |
|-------------------------|-------------------|--------------------|---------------------------------|------|------|------|
| Alkalinity expressed as | CaCO ₃ | NaHCO ₃ | Na ₂ CO ₃ | NaOH | HCl | NaCl |
| Factor F..... | 17.5 | 29.4 | 18.6 | 14.0 | 12.8 | 20.5 |

Direct Determination of Chlorides

As previously mentioned, chlorides in oils may be determined in other ways than by aqueous extraction methods. The direct titration and phosphoric acid distillation procedures are described below.

DIRECT ELECTROMETRIC TITRATION OF CHLORIDES

It should again be emphasized that this method should not be indiscriminately used on unknown crudes, and in cases of doubt the more accurate extraction or distillation methods should be used.

Requisites

1. Beckman pH meter or equivalent, silver electrode, reference electrode (mercurous sulfate cell), and air-driven mechanical stirrer. This apparatus has previously been described.
2. Titration beaker, (100 or 150 ml.) and grounded metallic shield surrounding it.

3. **Burette.** A 5-ml. burette graduated by 0.02 ml. divisions is most suitable.

4. **Solvent.** The solvent with which the oil is diluted is made up of 30 parts by volume of methyl alcohol (denatured is usually permissible), 150 parts *n*-butyl alcohol, 240 parts xylene, and 2 parts distilled water.

5. **Silver Nitrate.** Dissolve 1.453 g. of dry C.P. silver nitrate in 40 ml. distilled water and dilute with secondary butanol to 1 liter. 1 ml. of this solution is equivalent to 0.5 mg. of chloride as NaCl. The bottle containing this solution should be dark-colored and stored away from light.

6. **Sodium Chloride.** Dissolve 1 gram of dried C.P. sodium chloride (fused) in 1 liter of water.

Standardization of Silver Nitrate Solution

1. Pipette 10 ml. of the standard sodium chloride solution into 50 ml. of water contained in a 100 ml. beaker mounted in the titration assembly.

2. Add 0.5 ml. concentrated perchloric acid or 12 N. sulfuric acid.

3. Titrate slowly with the silver nitrate solution, taking the point of inflection on the titration curve as the endpoint.

4. Calculate the strength of the silver nitrate as grams of sodium chloride per liter.

Procedure

1. Inspect the electrode system to make sure it is in proper sensitive condition. A drop of solution should be drawn from the mercurous sulfate cell and then wiped off; the silver electrode should be clean and periodically rejuvenated by scraping the silver wire, dipping it in concentrated hydrochloric acid for a few seconds, and then thoroughly rinsing in order to put it into sensitive operating condition.

2. Accurately measure 10 ml. or less of the oil sample with a pipette into a 100 ml. beaker. A sample of less than 10 ml. may be needed if the oil contains much salt.

3. Add about 70 ml. of solvent, rinsing the pipette at least twice in the process.

4. Place the beaker in its shield, insert the electrodes, stir, and record the initial meter readings.

5. Add the silver solution slowly from a 5 ml. burette and record the corresponding meter readings at appropriate intervals so that a good titration curve can be established.

6. Remove the beaker and rinse the electrodes with xylene and acetone, and store in distilled water.

7. Plot the curve and read the silver nitrate consumption at the inflection point.

8. By the same procedure determine the blank to be subtracted from the value obtained in Step 7 by titrating the solvent alone.

9. Either pH or millivolt units may be plotted as read from the meter, since only the amount of reagent used at the inflection point is of interest.

DISTILLATION WITH PHOSPHORIC ACID

It has previously been mentioned that occasionally oil samples are found which present considerable difficulty in the extraction type of method, leaving the accuracy of the chloride determination somewhat

in doubt. This occurs especially when very heavy oils or residuums are encountered. Also, in the case of oils of very low chloride contents, the conventional procedures are not adequate. It is therefore desirable to have available an independent method which is suitable in such situations. Combustion bomb methods are not satisfactory, as the volume of sample permissible is so small that the amount of chloride obtained cannot be accurately measured, even by semi-micro methods. In the procedure here given, the sample is steam-distilled with phosphoric acid, thus liberating hydrochloric acid from any chlorides present, the chlorides being then determined in the distillate. As used in the Petreco laboratories, the method has been found to be considerably more sensitive and accurate than extraction procedures, and in cases where the extraction methods fail, or are inapplicable, the procedure is, of course, invaluable.

Apparatus

The equipment required is depicted in Fig. 9 and is there described in detail.

Procedure

The procedure is the same as that given in a subsequent section for the steam distillation tests on crude oils, with the following exceptions and additions:

1. Use 250 ml. oil sample.

2. Add, to the oil in the flask, 35 ml. of 85% C.P. phosphoric acid.

3. The caustic in the receiving bottle may be omitted, but it is desirable to retain the spiral wash bottle (containing caustic) in order to prevent the escape of sulfur compounds into the laboratory atmosphere.

4. Care should be taken to avoid foaming in the preliminary heating period, and the time schedule need not be followed accurately. The distillation is discontinued at 650°F. oil temperature.

5. Since only chlorides are to be determined the corresponding directions of the steam distillation method should be followed.

6. Phosphoric Acid Blank.

It has been found that the reagent grade phosphoric acid on the market may have an appreciable chlorine content which is not directly titrable as chloride ion, but which appears in the distillate when the acid is present during distillation under reducing conditions such as those encountered with crude oils. A blank determination is therefore essential. This is made by adding 0.5 g. of sucrose to 125 ml. of phosphoric acid and distilling by the procedure for a steam phosphoric acid distillation to 650°F. No attempt is made to follow the prescribed time schedule as the heating must be done very cautiously to prevent the foam from reaching the outlet tube. This method produces a strong reducing atmosphere which apparently is necessary to cause evolution of the chlorine as HCl.

The entire aqueous portion of the distillate is titrated for chlorides as described in the section on analysis of the aqueous extracts.

The blank correction to apply to the results of a steam phosphoric acid distillation made with this phosphoric acid is:

$$C = 0.392 A$$

Where C = the apparent hydrogen chloride evolution as NaCl, ptb caused by chlorine in the phosphoric acid.

A = the volume in ml. of silver nitrate solution used for the titration of chlorides from the sucrose blank.

It is convenient to note this blank directly upon the label of the phosphoric acid bottle.

The calculations for the concentration of chloride in the sample are made as indicated in the steam distillation method subsequently described.

Note: The phosphoric acid will gradually corrode the glass distillation flasks, and in the interest of safety these should therefore be discarded when the bottoms have become perceptibly thinned. As it is difficult to remove every trace of the acid when washing the flasks due to the etching effect, they should be marked and not used for any other distillation tests, such as the steam distillation assay elsewhere described.

ANALYSIS OF OIL FIELD WATERS

The refinery laboratory is often called upon to analyze samples of water which have been taken from various sources of refinery operations. Such samples may include brines, which have been settled from crude oil emulsions; effluents from dehydrators, desalters, and from water treating plants designed to improve the character of the fresh water used in desalting operations; etc. While it is not within the scope of these methods to describe in detail the various analytical procedures necessary for testing these waters, a short general discussion of the type of attack for such problems will be included.

SPECIFIC GRAVITY

It has been found that an accurate determination of the specific gravity of the water sample provides a very simple and reasonably accurate estimate of its total dissolved solid content. Furthermore, it serves as an independent check on any gross errors or omissions in the usual chemical analysis. In many cases a specific gravity determination combined with a chloride analysis, alkalinity, and pH determination provides sufficient information for evaluating the sample.

The usual apparatus for specific gravity determinations is a Westphal type of balance, which should be readable to one unit in the fourth decimal place. It is usually advisable to make a simultaneous determination on distilled water at the same temperature so that all balance errors can be eliminated in determining the true reading. Especial attention should be given to the avoidance of surface tension errors due to incomplete wetting of the platinum wire suspending the plummet. This has been described in the literature (30), and consists of adding a drop of 1% solution of detergent such as sodium lauryl sulfate to the surface of the water, thus providing free movement of the wire through the surface.

Calculation of Specific Gravity

Since oil gravities are generally reported in degrees API at 60°/60°F., it is desirable that water gravities be similarly stated. However, most plummets have Centigrade scales and are standardized for 20°C. It is therefore more desirable to operate with Centigrade degrees, and since an observed value corrected to a 20°/20°C. reading is very nearly equivalent to the corresponding 60°/60°F. value, the two types of determinations can be directly compared. Caution should be exercised that handbook values given at 20°/4°C. be not confused with those where the reference temperature is 20°C. On the assumption that the balance used is constructed to indicate specific gravities referred to water at 20°C., the following calculations are in order.

(a) Subtract the reading on the balance obtained with freshly distilled water from the values of the table below corresponding to the temperature of observation. This is a lump correction for all additive errors of the apparatus.

SPECIFIC GRAVITY OF WATER

| | | | | | | |
|--------------------|--------|--------|--------|--------|--------|--------|
| T, °C | 15 | 16 | 17 | 18 | 19 | 20 |
| Sp. Gr. T/20 | 1.0009 | 1.0007 | 1.0006 | 1.0004 | 1.0002 | 1.0000 |
| T, °C | 21 | 22 | 23 | 24 | 25 | |
| Sp. Gr. T/20 | 0.9998 | 0.9996 | 0.9993 | 0.9991 | 0.9988 | |

(b) Add this correction (which may be negative) to the observed value of the specific gravity of the sample. The result is now the corrected specific gravity at the temperature of measurement referred to water at 20°C.

(c) Since the temperature of observation will in general differ somewhat from 20°C., it is necessary to apply another correction to convert it to the proper value at this temperature. The proper coefficients, provided the deviation from 20°C. is not more than about 10°C., are given in the table below.

SPECIFIC GRAVITY CORRECTION PER DEGREE C.

| Approx. Sp. G. of Sample | If Obs. Temp. is over 20° Add | If Obs. Temp. is under 20° Subtract |
|-----------------------------|----------------------------------|--|
| 1.00 | 0.00026 | 0.00016 |
| 1.005 | 0.00028 | 0.00017 |
| 1.010 | 0.00029 | 0.00018 |
| 1.015 | 0.00030 | 0.00020 |
| 1.020 | 0.00031 | 0.00022 |
| 1.025 | 0.00032 | 0.00024 |
| 1.030 | 0.00033 | 0.00025 |
| 1.035 | 0.00034 | 0.00026 |
| 1.040 | 0.00035 | 0.00028 |
| 1.045 | 0.00036 | 0.00030 |

Calculation of Total Solids from Specific Gravity Values

These calculations are based on the specific gravities of sodium chloride solutions, but the errors involved usually will not be serious for the purposes of obtaining an approximation of the total salt content.

Conversion to Per Cent and Parts Per Million. Drop the figure 1 in front of the decimal point, move the latter 3 places to the right, and divide the resulting figure by 7. This will give the concentration of the salts in per cent. To convert to parts per million, the figure for per cent is multiplied by 10,000.

Conversion to Pounds Per Thousand Barrels. Drop the figure 1 in front of the decimal point, move the latter 6 places to the right, and divide the resulting figure by 2. This will give the concentration of the salts in pounds per thousand barrels.

Example: Sp. Gr. @ 20°/20°C. = 1.0217. The concentration of the equivalent sodium chloride solution will be 3.1%, 31,000 ppm., or 10,850 ptb.

HYDROGEN ION CONCENTRATION (pH)

The widespread development of the glass electrode pH meter has turned the measurement of hydrogen ion concentration into a simple, reliable procedure, yielding information which is often of great assistance in the control of refining or processing procedures.

No detailed description of the procedure will be necessary since the various types of meters and comparators give full instructions for their use.

Attention is called to the fact that there are available "high pH" glass electrodes for more accurate measurements in the alkaline range, and "high temperature" glass electrodes for measurements at well above ordinary room temperatures.

ALKALINITY AND ACIDITY

In addition to the pH, the alkalinity or acidity of a water sample is often an important property, since it provides information about the history of the process or, for example, the potential scaling characteristics of a wash water. Methods for determination of these constituents have been so well standardized that no detailed description here will be necessary. See especially refs. (27) and (28).

MINERAL CONSTITUENTS

Methods for determining chlorides, sulfides, sulfates, iron and aluminum, calcium, and magnesium have already been described in the section on "Analysis of Aqueous Extracts from Crude Oils," q.v.

DETERMINATION OF SOLIDS IN OILS

The designation "solids" as referring to impurities in crude oil may have various interpretations. Often it is taken to mean the non-volatile ash left after ignition of an oil sample, or it may refer to the heavy material (sediment) precipitated to the bottom of a centrifuge tube (below the water or emulsion layer) during the centrifuging procedure for water determination.

A knowledge of the various types and amounts of solids in crude oils and its products is of increasing interest and importance to the refiner in view of the serious adverse effects many of such solids have upon the refinery operations. In general, the solid materials fall into three classifications:

1. Solids insoluble in water or oil; dispersed in either the oil phase or in the brine droplets, or carried as an adsorbed film at the interfaces. The materials of this class are usually composed of finely divided sand, clay, corrosion products, and similar inert "sediment" which does not settle out of the crude oil during normal dehydration or in storage, either because it is so very finely divided that its settling rate is too slow, or because it is held in suspension in association with residual water droplets, or still further because it is associated with wax-like hydrocarbons which make for a very low gravity differential between such aggregates and the oil itself.

2. Water soluble solids, such as inorganic salts. These are the chlorides, sulfates, etc., which are dissolved in the brine particles.

3. Oil soluble solids of the organo-metallic type, which may be of the nature of soaps, such as those of sodium or calcium, if the oil has

been treated with an alkali. In many oils there are often present appreciable amounts of organo-metallic compounds of porphyrin structure which are actually in solution in the oil.

In the case of crude oils, it is usually desirable to make independent determinations of these three types of solids. The water soluble solids of Class 2 can be determined by first extracting them and then analyzing as previously described. The sediment can be determined by a centrifuging or filtering procedure subsequently given in detail. The oil soluble solids are best determined by an ashing method designed to avoid loss of the more volatile metallic constituents. The methods which have been used in the Petreco laboratories and found satisfactory for total ash and for "sediment" are presented below.

TOTAL ASH

The A.S.T.M. method of test for the ash content of petroleum oils, D482-46, is not suited to the determination of the total mineral constituents of crude oils, since the final severe ignition will tend to volatilize chlorides which may, and usually do, comprise the major portion of this material.

Since a determination of the total mineral content is often desirable as a supplement to the tests for water-extractible and suspended matter and as an indication of the possible presence of organo-metallic compounds, an ashing procedure has been developed which has been found to be reasonably satisfactory. This involves reduction of the crude oil to a coke in a platinum dish, followed by further heating and ignition in the presence of concentrated sulfuric acid, thereby converting the chlorides to sulfates and allowing a clean ignition of the ash. Since the melting point of the sulfates is much higher than that of the chlorides, there is much less tendency for loss by volatilization and for carbon to be occluded in the residue. Application of heat to the surface of the oil virtually eliminates spattering due, for example, to the presence of small amounts of water in the sample, and even crudes of fairly high water content can be satisfactorily ashed in this way.

In the case of distillates, the sulfation also avoids loss of organometallic compounds, appreciable quantities of which can be volatilized by the high temperatures required for the usual dry ashing methods.

Dry ashing methods have been carefully studied by Karchmer and Gunn (31) to determine their accuracy and limitations under various conditions. Their results indicate that an ignition procedure utilizing sulfuric acid will give results within about 10% of the actual values. The greatest source of the losses are probably the porphyrin type of compounds in which form the metals vanadium and nickel usually occur as they are partly volatilized by the temperatures of the direct ashing methods. The relative error introduced by volatilization of the heavy metal complexes will of course be much larger in distillates than in crude oils because of the much greater volatility of these compounds that have found their way into the distillates. Arsenic compounds are probably also volatile to some extent.

Numerous wet ashing methods have been proposed and these are referred to in the section on "Determination of Organometallic Compounds." The most recent trends along this line seem to be to ash the oil in the presence of about equal volumes of sulfuric acid, thus producing a wet oxidation

effect. Procedures that use modified Kjeldahl methods have the disadvantage of rather low sensitivity since the amount of sample which can be best digested is rather limited.

The procedure described below, and used for many years in the Petreco laboratories, is probably as satisfactory as most of those described for this purpose.

Procedure

Measure 75 ml. of crude oil (conveniently from a 100 ml. graduated cylinder) into a 30 gram platinum dish. (If the sample contains metals harmful to platinum, such as lead, a silica dish should be used instead.) Evaporate the oil in a hood under a 250 watt infra-red lamp until the rate of evaporation becomes very slow. Care must be exercised at first to avoid having the lamp too near the dish, as spattering may result if water is present. An initial distance of 8 to 10 inches has been found satisfactory, and this distance may be reduced from time to time, especially after the evaporation of any water present in the oil has been completed. Reduction of the oil volume in this manner requires a minimum of care and the surface heating avoids sudden bumping common to the ordinary burner method.

Carefully heat the dish with a small flame directed at its sides until the volatile and more readily combustible matter has been removed. With heavy crudes this procedure requires constant attention to avoid sudden foaming through small openings in the encrustation which forms, and which may cause a substantial part of the residual crude to be carried over the sides of the dish. Stronger heating may then be applied until only coke remains. Cool the dish, and gently break down the porous carbon mass with a pestle in order to consolidate it in the bottom of the dish. Carefully add 5 to 10 ml. of concentrated sulfuric acid to the carbonaceous mass; again carefully heat the dish until all the sulfuric acid has been driven off, as evidenced by the cessation of fumes.

Remove the dish to a muffle furnace and heat to 550°C for one hour. If all carbon has not burned off, aid the process with a slow stream of oxygen and continue the heating to a carbon-free residue. Cool the dish, weigh it, and determine the "total ash as sulfates," which is usually expressed as ptb. of crude oil.

The ash may be further analyzed for the various metals, such as sodium, vanadium, nickel, copper, iron, etc. by dissolving it in dilute hydrochloric acid and making the appropriate determinations on the resulting solution. Methods such as described by Lake (32) have been successfully used for such determinations.

FILTERABLE SOLIDS ("SEDIMENT")

Solids of this type present in crude oils are usually composed of sand or quartz, iron oxide, igneous and sedimentary rock constituents such as feldspar, calcium carbonate and calcium sulfate, ores of metals and some free metals such as lead, brass and iron. In some samples, organic resinous or bituminous solids are encountered which are insoluble in all ordinary organic solvents, and from which the inorganic solids are separable only by ashing the sediment. If the oil sample contains appreciable amounts of water, the two phases should be separated by centrifuging with an appropriate demulsifying chemical, and the two phases filtered separately.

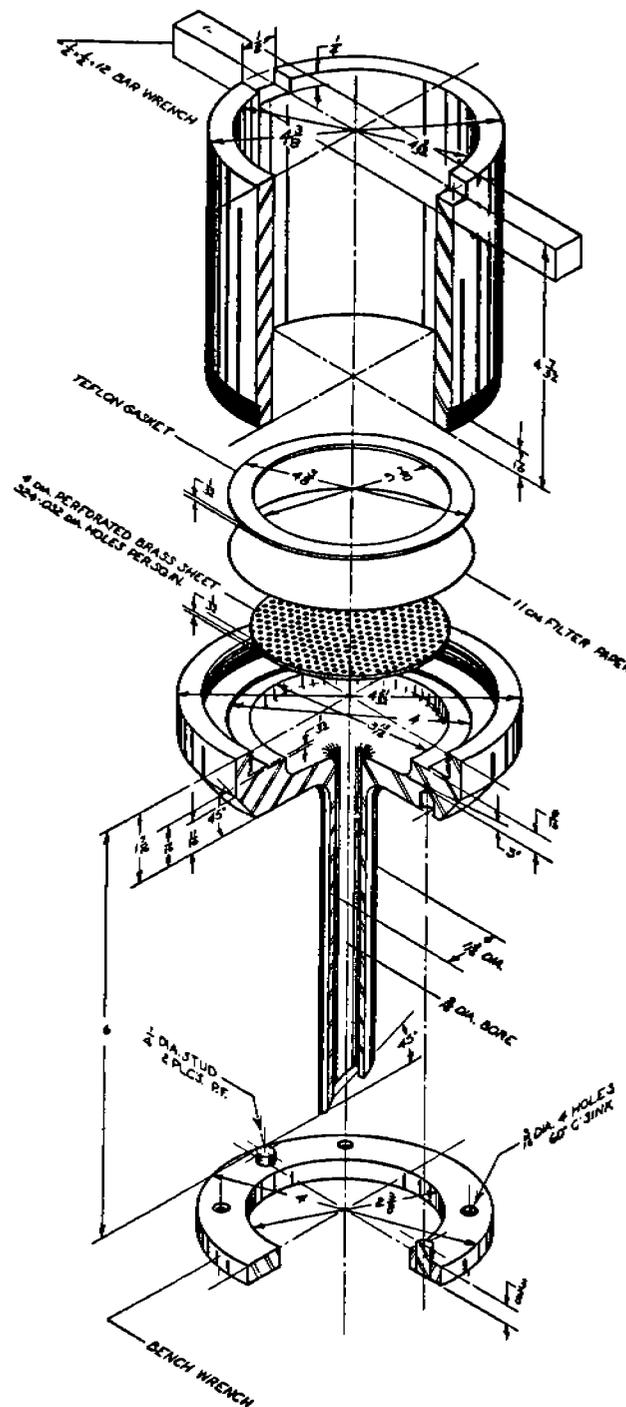


Fig. 10. Funnel for Filtering Sediments

These solids are most accurately determined by filtration of the oil and washing of the retained material with suitable solvents to remove residual waxes and other oily matter. The ordinary Buchner funnel method is not satisfactory for this filtration, because the filter paper does not adhere well to the funnel in the presence of the oil and solvents, so that it is best to use a modified funnel of the type described below. Furthermore, some heating is required to attain effective filtration and washing, and appropriate heating devices should be provided. The method described has been thoroughly tested and is believed to produce reliable results.

Requisites

1. Monel or stainless steel funnel as shown in Fig. 10. This funnel is constructed to accommodate standard 11 cm. filter papers. The paper is supported in the funnel by a perforated plate. The filter paper is sealed in the funnel by pressure of the cylindrical top pressing on the Teflon gasket. This Teflon gasket not only serves as a seal but due to its waxy surface acts as a cushion to prevent the edge of the metal cylinder from tearing the paper as it is tightened.
2. Bench wrench, as shown in the drawing, for assembling and disassembling the funnel.
3. Pyrex Suction Flask—4 liter, heavy wall, tubulated.
4. Rubber stopper to accommodate the funnel tip and flask.
5. A vacuum source such as a Cenco Pressovac or other suitable high capacity pump.
6. Three 8-liter stainless steel beakers.
7. Test tubes—18 x 150 mm.
8. Tapered Teflon stopper to fit the average test tube snugly.
9. Filter Paper—Reeve Angel #226—11 cm diameter.
Whatman #30—11 cm diameter.
10. A sealed electric hot plate.
11. Desiccator.
12. Solvents: Acetone, Benzene, Carbon Tetrachloride, Isopropyl Alcohol, Stoddard solvent, Distilled Water and Glacial Acetic Acid.

Procedure

Roll one circle of each grade of filter paper into a small cylinder, and insert in a numbered, clean, dry test tube. Heat to constant weight in an oven kept at 230°F. A heating time of approximately 3 hours is usually adequate.

Cool test tubes in a desiccator *without desiccant*, and weigh in advance of the filtration tests. Weighing is somewhat critical, as it is necessary to close the test tube immediately on removal from the desiccator with the Teflon stopper to prevent the dry filter paper from absorbing moisture. The Teflon stopper and beaker, to support the test tube on the balance, may be tared for convenience in weighing. *In all operations, the test tubes, once weighed, should be handled only with forceps, otherwise undue increases in weight may result.*

The sample to be analyzed may be of any volume, but in most cases one liter is adequate. If chemical analysis of the sediment is contemplated, a larger sample may be used and if the sediment content is high, a smaller sample will suffice.

Place the sample of oil to be tested in an 8 liter stainless steel beaker and dilute it with an equal volume of petroleum naphtha such as Stoddard Solvent or its equivalent. Heat the diluted sample on a suitable electric hot plate or steam bath to 130°F.

Remove the previously weighed 11 cm. Reeve Angel #226 filter paper from the test tube by means of forceps, unroll and place on the perforated disc in the funnel base resting in the bench wrench. Place the Teflon gasket on the filter paper and screw the cylindrical top snugly in place by means of the cross bar shown in drawing.

Connect the funnel to the flask and apply suction before pouring the heated diluted sample thereon. The diluted sample should be introduced into the funnel no faster than the rate at which the applied suction will remove it. This allows the observation of any tendency of the fluid to plug the filters and permits application of suitable solvents to remove the plug-forming constituents. A convenient device, not shown, for flowing the sample onto the filter is a stainless steel funnel fitted with a stopcock and suspended above the filter funnel at a convenient height. This funnel can be heated by means of an electric funnel heater jacket such as a Glas-Col funnel heater. The temperature of the funnel can be regulated by a suitable electric control.

For asphaltic oils, the temperature of the diluted sample should not exceed 150°F., and 130°F. has been found most satisfactory. For oils containing considerable wax, temperatures of the diluted samples must be 180-200°F. for best filtration. No set rule can be given for the best operating temperature, and the operator will have to determine this by experience.

If the filter paper becomes plugged, introduce small amounts as needed, of the following solvents onto the paper in the order mentioned. (1) Benzene, (2) Carbon Tetrachloride, (3) Stoddard Solvent, heated to 150°F., (4) Isopropyl Alcohol, (5) Acetone, and (6) Glacial Acetic Acid. In some refractory cases where a waxy emulsion appears to be the cause of plugging, liberal application of hot water is effective. The glacial acetic acid is used only if all other solvents fail to dissolve the residual organic matter.

On completion of the filtration, wash the filter paper and sides of the funnel with small portions of the petroleum solvent, benzene and carbon tetrachloride until all traces of oil are removed, as may be judged by the color of the filtrate. Then wash the filter paper with hot water to remove any soluble salts and finally wash with acetone to remove the water. Maintain suction until the paper appears dry.

Set aside the combined filtrate and washings for the second filtration.

Remove the funnel, place in the bench wrench and disassemble it. Brush solids clinging to the Teflon gasket onto the filter paper and carefully lift the paper at one edge by means of a spatula or knife, and roll it into a small cylinder, folding one end over to prevent loss of solids. Return the paper to the test tube used for its previous weighing and dry to constant weight in an oven at 230°F., which will again require about 3 hours.

After cooling in the desiccator, weigh the test tube as previously directed. The difference in weight represents the sediment content. *Do not handle the tubes with fingers; use only forceps!*

Process the filtrate and washings from the first filtration a second time, using a finer paper, such as a Whatman #30. Experience has indicated that one grade of filter paper will not satisfactorily remove all of the solids. For example, with most California oils the use of the finer filter paper for the first filtration results in considerable plugging difficulties.

Insert the weighed filter paper, 11 cm. Whatman #30, in the funnel as previously described. Heat the combined filtrate and washings to 100°F. and filter as before. As the diluted sample now contains very volatile and inflammable solvents, care should be exercised in heating the sample. If large quantities of acetone or benzene were required for washing, it may be impractical to heat the sample to 100°F. In general, little difficulty is encountered in the second filtration. If plugging occurs because of the introduction of water in the sample, this can be corrected by washing the filter paper first with benzene and then with acetone.

When the filtration is completed, wash the filter paper free of oil, as in the first filtration, with small portions of the solvents in the following order: Stoddard solvent, benzene, carbon tetrachloride and a final portion of hot water, followed by a liberal quantity of acetone to dry the filter paper.

Remove the funnel to the bench wrench, disassemble it and process the filter paper as noted for the first filtration.

With some oils, more than one filter paper of either the coarse or fine grade may be required to complete the filtration. In most cases where the first filtration indicates the presence of considerable amounts of sediment, it is expedient to discard the paper and start anew with a smaller sample. In some cases, where the first filtration appears difficult at the start, the sample should be further diluted with petroleum naphtha or benzene.

The combined differences in weights of the test tubes used for a given sample represent the weight of the sediment which may be expressed as pounds per thousand barrels or as parts per million, according to the following formula:

$$S = \frac{350 W}{V}$$

Where S = the amount in the sample, in ptb,

W = the weight of the filtered sediment, in mg.

V = the volume of the oil sample filtered, in ml.

If 1000 is substituted for the factor 350 in the formula, the results will be in mg. per liter, or approximately parts per million, ppm.

CENTRIFUGIBLE SOLIDS

The filtration method described above is somewhat tedious, and a simpler and more rapid determination of "sediment" can often be made by the centrifuge procedure outlined below. This will give all the solids which can be precipitated by centrifuging the diluted oil under the conditions

given. It should, however, be pointed out that in some cases the solids are so thoroughly associated with wax or resins that their gravity differs insufficiently from the body of the oil to allow of their being separated by centrifugal force in any reasonable time. The filtration method should therefore be preferably employed on an unknown oil if the total suspended solids are to be accurately determined. If the centrifuge method gives comparable results, it may then be used as a routine procedure.

The principle of the method is to dilute the oil with a solvent, separate the solids by centrifuging, then to wash the solids successively with acetone and water, so that most of the oily matter and water soluble salts are removed. The solids can then be dried and weighed, and finally ashed to remove any residual organic material. In this way there is no overlapping in values with those obtained by the aqueous extraction procedures. The water which is added and emulsified with the oil before the first centrifuging serves as a collector for the solid matter, which is often of such extreme subdivision that centrifuging without this step will not precipitate it to the bottom of the centrifuge tube.

The values determined by this procedure are: (a) dried solids, (b) ignited solids, and (c) sulfated solids.

The first is the weight of the solids after washing them free of as much of the oily matter as the solvents permit, and drying at 220°F.

The second is their weight after ignition, which will remove all organic matter and decompose any carbonates present. Since all water-soluble salts have been removed, no chlorides and only a negligible quantity of sulfates will in general be present.

The third is the weight of the solids from (b) after evaporation with sulfuric acid. This step converts any non-siliceous matter (such as alkaline-earth oxides which were originally present as carbonates) to the sulfates.

From these values a rough estimate of the organic matter, carbonates, and inert matter present in the dried solids can readily be made. This information is often of value for a qualitative picture of the solid suspended matter.

Procedure

1. Measure a suitable volume of the sample (depending upon the amount of suspended matter) into a tall-form glass cylinder. 350 ml. is convenient, as the final weights in mg. will correspond to the pounds per thousand barrels of oil. Add an equal volume of benzene, then a quantity of distilled water equivalent to 2% of the oil volume, and emulsify the mixture thoroughly with the aid of a piston made from a rod and a disc having a small clearance in the cylinder.

2. Pour the emulsion into 100 ml. centrifuge tubes and heat in a water bath to about 120°F. Then centrifuge for 30 minutes at 1500-1800 r.p.m.

3. Remove the tubes from the centrifuge, and carefully decant the supernatant fluid so that the precipitated emulsion and solid matter are not disturbed. Then transfer all the precipitates to a single centrifuge tube by dispersing them (by thorough shaking) in a small amount of benzene, using several successive rinsings if necessary to insure that all

of the emulsion is completely removed. Fill the tube with benzene, heat to 120°F., centrifuge for 5 minutes, and decant the liquid.

4. Fill the tube with acetone, shake to disperse the solids, heat to 120°F., and centrifuge for 5 minutes. Decant, refill the tube with acetone and repeat the heating and centrifuging. *Note: As in all instances where a volatile solvent is shaken in a centrifuge tube, especially if hot, care must be taken to avoid a build-up of excessive pressures in the tube. The tube should first simply be turned over once or twice, the pressure relieved, then gently shaken and pressure again relieved. Subsequently more violent shaking is then usually permissible.*

5. Decant the acetone, add 75 ml. of distilled water to the tube, and shake it thoroughly. If any of the solids tend to float on the surface (due to the presence of residual organic matter) add 25 ml. acetone, shake the mixture, heat to 120°F., and centrifuge for 5 minutes. If the solids are all heavier than water (no indication of flotation), the acetone addition should be omitted, as it tends to decrease the solubility of the water-soluble salts. Repeat the extraction, heating, and centrifuging, with the water-acetone mixture or with water alone, whichever was used, and decant the liquid.

6. Add about 1 ml. acetone to the tube, and with the aid of an elongated medicine dropper disperse the solids and transfer the mixture to a weighed platinum crucible. Add successive portions of acetone and repeat the transfer until all the solids have been removed. Carefully evaporate the acetone on a warm plate and finally dry at 220°F. in an oven for 2 hours. Weigh the crucible and compute the weight of the dried solids.

7. Ignite the solids over a burner or in a muffle furnace at 950-1000°C. for about 1 hour. Cool, weigh, and record as ignited weight.

8. To the cool crucible add 2 ml. of concentrated sulfuric acid, and evaporate until no more fumes of SO₃ are evolved. Ignite, cool, and weigh the sulfated solids.

Calculations

$$\text{Carbonates as CaCO}_3, \text{ ptb.,} = \frac{438}{V} (S - I)$$

$$\text{Organic Matter, ptb.,} = \frac{350}{V} (D - 0.45 I - 0.55 S)$$

$$\text{Inert Matter, ptb.,} = \frac{350}{V} (1.7 I - 0.7 S)$$

Where V = volume in ml. of oil sample,

D = weight in mg. of dried solids,

I = weight in mg. of ignited solids,

S = weight in mg. of sulfated solids.

If a quantitative analysis of the solids is desired, the sulfated material can be evaporated with 2 ml. of hydrofluoric acid and a few drops of sulfuric acid (platinum crucible must be used), until no more fumes of SO₃ appear, then ignited and weighed, the loss representing silica. The residue is then dissolved in concentrated hydrochloric acid, diluted, and the various cations determined by the usual procedure.

DETERMINATION OF ACIDITY IN OILS

The presence of acids in a crude charging stock is often of interest to the refiner, since such impurities, especially if inorganic salts are present, can contribute considerably to the corrosion produced by the oil in the refining process. A knowledge of these acidities is therefore highly desirable as a basis for correlation with refinery corrosion, characteristics of the thermal decomposition of the salts in oil, and properties of the products. Both strong and weak acidity may be present in the crude oil sample. The presence of strong acids is usually the result of some processing connected with production methods, such as the increasingly common practice of acidizing wells with hydrochloric acid, leaving highly acidic residual brine particles in the oil. Acidic treating agents used for demulsification of the crude may also be the source of some residual strong acidity. Weak acidity is generally due to the presence of organic acids of the naphthenic acid type and to hydrolyzable salts in the brine particles.

The refiner is also often interested in the acidity of the petroleum products, both in the lighter fractions and in the lube oils. Naphthenic acids in the latter are objectionable because they interfere with caustic washing procedures by forming soaps and thereby promoting emulsion formation. Acids in the lighter gas oils and in kerosine have economic value and are therefore sometimes extracted for that reason. In catalytically cracked naphthas, acids in the form of cresols and thiocresols have adverse effects on the finished gasoline, such as promoting gum formation, etc. It is therefore also desirable to determine the acidity in many of these products, and the methods given below are designed to serve that purpose.

Methods for the direct electrometric titration of acidity in petroleum oils have been published in the literature, see e.g. references (2), (39) and (40), and they have the advantage over the older colorimetric procedures in that they are applicable to dark oils, such as crude oils. By plotting the titration curves it is possible to determine not only the amount but also the type of acidity present.

Titration of petroleum distillates is generally simple and straightforward, but some additional factors must be considered in the case of crude oil samples. It should be kept in mind that the alkali-consuming power of a crude oil may be due not only to the acidity of the oil phase itself, but in addition, to acidic components in the dispersed brine particles. For purposes of studying the effects of salts in crude oils it is often desirable to determine this total acidity as well as that due to the dissolved oil-soluble acids alone. This can be done by making a separate determination on the crude oil sample as received, followed by one in which the dispersed material is first removed by centrifuging. Thus, the contribution of the brine to the total acidity may readily be determined. The acidity of this brine may be due to hydrolyzable salts such as iron and magnesium chloride, although if the salt content is quite high a pseudo-acidity is sometimes obtained which is apparently due to the precipitating characteristics of the salts.

For obtaining the net oil acidity of the sample, the latter is mixed with the solvents, as described in the procedure, and centrifuged for 5 minutes at 1500 to 1800 r.p.m., the supernatant oil being decanted from the precipitated matter and then titrated as directed.

The method described below is that originally developed in the Petreco laboratories (2) and has been found to be satisfactory on a large variety of crude oils, distillates, and residual oils.

ACIDITY BY ELECTROMETRIC METHOD

Apparatus

1. *Potentiometer.* Since the solvent system necessary to assure complete solution of the crude oil introduces a high resistivity into the measuring system in addition to the high resistance of the glass electrode, it is essential that the potentiometer and electrode system used have a very high sensitivity. A Beckman Model G pH meter, or equivalent, will be quite satisfactory for the purpose.

2. *Electrodes.* The large size (5") shielded glass electrode suitable for high pH measurements with shielded cables should be used, together with a calomel cell.

3. *Titration Beaker.* A grounded metal shield should be provided for the 100 ml. titration beaker. This shield can conveniently be made of brass tubing of such size that the beaker will fit snugly into it. The adapter terminals and metal lining of the meter box should be connected to the same ground. It is desirable to support the beaker in such manner that it may be removed without disturbing the electrode system. This may be done simply by supporting it upon a 3" wooden block or by a mechanical support which allows the beaker to be racked up and down.

4. *Air Driven Stirrer.* Ordinary electric motors cause interference with the sensitive meter circuits and should be kept away from the system. However, some of the recently available electric stirrers especially designed for potentiometric set-ups are probably suitable. If an electric motor is used, the frame should be grounded and the shaft extension should be made of glass.

5. *Burette.* A 5 or 10 ml. burette with .02 ml. divisions is satisfactory.

Solutions

1. *Alcoholic KOH.* This is a solution prepared by dissolving 3.5 g. of C.P. KOH pellets in 100 ml. of C.P. methanol and adding 400 ml. of C.P. secondary butanol. The precipitate which forms may be removed by centrifuging; it is equally satisfactory to allow it to settle to the bottom of the bottle and use the reagent without stirring up the sediment. It is standardized by titrating 5.0 ml. of 0.1 N. benzoic acid in xylene mixed with 50 ml. of secondary butanol containing 4% water. Standardizations should be frequently made, as the solution slowly changes in strength. This mixture of alcohols has been found by experiment to be more stable with 0.1 N. KOH than any pure alcohol, with the exception of methanol. The latter, however, has the disadvantage that it will tend to concentrate the solution by evaporation, and is difficult to hold by burette stopcocks which have been exposed to alkali for a few weeks. The mixture also has the at least partially compensating characteristics of tending to become stronger due to evaporation of methanol, and to become weaker due to oxidizing effects on the butanol.

2. *Titration Solvent.* This consists of a mixture of equal volumes of purified xylene and of secondary butanol, the butanol having had water added in the amount of 4% of its volume. If it is desired to substitute a technical grade of secondary butanol, it is advisable to purify by agitating for 30 minutes with 2% of powdered calcium hydroxide and then to filter bright, using some suitable siliceous filter aid. The criterion of suitability of the solvent is that the blank titration to pH 11, as described under "Procedure," should not exceed 0.15 ml. For the titration of distillates, the secondary butanol alone (to which 4% of distilled water has been added) may be used as the titration solvent.

3. *Standard Buffer.* This is made by dissolving C.P. potassium acid phthalate in CO₂-free water to make a 1% solution, giving a buffer with a pH of 4.0. Prepared buffers having various standard values are now readily available.

Procedure

1. Inspect the electrodes and allow a drop of potassium chloride to escape from the calomel cell by slightly loosening the glass sleeve. Rinse with distilled water, immerse both electrodes in the potassium acid phthalate buffer solution, and with the stirrer revolving at moderate speed, observe whether the electrode system and pH meter are functioning properly, as indicated by a definite reading in the neighborhood of pH 4 without fluctuation. Set the temperature compensating knob to room temperature and adjust the meter to read pH 4.0. This preliminary check with potassium phthalate buffer is desirable because the glass electrode functions best when it has been in contact with an acid system immediately before a titration. Remove buffer solution, rinse electrodes thoroughly, and dry with tissue.

2. Into 50 ml. of titration solvent contained in a 100 ml. beaker, pipette 25 ml. of the oil sample. In the analysis of a crude oil containing substantial amounts of salts, a separate titration should be made on a sample in which the mixture of titration solvent and oil has been centrifuged and the oil decanted from the sedimented material. Any water obtained by this centrifuging may be separately titrated for strong and weak acidity.

3. Raise the beaker into position so that the electrodes and stirrer are sufficiently immersed, and stir vigorously (but not so violently as to mix air into the solution) for three minutes, to allow the system to come to equilibrium.

4. Record the initial pH reading. Add the 0.1 N. alcoholic potassium hydroxide solution in suitable increments, recording the pH reading after each addition. At least one minute should be allowed for equilibrium before recording the meter reading, especially in the higher pH range. It is difficult to specify a proper waiting period between increments as oils vary in their behavior when titrated. Frequently good precision is obtained by using uniform increments of alkali and taking readings after the upward "drift" has become small. If the reading reverses its drift after an upward trend, it is well to read the meter as soon as this is seen to occur and then to add the next increment. This reduces errors from hydrolytic effects and prolonged contact with air containing carbon dioxide which are probably occurring when the pH indication shows a falling tendency.

5. Stop the titration at an indicated pH of 12, remove the beaker, thoroughly rinse the electrodes with benzene or xylene, then with acetone, and finally with water. Between titrations the electrodes should be stored in tap water or in the buffer solution recommended by the manufacturer.

6. Plot the titration curve and determine the alkali consumption at indicated pH 7 and 11. Record the first as the equivalent of the strong acidity, the difference between the two as that of the weak acidity.

7. A blank titration should be made on 50 ml. of titration solvent, omitting the oil sample. Subtract the results of this titration at pH 7 and 11 from the results obtained with the oil sample. Only one blank titration need be made with a given batch of titration solvent.

Discussion

When these titrations are made for the first time it is desirable to begin with the titration of a known acid, such as oleic or stearic, so that the operator will become familiar with the behavior of the system in the weak acidity range and may thus proceed with more confidence in the titration of oil samples. The endpoints designated are somewhat arbitrary and may be varied to suit any particular interest, but they have been found in pure systems to be quantitatively satisfactory. The indicated pH of 11 corresponds to the equivalence point for carboxylic acids, such as oleic or naphthenic acids, while the value of pH 7 corresponds to strong inorganic acids.

ACIDITY BY COLORIMETRIC METHOD

Most petroleum distillates are sufficiently light in color to permit titration to a colorimetric endpoint. Since this method is considerably more rapid than the electrometric procedure, it is usually preferred for routine test purposes.

Procedure

The titration solvent used for the titration of distillates is simply secondary butanol, purified if necessary as indicated in the previous method. The solvent contains 75 mg. of bromthymol blue indicator per liter of solvent.

50 ml. of solvent and 25 ml. of the sample are mixed together and titrated with alcoholic potassium hydroxide prepared as directed in the previous section. The solution is of course stirred if in a beaker or shaken if in a centrifuge tube, after the addition of each increment of caustic. The endpoint is a green color which the solution takes on just before the dark blue color that appears when a slight excess of caustic is present.

Calculations

The manner of expressing the results will depend upon the use to which the data are to be put. In many cases it will be desired to find the amount of caustic soda required to neutralize the oil. In others it may be more effective to calculate the "Acid Number," which is defined as the number of milligrams of KOH required to neutralize 1 gram of the oil. The formulas for making these calculations are as follows:

$$N = KAC$$

Where N = acidity in units given in table below,

K = constant as given in table below,

A = ml. of KOH used to titrate a 25 ml. sample,

C = normality of KOH

| Units of N | K | Units of N | K |
|---|------|------------|-----|
| NaOH, ptb. | 560 | NaCl, ptb. | 818 |
| KOH, ptb. | 784 | HCl, ptb. | 510 |
| Naphthenic Acids, ptb. (Mol. w't. 300) | 4200 | | |

Acid No. = mg. KOH per gram of oil

$$= \frac{2.24 AC}{s}$$

Where s is the specific gravity of the oil.

It may be noted that the oil acids in light distillates have molecular weights of about 300, so that their concentration in the oil can be readily approximated, as indicated in the table.

DETERMINATION OF PHENOLS AND THIOPHENOLS IN DISTILLATES

Most thermally or catalytically cracked distillates contain appreciable amounts of weakly acidic materials, usually referred to as "acid oils," "cresols," "phenols," etc., and consisting principally of a mixture of phenolic types of substances. These are usually accompanied by additional weak acids of thiophenolic character. It is often desirable to determine the amounts of these compounds present, and a number of methods have been suggested for this purpose, typically UOP Method N-262-48-1. In this the oil is extracted with caustic and the optical density of the extract measured with an ultraviolet spectrophotometer at appropriate wave lengths.

A comparison of analytical methods for the determination of phenolic materials together with an evaluation of their general applicability has been made by Mohler and Jacob (41) who found that the Emerson Method using 4-aminoantipyrine reagent is the most precise and accurate even in the low parts-per-billion range. However, this method will not determine phenols substituted in the para position, and since such materials are probably often present in petroleum distillates, the method must be used with caution. These investigators also found that the ultra violet absorption method, such as has been described by Schmauch and Grubb (42) does not have this limitation, but it is more tedious and involves errors due, for example, to the necessity for assuming arbitrary average absorptivities for the many different kinds of phenolic materials usually present in petroleum samples.

Thiophenols are considerably stronger acids than phenols and can be titrated with alkaline solutions. However, their strength does not differ sufficiently from those of naphthenic acids, for example, to make possible a differentiation between the two. If carboxyl acids are absent, the thiophenols can be titrated very satisfactorily in pyridine solution with tetraethylammoniumhydroxide to a thymol-blue endpoint. Thiophenols can also be determined by argentometric titration but aliphatic mercaptans of course will interfere.

Considerable improvements in methods for determining these materials in distillates is required if the needs of the refiner for detailed knowledge of their significance are to be met.

DETERMINATION OF NITROGEN IN OILS

The types of nitrogen compounds present in petroleum and its various fractions have already been briefly described. Total nitrogen is usually determined by a Kjeldahl method modified to suit the difficultly digestible petroleum oils. However, refiners are now interested in nitrogen concentrations as low as a few parts per million, and these traces are difficult to determine accurately on the small samples which the methods usually require. Wankat and Gatsis (43) used a high pressure catalytic hydrogenation process for these determinations with good results. Noble (44) has reported a refined Kjeldahl procedure accurate to 1 ppm. on a 5-gram sample by extremely careful procedural steps and purification of reagents. Bond and Harritz (45) were able to make accurate determinations in the 1 to 10 ppm. range by first adsorbing the nitrogen compounds on silica gel and then subjecting the silica column to the usual Kjeldahl digestion. This has of course the advantage of permitting operation on much larger samples than those in which all of the sample must be decomposed. Other analytical methods, employing the mass spectrograph, chromatography, and ultraviolet spectrographs have also been used, and are described in the work of Sauer et al. (7).

However, it appears that the basic nitrogen compounds are primarily responsible for the adverse effects on refinery operations (11), and considerable work has been done to devise methods for their determination that are reliable. Direct titration of the bases in petroleum distillates has been attempted, and the method of Wittmann (46) and modifications have been used satisfactorily (47), especially on high-nitrogen content distillates, such as those from shale oil (48). The method consists essentially of an electrometric titration of the oil, dissolved in glacial acetic acid, with perchloric acid.

The method described below is intended for the determination of low concentrations (a few parts per million) of those basic nitrogen compounds in petroleum fractions which react with perchloric acid. It follows the methods cited, with some modifications to allow for increased sample size so as to give greater accuracy.

DIRECT TITRATION METHOD

Requisites

pH meter or potentiometer with a range of 400-800 mv., fitted with a glass and calomel electrode set. The amplifier control knob setting may be changed in some instruments if the voltage is outside the meter range.

Titration Assembly. 600 ml. beaker, stirrer, and grounded metallic shield or the breaker.

Perchloric Acid, 0.1 N. Dissolve 8.5 ml. of 70-72% perchloric acid in liter of glacial acetic acid. Water may be removed from this solution by adding about 14 grams of acetic anhydride and allowing to stand overnight. Standardize against potassium acid phthalate dissolved in glacial acetic acid.

Acetic Acid, glacial

Procedure

Weigh the sample into the 600-ml. beaker and add 400 ml. of glacial acetic acid. (As much as 100 grams of sample may be taken for very low concentrations of basic nitrogen.) Place the beaker in the titration assembly and adjust the electrical conditions, if necessary, to give a reading in the high range of the pH scale. Add suitable increments of standard perchloric acid solution and record the meter reading after each addition.

Plot the titration curve and determine the endpoint at its inflection, which occurs between about 500 and 600 mv. on samples containing appreciable amounts of basic nitrogen, say 25 ppm. or more. When very small quantities are present the inflections may be poorly defined and the endpoint must therefore be chosen at the same e.m.f. at which it occurs in samples containing the larger quantities. A suitable blank should be run, following the procedure without the addition of the base sample, and the final titration result corrected accordingly.

Note: The usual precautions for manipulating perchloric acid in the presence of organic substances should be observed, i.e. operate with dilute solutions and at room temperatures. Wastes should be disposed of promptly and with high water dilution.

Calculations

Calculate the percent basic nitrogen as follows:

$$B = \frac{1.4 AN}{W}$$

Where: B = weight percent of bases expressed as Nitrogen,
 A = net volume of perchloric acid solution used, ml.
 N = normality of perchloric acid solution,
 W = weight of sample, grams

The direct titration method is usually quite satisfactory for the lighter distillates, but for diesel and gas oils it may give poor results. In such cases it is therefore desirable to extract the bases first from the oil with a mineral acid, recovering the extract and titrating it in a suitable solvent. This method also isolates the bases for further inspection, if desired, and makes possible a direct estimation of the amount and kind of material which will be removed from the oil in a commercial acid-wash operation.

EXTRACTION METHOD

The method described below has been tried on a large variety of oils and found to be satisfactory for estimating their nitrogen base contents.

Requisites

| | |
|--|--|
| 40% Sulfuric Acid | Sodium Hydroxide, 25° Be. solution |
| Acetone | Sodium Chloride, saturated solution |
| Ethyl Ether | Potassium Sulfate, saturated solution |
| Petroleum Ether | pH indicator paper |
| 1-liter separatory funnel | 250-ml. glass cylinder and piston |
| 100-ml. centrifuge tubes | 0.1 N perchloric acid in glacial acetic acid |
| 10-ml. burette | Glacial acetic acid |
| Electrometric acid-base titration apparatus and shielded titration beaker, such as described in the section on the determination of acidity in oils. | |

Procedure

Place 200 ml. of the oil sample in a 250 ml. pyrex cylinder and add 4 ml. of 40% (10N.) sulfuric acid.

Place the cylinder in a water bath heated to about 150°F., and emulsify the contents by pumping carefully with a close-fitting piston for a total of 100 strokes at the rate of about 60 strokes per minute. This piston should preferably be of stainless steel or glass, and can be simply made by affixing a disk nearly the diameter of the cylinder transversely to the end of a 1/4-inch rod, the end of which is bent to form a handle.

After the mixture has been brought to temperature and emulsified, pour the emulsion into two centrifuge tubes (100 ml. in each) and centrifuge for 5 minutes to separate the sludge formed.

Decant the oil layer from the tubes back into the emulsification cylinder, add an additional 4 ml. of 40% sulfuric acid, and repeat the procedure of emulsification and centrifuging, using the same centrifuge tubes as previously. If the sludge is fluid and has a tendency to pour as the oil is being decanted, cool just the sludge portion of the centrifuge tube in ice cold water. This will stiffen the sludge and permit a clean separation. It has been found that additional extractions do not result in the removal of appreciable further amounts. Again decant the oil from the centrifuge tubes carefully to avoid loss of sludge, and discard the oil layer.

Wash the piston and cylinder with about 100 ml. of petroleum ether and transfer any residual sludge in this manner to the centrifuge tubes.

Shake the centrifuge tubes carefully, releasing any pressure developed after a preliminary gentle agitation, then shake thoroughly to mix the sludge and ether in order to extract as much of the oil as possible.

Again centrifuge the tubes, and pour off and discard the ether layer.

Add 25 ml. of acetone to each centrifuge tube, agitate gently at first, then cork each tube, shake it thoroughly, and transfer the mixture to a 1 liter separatory funnel. Repeat this procedure with two or three additional doses of acetone to make sure that all of the sludge has been transferred.

Add 100 ml. of petroleum ether and 20 ml. of 25° Be. (6N) sodium hydroxide to the separatory funnel, and mix the contents by gentle agitation.

Add 100 ml. of distilled water and again agitate the mixture. The insolubility of the sodium sulfate formed tends to promote emulsion formation, and if an emulsion is encountered, add one or more additional 100 ml. portions of water.

Withdraw the aqueous layer into a 2 liter beaker and save for a second extraction with ethyl ether.

Wash the petroleum ether layer alternately with 100 ml. portions of saturated sodium chloride and potassium sulfate solutions by vigorous agitation until the aqueous phase is neutral to pH indicator paper. Some stubborn emulsions may require the addition of a mixture of the two saturated solutions in order to obtain good resolution.

After the final wash, withdraw all the water, and centrifuge the petroleum ether layer to precipitate any water carried over in the transfer.

Remove this small amount of water with the aid of a capillary pipette made by drawing a medicine dropper to a long capillary tip which will reach the bottom of the centrifuge tube.

Evaporate the water-free petroleum ether on a hot plate in a 200 ml. beaker, accurately weighed and containing a boiling tube. The ether should be carefully evaporated at low heat until active boiling ceases, and the beaker retained for evaporation of the subsequent ethyl ether extract.

Reduce the combined water washes from the petroleum ether extraction by evaporating to approximately 600 ml. Take care that the vapors do not come near a flame, as they contain combustible components, such as acetone, ether, etc. Cool the beaker and transfer its contents to a 1 liter separatory funnel, and add 100 ml. of ethyl ether.

Agitate the mixture, gently at first, with repeated release of pressure, then vigorously. Allow the ether layer to separate, and draw off the aqueous phase. Wash the ether layer twice with a 50-50 mixture of saturated sodium chloride and potassium sulfate, using approximately 100 ml. of the mixed saturated solutions for each wash. Transfer the ethyl ether extract to a centrifuge tube and centrifuge it to remove any entrained water in the manner described above for the petroleum ether extract. Pour the ethyl ether extract from the centrifuge tube into the beaker containing the petroleum ether residue, and carefully evaporate on a low temperature hot plate until all of the ether has been removed.

Cool and weigh the residue, thus obtaining a first approximation of the nitrogen base content of the oil.

Titration. This extract can be titrated for its base content by the method described above. However, the amount of sample need be only about 0.5 g. and the amount of glacial acetic acid used can be reduced to 100 ml. The calculation is also modified, as follows:

$$B = \frac{1.4 ANW}{wVs}$$

- Where B = weight percent of base in the oil, as Nitrogen,
 A = net volume of acid used in titration, ml.
 N = its normality,
 W = total weight of bases extracted, g.,
 w = weight of bases used for the titration, g.,
 V = volume of oil used for the extraction, ml.,
 s = its specific gravity.

Calculation of Results. The results obtained may be used to express the nitrogen base content of the oil in a number of ways. One is to calculate a "base number," corresponding to the more commonly determined "acid number" of the oil. Another way is to calculate the percent of nitrogen bases present (weight basis), either as Nitrogen, or as Nitrogen Bases, using an arbitrary equivalent weight, depending upon the nature of the oil used. A figure of 300 for this equivalent weight appears to be a good average for the nitrogen bases extractable from petroleum distillates. The formulas are as follows:

B = Base No. = Amount of acid required to neutralize 1 g. of oil, expressed as mg. of KOH

$$\frac{56vNW}{wVs}$$

Where: **v** = the volume of perchloric acid required in the titration,
N = its normality,
W = total weight of the extract obtained,
w = weight of the extract used for titration,
V = volume of the oil sample extracted,
s = specific gravity of the oil

C = Weight percent of Nitrogen Bases, as such, present in the oil, assuming an average molecular weight of 300.

$$C = 0.536B = \frac{30vNW}{wVs}$$

N = Weight percent of Nitrogen bases present, expressed as Nitrogen

$$N = .025B = .0467C$$

DETERMINATION OF MERCAPTANS IN DISTILLATES

When sour distillates are to be sweetened or otherwise treated to get rid of the odoriferous mercaptans, it is necessary to analyze for their mercaptan content so that the proper treating conditions can be determined. Probably the most satisfactory method for their quantitative determination is to titrate the mercaptans with silver nitrate solution, in an organic solvent in which the distillate is completely soluble, following the titration electrometrically.

After a distillate has been treated to remove mercaptans or to "sweeten" them, specifications usually call for a "Doctor" test, which is very sensitive and designed to show merely the presence of any residual mercaptans. The test is based on the fact that mercaptans react with an alkaline solution of sodium plumbite to form a brown or reddish lead mercaptide, which on the addition of powdered sulfur will precipitate the lead as a black lead sulfide. It is generally sensitive to about .0005% mercaptan sulfur content and is described in the ASTM procedure D484-52 and in the UOP test method H-41-40.

Both methods are described below.

MERCAPTANS BY ELECTROMETRIC TITRATION

Requisites

The meter and electrode requirements are the same as those described in the section on Electrometric Chloride Titration.

Silver electrode. This is sensitized by dipping in concentrated HCl and rinsing, as for the chloride titration. In addition, it is next dipped into a small vial containing saturated sodium sulfide solution, after which it is thoroughly rinsed and dried with absorbent paper.

A mechanical stirrer, preferably air-driven to avoid electrical interference. It should be thoroughly grounded electrically.

Burette. A 25-ml. burette graduated in 0.1-ml. divisions is most suitable.

Standard Sodium Chloride Solution. Dissolve 1 g. of dried sodium chloride in 1 liter of distilled water.

Silver Nitrate Solution, .01 N. Dissolve 1.700 g. of dried C.P. silver nitrate in 3 ml. of distilled water and add secondary butanol to make one liter. Agitate the mixture until all aqueous phase has dissolved. This alcoholic solution loses strength rather rapidly, but the deterioration can be markedly reduced if it is kept refrigerated when not in use. Standardize by titrating a solution of 50 ml. of secondary butanol containing 4 ml. of standard aqueous sodium chloride solution, using the electrometric set-up. It is usually more convenient to use the pH scale for the readings, although the millivolt scale can of course also be used. The titration curve of indicated "pH" or mv. versus ml. silver nitrate solution used should be plotted and the point of inflection taken as the endpoint.

Procedure

1. Pipette a suitable volume (normally 25 ml.) of the oily distillate into a 100 ml. beaker, add xylene, if required, to make the volume about 25 ml., then add 25 ml. of secondary butanol. Place the beaker in a grounded metal shield and raise into position so that the electrodes are well immersed.

2. Start the stirrer, and record the e.m.f. of the cell. The initial reading if observed on the pH scale may be off-scale on the low-reading end. On the millivolt scale voltages of about 450-550 mv. with the silver electrode negative may be observed. If the reading is below pH 0 (470 mv.), the solution should be titrated to this point and this volume used as the starting point of the mercaptan titration. This is because readings below pH 0 (higher than 470 mv.) indicate the presence of some residual H₂S in the oily distillate. Add the silver nitrate in small increments, and record the meter reading after equilibrium has been obtained upon each addition. Continue the titration to an indicated pH of 7.5, or 20 mv. (silver wire negative).

3. Plot the curve, take the titration volume at the point of inflection as the endpoint, and compute the mercaptan content by the formula given below. The inflections occur at an indicated pH of about 6.3 (90 mv.) for amyl and benzyl mercaptans, but the endpoints on distillates from crudes may vary between pH 5 and 6 (170-100 mv.). Occasionally the curves show no inflections; in such cases the readings at an arbitrary indicated pH of 6.3 are taken as the endpoints.

Blanks on the solvent system above should, of course, be determined and subtracted from the titration of the sample.

Calculations

$$M = \frac{3.2 AN}{V_s}$$

Where **M** = weight percent of mercaptan in the distillate, expressed as sulfur,

A = ml. of silver nitrate used,

N = its normality

V = volume of distillate titrated, ml.

and **s** = its specific gravity

SODIUM HYDROXIDE

Densities and Concentrations
at 60/60°F

Caustic Soda (NaOH)

| Degrees Baume | Specific Gravity | Weight % | Grams per Liter | Pounds per Gallon | Normality |
|---------------|------------------|----------|-----------------|-------------------|-----------|
| 1.0 | 1.007 | 0.60 | 6.04 | 0.05 | 0.15 |
| 2.0 | 1.014 | 1.22 | 12.35 | 0.10 | 0.31 |
| 3.0 | 1.021 | 1.86 | 18.97 | 0.16 | 0.47 |
| 4.0 | 1.028 | 2.50 | 25.68 | 0.21 | 0.64 |
| 5.0 | 1.036 | 3.15 | 32.61 | 0.27 | 0.81 |
| 6.0 | 1.043 | 3.81 | 39.70 | 0.33 | 0.99 |
| 7.0 | 1.051 | 4.50 | 47.25 | 0.39 | 1.18 |
| 8.0 | 1.058 | 5.18 | 54.75 | 0.46 | 1.37 |
| 9.0 | 1.066 | 5.88 | 62.62 | 0.52 | 1.56 |
| 10.0 | 1.074 | 6.60 | 70.82 | 0.59 | 1.77 |
| 11.0 | 1.082 | 7.31 | 79.02 | 0.66 | 1.97 |
| 12.0 | 1.090 | 8.05 | 87.67 | 0.73 | 2.19 |
| 13.0 | 1.098 | 8.79 | 96.43 | 0.80 | 2.41 |
| 14.0 | 1.107 | 9.54 | 105.51 | 0.88 | 2.64 |
| 15.0 | 1.115 | 10.30 | 114.74 | 0.96 | 2.86 |
| 16.0 | 1.124 | 11.09 | 124.54 | 1.04 | 3.11 |
| 17.0 | 1.133 | 11.88 | 134.48 | 1.12 | 3.36 |
| 18.0 | 1.142 | 12.69 | 144.79 | 1.21 | 3.62 |
| 19.0 | 1.151 | 13.51 | 155.36 | 1.30 | 3.88 |
| 20.0 | 1.160 | 14.33 | 166.08 | 1.39 | 4.15 |
| 21.0 | 1.169 | 15.17 | 177.17 | 1.48 | 4.42 |
| 22.0 | 1.179 | 16.02 | 188.70 | 1.57 | 4.71 |
| 23.0 | 1.189 | 16.89 | 200.64 | 1.67 | 5.01 |
| 24.0 | 1.198 | 17.78 | 212.81 | 1.78 | 5.32 |
| 25.0 | 1.208 | 18.68 | 225.45 | 1.88 | 5.63 |
| 26.0 | 1.218 | 19.61 | 238.63 | 1.99 | 5.96 |
| 27.0 | 1.229 | 20.55 | 252.33 | 2.11 | 6.31 |
| 28.0 | 1.239 | 21.50 | 266.15 | 2.22 | 6.65 |
| 29.0 | 1.250 | 22.47 | 280.62 | 2.34 | 7.01 |
| 30.0 | 1.261 | 23.46 | 295.57 | 2.47 | 7.38 |
| 31.0 | 1.272 | 24.46 | 310.84 | 2.59 | 7.77 |
| 32.0 | 1.283 | 25.50 | 326.67 | 2.73 | 8.17 |
| 33.0 | 1.295 | 26.52 | 343.13 | 2.86 | 8.57 |
| 34.0 | 1.306 | 27.61 | 360.26 | 3.01 | 9.00 |
| 35.0 | 1.318 | 28.71 | 378.06 | 3.15 | 9.45 |
| 36.0 | 1.330 | 29.86 | 396.78 | 3.31 | 9.91 |
| 37.0 | 1.342 | 31.00 | 415.78 | 3.47 | 10.39 |
| 38.0 | 1.355 | 32.21 | 436.05 | 3.64 | 10.90 |
| 39.0 | 1.368 | 33.42 | 456.78 | 3.81 | 11.41 |
| 40.0 | 1.381 | 34.67 | 478.36 | 3.99 | 11.95 |
| 41.0 | 1.394 | 36.00 | 501.50 | 4.19 | 12.53 |
| 42.0 | 1.408 | 37.31 | 524.85 | 4.38 | 13.12 |
| 43.0 | 1.422 | 38.70 | 549.81 | 4.59 | 13.74 |
| 44.0 | 1.435 | 40.00 | 573.28 | 4.78 | 14.33 |
| 45.0 | 1.450 | 41.61 | 602.80 | 5.03 | 15.07 |
| 46.0 | 1.464 | 43.00 | 628.76 | 5.25 | 15.71 |
| 47.0 | 1.480 | 44.68 | 660.66 | 5.51 | 16.51 |
| 48.0 | 1.495 | 46.27 | 691.11 | 5.77 | 17.28 |
| 49.0 | 1.511 | 48.00 | 724.72 | 6.05 | 18.11 |
| 50.0 | 1.526 | 49.60 | 756.21 | 6.31 | 18.90 |
| 51.0 | 1.543 | 51.32 | 791.14 | 6.60 | 19.77 |
| 52.0 | 1.559 | 53.10 | 827.08 | 6.90 | 20.67 |

SULFURIC ACID

Densities and Concentrations
at 60/60°F

| Degrees Baume | Specific Gravity | H ₂ SO ₄ Wt. % | lbs. H ₂ SO ₄ per gal. | Degrees Baume | Specific Gravity | Wt. % H ₂ SO ₄ | lbs. H ₂ SO ₄ per gal. |
|---------------|------------------|--------------------------------------|--|---------------|------------------|--------------------------------------|--|
| 0 | 1.0000 | 0.00 | 0 | 36 | 1.3303 | 42.63 | 4.73 |
| 2 | 1.0140 | 2.08 | .18 | 38 | 1.3551 | 45.35 | 5.12 |
| 4 | 1.0284 | 4.21 | .36 | 40 | 1.3810 | 48.10 | 5.54 |
| 6 | 1.0432 | 6.37 | .55 | 42 | 1.4078 | 50.87 | 5.97 |
| 8 | 1.0584 | 8.55 | .75 | 44 | 1.4356 | 53.66 | 6.42 |
| 10 | 1.0741 | 10.77 | .96 | 46 | 1.4646 | 56.48 | 6.90 |
| 12 | 1.0902 | 13.01 | 1.18 | 48 | 1.4948 | 59.32 | 7.39 |
| 14 | 1.1069 | 15.25 | 1.41 | 50 | 1.5263 | 62.18 | 7.91 |
| 16 | 1.1240 | 17.53 | 1.64 | 52 | 1.5591 | 65.13 | 8.47 |
| 18 | 1.1417 | 19.89 | 1.89 | 54 | 1.5934 | 68.13 | 9.05 |
| 20 | 1.1600 | 22.25 | 2.15 | 56 | 1.6292 | 71.17 | 9.67 |
| 22 | 1.1789 | 24.61 | 2.42 | 58 | 1.6667 | 74.36 | 10.3 |
| 24 | 1.1983 | 27.03 | 2.70 | 60 | 1.7059 | 77.67 | 11.0 |
| 26 | 1.2185 | 29.53 | 3.00 | 62 | 1.7470 | 81.30 | 11.8 |
| 28 | 1.2393 | 32.05 | 3.31 | 64 | 1.7901 | 85.66 | 12.8 |
| 30 | 1.2609 | 34.63 | 3.64 | 65 | 1.8125 | 88.65 | 13.4 |
| 32 | 1.2832 | 37.26 | 3.99 | 66 | 1.8354 | 93.19 | 14.3 |
| 34 | 1.3063 | 39.92 | 4.35 | | | | |

OLEUM TABLE

| Free SO ₂ % | H ₂ SO ₄ % | Free SO ₂ % | H ₂ SO ₄ % | Free SO ₂ % | H ₂ SO ₄ % |
|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|----------------------------------|
| 0 | 100.00 | 34 | 107.65 | 68 | 115.30 |
| 2 | 100.45 | 36 | 108.10 | 70 | 115.75 |
| 4 | 100.90 | 38 | 108.55 | 72 | 116.20 |
| 6 | 101.35 | 40 | 109.00 | 74 | 116.65 |
| 8 | 101.80 | 42 | 109.45 | 76 | 117.10 |
| 10 | 102.25 | 44 | 109.90 | 78 | 117.55 |
| 12 | 102.70 | 46 | 110.35 | 80 | 118.00 |
| 14 | 103.15 | 48 | 110.80 | 82 | 118.45 |
| 16 | 103.60 | 50 | 111.25 | 84 | 118.90 |
| 18 | 104.05 | 52 | 111.70 | 86 | 119.35 |
| 20 | 104.50 | 54 | 112.15 | 88 | 119.80 |
| 22 | 104.95 | 56 | 112.60 | 90 | 120.25 |
| 24 | 105.40 | 58 | 113.05 | 92 | 120.70 |
| 26 | 105.85 | 60 | 113.50 | 94 | 121.15 |
| 28 | 106.30 | 62 | 113.95 | 96 | 121.60 |
| 30 | 106.75 | 64 | 114.40 | 98 | 122.05 |
| 32 | 107.20 | 66 | 114.85 | 100 | 122.50 |

CONVERSION FACTORS FOR CONCENTRATION OF SALTS IN CRUDE OILS (1 barrel = 42 U.S. Gallons)

| Mg. per liter | Pounds per 1000 Bbls. | Grains per U. S. Gallon | Grains per B. I. Gallon |
|---------------|-----------------------|-------------------------|-------------------------|
| 1 | .350 | .0584 | .0701 |
| 2.85 | 1 | .167 | .200 |
| 17.1 | 6.00 | 1 | 1.20 |
| 14.3 | 5.00 | .833 | 1 |

Note: Mg./liter is equivalent to grams/kiloliter.

Mg./liter can be converted to parts per million (ppm.) by dividing mg./l. by the specific gravity of the oil.

Ppm. is also equivalent to grams/metric ton.

the residue at 1500°F., and obtained good recovery when using naphthenates of the metals in their control tests.

Another ashing procedure designed to avoid losses of the metallic elements and applicable to various petroleum fractions has been described by Karchmer and Gunn (31). Careful heating of the sample, with a final ignition temperature of 1000°F. for several hours, is prescribed to avoid metal loss. Comparison of results on a sample by this method with a wet ashing procedure showed good agreement, the latter giving only about 3% higher values in total ash. The various metals were determined colorimetrically and spectrographically in the residual ash.

Tests of the effect of ashing methods on the determination of porphyrins in oils have been made by Horeczy et al, (35) who used synthetic metalloporphyrins for the purpose. They found that the dry ash procedure was quite deficient in recovering the metals. 40% of the nickel, 12% of vanadium, 28% of iron and 55% of the copper was lost in the dry ash technique. Considerable care must therefore be exercised in the analysis of these materials, especially when present in small amounts.

The Petreco procedure detailed in the section on "Total Ash" is a semi-wet ash method and should be suitable for most determinations of organometallic compounds.

Arsenic is in a class by itself as a metallic impurity in petroleum distillates, as its adverse effect on catalysts, especially those of the platinum variety, is pronounced even when the arsenic concentration is in the low parts per billion. A method applicable to petroleum as well as to catalysts has been devised by Jay and Dickson (36), employing a wet oxidation method.

A method for arsenic in naphthas has also been developed by the Universal Oil Products organization. This method utilizes an extraction with acid to remove the arsenic, the organic matter which is simultaneously extracted being then eliminated by a wet-oxidation procedure. Jay and Dickson reported that acid extraction was not satisfactory for the samples with which they worked, and undoubtedly the nature of the oil has a considerable influence upon the suitability of any particular method.

The determination of lead in distillates is frequently required, and a number of methods are available. The Ethyl Corporation procedure utilizes a bromination step followed by a colorimetric estimation of the extracted lead by the dithizone reaction. A more recent method, described by Griffing (37), is sensitive in the 10 to 100 parts-per-billion range. It is based on similar analytical principles.

Since these methods are described thoroughly in the references given, and since they have not been thoroughly tested in the Petreco laboratories, they will not be presented here in detail.

DETERMINATION OF SODIUM

In the treatment of distillates with caustic solutions care must be exercised to minimize the amount of sodium which remains in the distillate after treatment. This residual sodium can be in the form of minute dispersed caustic droplets or as dissolved sodium soaps, which latter is often the case in heavy distillates in which the sodium soaps are more soluble. Treatment with high caustic concentrations or washing through a salt filter also tend to drive the soaps from aqueous droplets back into the oil phase. The

presence of residual sodium hydroxide is very undesirable since it has ash-forming tendencies and poisons catalysts, and its caustic nature tends to promote sediment formation and degradation of color. Normally about one part per million of sodium is all that can be tolerated without harm to the distillate properties. It is therefore important to analyze the treated distillate to make certain that an excessive amount of sodium is not present.

Sodium is best determined by flame photometry on a dilute hydrochloric acid solution of the metal. The actual measurement with a suitable spectrometer presents no particular difficulty, but the preparation of the sample for the test must be carefully carried out.

If the hydrocarbon can be collected directly from the process line (as in pilot plant testing) a sample of approximately 100 grams should be caught in a large platinum or silica dish. The sample is weighed and then ignited and allowed to burn to a carbonaceous residue, the latter being further reduced to inorganic ash in a muffle furnace at a maximum temperature of 550°C. The sodium compounds are extracted from the ash by adding 2 ml. of dilute (1 to 4) hydrochloric acid solution (sodium free) to the dish, the ash being macerated gently with a stirring rod in order to obtain good contact with the acid. The acid is poured into a 10-ml. volumetric flask and the extraction is repeated with an additional 2 ml. of acid. The ash is then washed successively with about 1-ml. portions of distilled water until the flask has been filled to the mark. Small particles of ash which may be swept into the flask are simply allowed to settle before the aliquot for the analysis is removed.

If the distillate can not be analyzed immediately as above, it should be taken in a clean, dry polyethylene bottle of at least one pint capacity and filled only to within two inches of the neck. 50 ml. of dilute (1 to 4) hydrochloric acid is measured with a pipette directly into the bottle, the bottle then capped and shaken vigorously to assure good contact between the oil and water phases. For quart-size samples, double the amount of acid is used. The aqueous phase is separated from the oil by means of a separatory funnel and is then ready for analysis.

The sodium content of the acid solutions obtained can be determined in the routine procedures prescribed for this element in spectrophotometric analysis methods. Suitable concentration-transmittance curves must of course be first determined and proper blank corrections made. Knowing the weight or volume of the total oil sample and the volume of the dilute acid added, calculation of the original sodium concentration in the hydrocarbon is readily made.

Tests on numerous samples by both methods have shown agreement to within .1-.2 ppm. in the 1 ppm. range.

ANALYSIS OF COKES

Due to the generally recognized adverse effect which salts in charging stocks have upon not only the amount of coke formation in still tubes, but also on the character (increased hardness) of this material, it is quite often desirable to analyze coke samples obtained from still tube clean-outs in order to determine the amount of salts and other solids present. Such analyses are often made before and after desalting in order to determine the degree of the beneficial effects derived from the desalting operation on this phase of the refining operations.

Samples of coke and similar materials are diverse in nature and may require special methods of treatment. The following scheme of analysis is valid for most of these substances, but variations may be necessary in handling certain specific cases.

Sampling. The coke samples are broken into pieces and ground in a large mortar to a coarse powder. This powder is sampled by quartering and the quarters further ground to pass a 200-mesh sieve. In cases where a high content of oily matter is present in the coke, it is best mixed and sampled with a steel spatula on a glass slab.

Determination of Free Iron and Magnetite. The prepared sample, if in powdered form, is examined magnetically for free iron and magnetite. The magnetic pieces from a weighed uniform sample of the material are separated and weighed. If they consist principally of magnetite (Fe_3O_4), they should be analyzed for iron.

Determination of Oil. Oily material in the coke is best determined by making a Soxhlet extraction with benzene on 10 or 20 g. of the prepared sample. The extracted material is dried in an oven at 100°F . and weighed, the loss of weight representing the benzene-soluble matter.

Determination of Total Volatile Portion. The total "volatile" portion of the coke may be determined by ashing about 0.5 g. in a platinum crucible. In most cases, it is best to carry out the ignition in the presence of oxygen, introducing a gentle stream of oxygen into the crucible by means of an alundum or porcelain tube. The ignition is continued to constant weight and the resultant ash then treated with 2 to 3 drops of concentrated sulfuric acid. The crucible is heated on the hot plate until the evolution of SO_3 fumes ceases and is then reignited to constant weight. The increase in weight obtained, if any, permits calculation of carbonates in the sample.

Determination of Silica. The sulfated and ignited ash is analyzed for silica by treating it with 5 drops of 6 N. sulfuric acid and 5 ml. of 48% hydrofluoric acid. The acids are evaporated on the hot plate just below the boiling point to avoid spattering, until sulfuric acid fumes are evolved; the crucible is then carefully ignited over a Meker burner for 15 minutes. The loss in weight represents the quantity of silica present.

Determination of Sulfur. Approximately 0.25 of the sample is weighed out and burned in a Parr peroxide bomb, using a nickel cup, with 1 Parr measure of sodium peroxide and 1 g. of sucrose. If iron is to be determined on this same combustion, the magnetic iron should be removed before the sample is weighed out. A blank determination should be run simultaneously on the sucrose. The contents of the bomb are dissolved in 50 ml. water in a beaker and acidified with concentrated hydrochloric acid (about 30 ml. are usually required). The acidified solution is made up in a volumetric flask to 500 ml. If constituents other than sulfur are to be determined, a 200 ml. aliquot is taken for the sulfur determination, the usual procedure of precipitation as barium sulfate being used.

Determination of Metals. The remainder of the solution from the peroxide bomb combustion left from the sulfur analysis, as described in the preceding section, is analyzed for iron, aluminum, calcium and magnesium according to the procedures for these constituents given elsewhere in these methods.

The large amount of salts present in the solution obtained from the

peroxide bomb combustion causes considerable contamination of the precipitates obtained from it, so that it is necessary to dissolve and reprecipitate the iron, calcium and magnesium precipitates. The iron precipitate is conveniently redissolved by placing the washed filter paper in a 250 ml. beaker, adding 5 ml. of concentrated hydrochloric acid, macerating the paper, and adding water to 150 ml. From this point on the technique is the same as the regular iron procedure, excepting that the oxidizing step employing bromine water may be omitted. The presence of the macerated filter paper will facilitate the filtration and ignition of the reprecipitated ferric hydroxide.

The calcium oxalate and the magnesium ammonium phosphate precipitates may each be dissolved in 5 ml. of 6 N. hydrochloric acid, diluted to 250 ml. and 400 ml., respectively, and the regular precipitation procedures repeated.

Determination of Chlorides and Soluble Sulfates. Ten grams of the powdered coke sample are mixed with 50 ml. of benzene and 25 ml. of acetone and heated to 120°F . in a 250 ml. graduate. It is best to let the hot mixture soak for about 15-30 minutes. 75 ml. of distilled water are added and after allowing the temperature to rise again to 120°F ., the system is emulsified with a piston. The analysis is made according to the Petreco salt extraction method, except that the aqueous extract is divided into two equal portions, one-half being titrated for chlorides, and the other half analyzed for sulfates, as previously described.

Calculations. In all of the following,

W = the weight of coke sample taken, in grams.

$$\% \text{ Benzene Soluble Matter} = \frac{100 L}{W}$$

Where L = loss in weight of extract when ashed, in grams.

$$\% \text{ Total "Volatile" Matter} = \frac{100 L}{W}$$

Where L = loss in weight of sample when ashed, in grams.

$$\% \text{ Carbonates as } \text{CO}_2 = \frac{167 G}{W}$$

Where G = gain in weight caused by sulfuric acid treatment, in grams.

$$\% \text{ Silica as } \text{SiO}_2 = \frac{100 L}{W}$$

Where L = loss in weight caused by HF treatment, in grams.

$$\% \text{ Sulfur (Parr Bomb Analysis)} = \frac{6870 B}{VW}$$

Where B = weight of barium sulfate precipitate, in grams,
 V = volume in ml. of aliquot taken from 500 ml. flask for analysis.

$$\% \text{ Chlorides as NaCl} = \frac{0.1 AC}{WF}$$

Where A = volume of silver nitrate used to titrate chlorides, ml.,
C = its concentration as grams NaCl per liter,
F = fraction of extract analyzed for chlorides.

$$\% \text{ Sulfates as Na}_2\text{SO}_4 \text{ (Aqueous Extraction)} = \frac{60.9 B}{WF}$$

Where B = weight of barium sulfate precipitate, in grams,
F = fraction of extract analyzed for sulfate.

$$\% \text{ R}_2\text{O}_3 = \frac{50,000 R}{WV}$$

Where R = weight of mixed iron and aluminum oxides, in grams,
V = volume in ml. of aliquot taken from 500 ml. flask for analysis.

$$\% \text{ Calcium as NaCl} = \frac{104,200 C}{WV}$$

Where C = weight of calcium oxide precipitate, grams,
V = volume in ml. of aliquot taken from 500 ml. flask for analysis.

$$\% \text{ Magnesium as NaCl} = \frac{52,500 M}{WV}$$

Where M = weight of magnesium pyrophosphate, in grams,
V = volume in ml. of aliquot taken from 500 ml. flask.

Reporting Results. In reporting the analytical results, it is customary to assume various hypothetical combinations among the ions. This is done by dividing the percentage of each component calculated as shown above by its equivalent weight, thus obtaining the number of equivalents of that component per hundred grams of coke. The first step is to subtract the sulfate sulfur from the total sulfur and to assign this remaining sulfur to iron, in this manner calculating the number of equivalents of iron sulfide assumed to be in the coke originally. Any excess of iron over sulfur is reported as iron oxide, and any excess of sulfur over the iron (as in the following example) is considered to be organic sulfur and hence a part of the total "volatile matter." Calcium is commonly assigned to carbonate and the percentage calcium carbonate in the coke calculated. If there is an excess of carbonate over that equivalent to calcium ion, the remaining carbonate is assigned to magnesium and the per cent magnesium carbonate in the sample obtained. Calcium and magnesium ions, in excess of carbonate, are calculated as sulfates. If the quantity of sulfate ion is not sufficient to combine with all the calcium and magnesium in excess of carbonate, any magnesium ion left over is assigned to the chloride ion. In the event that the sulfate ion is more than equivalent to the sum of the calcium and magnesium ions (in excess over carbonate ion), the excess sulfate ion is assigned to sodium. Chloride ion is assumed to combine with calcium and magnesium ions if there is an excess of these after combination with carbonate and sulfate. The remaining chloride ion is

reported as sodium chloride. If desired, the difference between the total "R₂O₃" and the ferric oxide may be determined by separate titration of the iron, and reported as alumina. (Nickel contamination from the bomb is not precipitated in any of the analytical steps.)

After the equivalents of each hypothetical component have been calculated, multiply each by its equivalent weight to obtain the percentage of that component contained in the original coke.

The per cent total volatile matter should be corrected by subtracting 70.3% of the percentage of carbonates expressed as CO₂ and 9% of the iron sulfide, as these two components are responsible for these corresponding weight losses of the sample on ignition. This corrected component should then be reported as organic matter, carbon, etc.

The following table shows the manner in which the determined constituents are treated to obtain the final composition or arrangement of the coke.

EXAMPLE OF CALCULATION OF HYPOTHETICAL COKE COMPOSITION

| Original Data | | | Combinations | | | |
|--|-------|------------------------|--|---|---------------------|------------------|
| Constituent of Analysis | % | Equivalents per 100 g. | Constituent (Org. S) (SO ₄) | Eq./100 g. (0.3364) (0.0010) ^c | (Final Report) % | (Final Report) % |
| S (total) | 6.00 | 0.3750 | (Org. S) | (0.3364) | (5.38) ^f | |
| SO ₄ as Na ₂ SO ₄ | 0.05 | 0.0010 | (SO ₄) | (0.0010) ^c | | |
| Fe ₂ O ₃ | 1.50 | 0.0376 ^a | FeS | 0.0376 | 1.65 | 1.65 |
| CO ₂ | 0.80 | 0.0266 | | | | |
| Ca as NaCl | 1.25 | 0.0214 ^b | CaCO ₃ | 0.214 ^d | 1.07 | 1.07 |
| | | 0.0068 ^b | MgCO ₃ | 0.0052 ^d | 0.22 | 0.22 |
| | | | MgSO ₄ | 0.0010 | 0.06 | 0.06 |
| Mg as NaCl | 0.40 | | MgCl ₂ | 0.0006 ^e | 0.03 | 0.03 |
| Cl as NaCl | 0.30 | 0.0051 ^b | NaCl | 0.0045 ^e | 0.26 | 0.26 |
| SiO ₂ | 0.01 | 0.0003 | SiO ₂ | 0.0003 | 0.01 | 0.01 |
| Total Volatile | 97.27 | | Organic matter, carbon, sulfur, etc. (g) | | 96.56 | 96.56 |
| | | | | | 99.86 | 99.86 |

(a) Calculated with valence of 2 because iron in coke is divalent; (b) Calculated with equivalent weight of NaCl; (c) Included in MgSO₄; (d) CaCO₃ plus MgCO₃ equals CO₂; (e) MgCl₂ plus NaCl equals Cl as NaCl; (f) Included in organic matter; (g) Calculated from total volatile by subtracting 70.3% of CO₂ and 9% of FeS.

DECOMPOSITION OF SALTS DURING DISTILLATION OF CRUDE OILS

It is well recognized that the origin of the extremely corrosive hydrochloric acid which is evolved during distillation of crude oils can only be the chlorides which are present in the original charging stock. Quantitative laboratory studies of the character of this decomposition have already been reported (2), (3). The distillation method used was essentially that described by Davis, Jones and Neilson (38). It involves the steam distillation of the oil sample at a definite rate to 650°F and titration of the evolved hydrochloric acid either acidimetrically or as the chloride. Since this method is very useful in providing information regarding the

evolution of hydrochloric acid under topping conditions, it will be described below. A general indication of the hydrogen sulfide and mercaptan evolution can also be obtained by suitable analysis of the overhead products if desired.

STEAM DISTILLATION METHOD

In this method, interest is focused upon the amount of hydrochloric acid evolved as a result of the hydrolysis of the salts contained in the oil. This may then be correlated with the corrosion of refinery fractionating equipment when the crude is subjected to ordinary straight-run distillation. No attempt is made to distinguish between chlorides and the other halogens, since the proportions of the latter are negligible. The quantities of hydrogen sulfide and mercaptans evolved can also be used for correlation with the corrosion of the pipe stills, and the amounts of sulfur compounds in the distillates resulting from the refinery distillation pro-

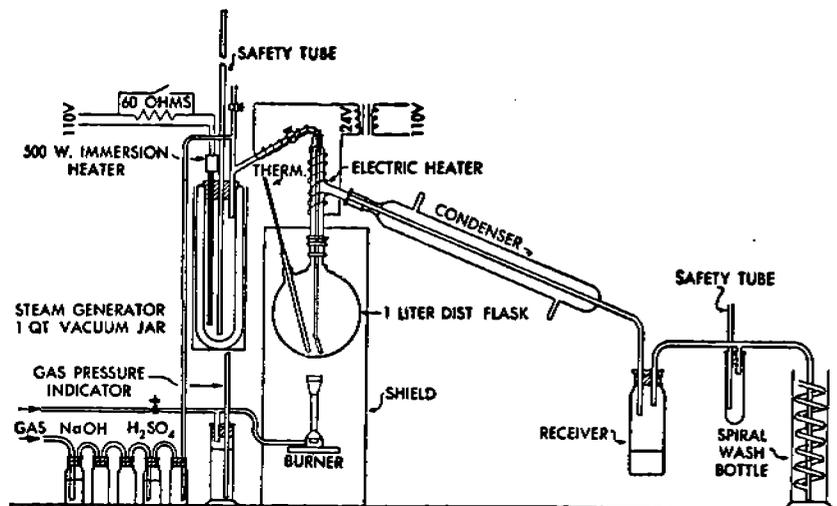


Fig. 11. Apparatus for H_2S and HCl Evolution.

cess. It should, of course, be kept in mind that for comparison with any particular commercial still, more directly comparable results will be obtained if the end temperatures are held to similar values.

In the method described below, provision is made for determining the amount of hydrochloric acid, hydrogen sulfide, and mercaptans evolved, as well as the gravity and volume of the distillate. If, as is often the case, only the HCl evolution is of interest, the method can be simplified by omitting the caustic in the receiver bottle. It is usually desirable to retain the gas wash bottle in the train, however, in order to prevent escape of sulfur compounds to the laboratory atmosphere.

Apparatus

The distillation apparatus is shown in Fig. 11. An itemized description follows:

Distillation Flask. The distillation flask is a 1 liter spherical flask which is provided with a standard taper 29/42 female fitting and a sealed-in thermometer well.

Condenser. The condenser is a 400 ml. Liebig condenser provided with 29/42 standard taper fittings and having the discharge tube bent at an angle of 105° so as to discharge vertically into the receiver.

Adapter. The adapter which serves to couple the flask and condenser is provided with two 29/42 fittings, and a 10/30 female fitting to take the steam inlet tubing.

Thermometer. This is a standard A.S.T.M. high-distillation thermometer.

Receiver. This consists of a 16-oz. screw cap bottle connected to the system by means of a bored rubber stopper.

Gas Wash Bottle. This wash bottle may either be a spiral tube gas wash bottle or one of the Milligan type. Its capacity should be about 150 ml. Fritted glass types of gas wash bottles are unsuitable because of excessive back pressure.

Steam Generator. The steam generator consists of a 1 qt. vacuum food jar provided with a large stopper through which is inserted a 500 watt immersion heater which serves to boil the distilled water contained in the jar. The immersion heater is connected to a switching system and a resistor of such size that when connected in series with the heater, the system generates steam at the rate of 40 g. in 45 minutes. The switches are so arranged that full voltage may be applied to the heater to allow quick warm-up to the steam generating point. A glass safety tube extends from near the bottom of the jar through the stopper to about 12 inches above the pressure in the jar. This serves as a vacuum release and as an indication of the pressure in the jar. The steam generated within the jar passes out through another glass tube and through a 4 mm. bore Pyrex stopcock and, by way of the lead-in tube, into the flask. The generator is conveniently refilled and its level tested by means of a rubber bulb and long glass tube which may be inserted through the safety tube into the water. Frequent removal of the large cork is conducive to leaks and should be avoided.

Purging Gas Wash Bottles. The gas used for purging the system at the end of the run is preferably a good grade of nitrogen, and may be used directly as it comes from the cylinder. If illuminating gas is used, it should be purified by first passing it through four 2 oz. bottles, the first of which contains 6 N. sodium hydroxide solution, the second and third being empty, and the fourth containing concentrated sulfuric acid. The first and fourth bottles have their inlet tubes reaching to the bottom of the bottle, while the second and third bottles have both inlet and outlet tubes cut flush with the inside of the stoppers. The empty tubes serve to prevent accidental mixing of the strong acid and alkali. The outlet from this wash bottle system is joined by means of a short length of rubber tubing to a glass tee in the tube conducting the steam to the flask. Except when purging the system at the end of a run, a pinch clamp on the short length of rubber tubing isolates these bottles from the steam line.

Meker Burner. Heat for the distillation is provided by a Meker burner. The pressure of gas applied to the burner is measured by means

of a manometer which enables delicate adjustment of the burner. An electric heater may be used in place of the Meker burner, but is less suitable because it is not so immediately responsive under adverse conditions, such as when the oil shows a tendency to foam over.

Vacuum Release. A vacuum release is provided between the gas wash bottle and the receiver to prevent the contents of the former from being drawn into the receiver when the heat is removed from the flask at the end of a distillation. This consists of a small water column manometer which prevents escape of gas from the system when under pressure but allows air to bubble back in when a vacuum is created.

Prevention of Condensation. To prevent condensation of steam in the adapter and steam line, these are wrapped with asbestos which is fastened by means of sodium silicate solution and then bound with a total of 3 ft. of No. 26 nichrome wire which is connected in series with a 40 ohm resistor to the 110 volt power supply. Condensation difficulties are further minimized by sloping the steam line in such direction as to drain toward the steam generator.

Interval Timer. An interval timer capable of reading up to one hour by minutes is desirable and is made still more convenient by inscribing the temperatures on its dial in such manner that the timer indicates directly the temperature which should be reached at any instant, as specified in the following distillation procedure.

Shield. The distilling flask and burner should be surrounded by a Transite shield to protect it from drafts and to keep the upper parts of the flask hot enough to reduce condensation.

Procedure

1. Heat the water in the steam generator to boiling and throw switch to the running position. Vent the steam until needed for the distillation.
2. Place 500 ml. of oil sample in the distilling flask and assemble the apparatus. It is better to weigh the oil than to measure its volume, as higher accuracy and freedom from sedimentation of emulsion are thus attainable. Before assembling the apparatus, coat the ground glass fittings with a thin layer of glycerine to prevent sticking.
3. Place 25 ml. of 1 N. sodium hydroxide in the receiver bottle and fill the spiral wash bottle with the same solution.
4. Switch on the wire heater around the steam inlet and adapter. Start the water through the condenser.
5. Light the burner and heat the flask so that the oil temperature rises about 18°F. per minute. When the temperature of the oil reaches 250°F., close the steam vent, and when the water has risen a few inches above the stopper in the steam generator manometer, open the stopcock leading to the distilling flask. From here on, reduce the rate of temperature rise to about 9°F. per minute. A test for complete absorption of H₂S may be made with lead acetate paper on the gases issuing from the wash bottle.
6. At 650°F. turn off the burner. Close the steam stopcock, vent the steam to the atmosphere, and disconnect the steam inlet tube after the system has cooled a little.

7. Flush the system for 5 minutes with nitrogen or with illuminating gas which has been passed through the four wash bottles.

8. Disconnect the receiver, quickly cap it, and shake thoroughly so that all residual hydrogen sulfide will be absorbed by the alkali. Wash the condenser with a few ml. of distilled water, collecting the rinsings in the receiver.

9. When chlorides only are to be determined, the contents of the receiver (but not of the absorber) are poured into a separatory funnel, the receiver rinsed, 3 ml. of 12 N. sulfuric acid added, the funnel shaken, and the aqueous layer withdrawn to a 100 ml. volumetric flask. The oil layer is washed by shaking with 25 ml. of distilled water and this extract combined with the preceding one. The flask is filled to the mark with distilled water and the contents thoroughly mixed. A suitable aliquot (50 ml. or less) is then analyzed for chlorides, as previously described.

10. When chlorides, hydrogen sulfide, and mercaptans are to be determined, mix the contents of the receiver and absorber in a separatory funnel, and add to the aqueous layer 0.5 ml. of 1% thymolphthalein indicator. Then add 6 N. sulfuric acid dropwise with gentle agitation of the separatory funnel contents, until the blue color is almost discharged. (If the two phases are vigorously shaken together in the acid condition the indicator may pass into the hydrocarbon layer, necessitating further addition of indicator to the aqueous layer to permit the final pH adjustment.) If the blue color is entirely discharged, a little 1 N. sodium hydroxide should be added to the aqueous layer to restore the color. When the color is believed to be correct the oil and water layers are emulsified by shaking, and the indicator color again adjusted after the water layer has completely settled. The final result is an oil layer which is in equilibrium with a light greenish water layer. If the proper endpoint has been obtained the aqueous phase will have a pH of 9.3 (± 0.2), and it is desirable when carrying out this procedure for the first time to check this with a pH meter.

11. When the aqueous layer is completely separated, withdraw it into a 500 ml. volumetric flask and wash the oil layer with 25 ml. of a 0.01 N. borax solution, draining this also into the same volumetric flask. Make up to the mark with distilled water.

12. Dilute a 50 ml. sample from the flask to about 100 ml. and determine total sulfide and chloride content by the electrometric method, as previously described. The aliquot taken may be reduced to as little as 5 ml. if the sulfur evolution was high.

13. Analyze another 50 ml. aliquot from the volumetric flask by treating for removal of sulfides and determining chlorides as previously directed. Calculate results by the formula given below under "Calculation of Chlorides, Sulfides and Mercaptans."

14. Measure the volume of the oily distillate in a graduated cylinder and determine its gravity by means of the specific gravity balance.

15. Analyze the oil layer for mercaptans by the following procedure.

Procedure for Mercaptans in the Distillate

The oil phase of the distillate is analyzed for mercaptans by titration with silver nitrate in secondary butanol. This method has already been

described under the section on the determination of mercaptans in distillates, q.v.

Calculation of Chlorides, Sulfides, and Mercaptans

The following are the formulas for the calculation of evolved hydrogen chloride, hydrogen sulfide, and mercaptans.

Hydrogen Chloride

$$S = \frac{350 ACM}{UV}$$

- Where S = the hydrogen chloride evolved, as sodium chloride, in ptb.,
 A = ml. of silver nitrate used to titrate chloride only,
 C = its concentration expressed as grams of sodium chloride per liter,
 M = capacity, in ml., of volumetric flask used in make-up,
 U = volume in ml. of oil charged to the distilling flask,
 V = volume in ml. of aliquot of aqueous phase titrated.

Hydrogen Sulfide

$$H = \frac{102 BCM}{UV'} - 0.291 S$$

- Where H = the hydrogen sulfide evolved, as H₂S, ptb.,
 B = ml. of silver nitrate required to titrate both chlorides and sulfides,
 C = its concentration expressed as grams per liter of NaCl,
 M = capacity, in ml., of volumetric flask used in make-up,
 U = volume in ml. of oil charged to the distilling flask,
 V' = volume in ml. of aliquot of aqueous phase titrated,
 S = the hydrogen chloride as calculated above.

Mercaptans

$$M = \frac{204 ACD}{UV}$$

- Where M = the mercaptans evolved as H₂S, ptb.,
 A = ml. of silver nitrate used to titrate the mercaptans,
 C = its concentration as grams per liter of NaCl,
 D = volume in ml. of the oily distillate,
 U = volume in ml. of oil charged to the distilling flask,
 V = volume in ml. of distillate titrated.

Discussion of Formulas

These calculations yield results which are based upon the original charge of oil rather than concentrations in the distillates. While the latter are the usual basis in refinery work, the present tests are generally made for reasons other than the determination of the quality of the distillates. Mercaptans are here calculated as pounds per thousand barrels of hydrogen sulfide on the basis of their sulfur content, (i.e., a quantity of mercaptans is regarded as equivalent to a quantity of hydrogen sulfide containing the same amount of sulfur). However, because the sulfur in mer-

captans is effectively monovalent, while in hydrogen sulfide it is divalent upon titration, a single atom of sulfur in the former condition will neutralize only one molecule of silver nitrate, whereas a single atom of sulfur as hydrogen sulfide will require two molecules of silver nitrate for its titration. Hence, in the calculation of the above formulas, the equivalent per ml. of silver nitrate used in the titration is only half as great for hydrogen sulfide as for mercaptans. If it is desired to convert hydrogen sulfide equivalents to sulfur, as for refinery work, multiply by 0.942. To convert to distillate concentrations, divide by the fraction of the total charge which appeared in the distillate.

TESTS FOR FOULING POTENTIALITY OF SETTLED ALKYLATES

Alkylates which contain residual dispersed sulfuric acid which has not been removed by the settling process tend to produce fouling of tubes in the alkylate reboilers, exchangers, etc., and to cause corrosion in the overhead vapor lines of depropanizers and debutanizers. The determination of the free sulfuric or sulfonic acid content of the alkylate is relatively simple, since it can be readily accomplished merely by titrating the strong acidity present in the sample. However, other materials contribute to this fouling also, such as the neutral esters formed in the process, and these are usually most responsible since they are not removed by the conventional settling and caustic washing procedures. The quantitative determination of these materials is more difficult, although various approximate procedures have been proposed. The most realistic and at the same time simplest test for a rough indication of the fouling tendencies of an alkylate is probably the Engler flask test, described by Brant (49).

ENGLER FLASK FOULING TEST

Procedure

Place 100 ml. of the weathered alkylate into an Engler flask and distil to the endpoint, as in a naphtha distillation. Observe the brown residue or stain in the bottom of the flask after cooling. The intensity of the discoloration is a rough measure of the amount of fouling to be expected from the sample.

TOTAL SULFATES BY KOH DIGESTION

Since it is sulfuric acid or its reaction products which are primarily the cause of the fouling tendencies of the alkylates, a simple method of estimating the potential fouling is to determine the total sulfate present in the sample. The usual procedures for sulfur are not directly applicable, but it has been found that digestion of the sample with alcoholic potassium hydroxide is effective in hydrolyzing the sulfate esters present, thereby converting them to sulfates which can then be determined by the usual quantitative procedures.

Tests with this method have shown that virtually complete hydrolysis of the esters is obtained by the prescribed digestion, since the Engler flask test mentioned above shows no carbonaceous residue or acidity in a fouling alkylate after it has been thus treated.

The following method is suggested for making this determination on weathered alkylate samples.

Requisites

- 500 ml. round-bottom flask
- Alcoholic KOH (20 g. KOH per liter of methanol)
- Heating mantle with variable voltage control
- Reflux condenser
- Separatory funnel
- 1 N Hydrochloric acid solution

Procedure

Place 100 ml. of the weathered alkylate and an equal volume of the alcoholic KOH in a 500 ml. round-bottom flask. Attach a condenser and heat the mixture until it refluxes, then adjust the temperature to a gentle reflux condition. Reflux the mixture for three hours and then transfer it to a separatory funnel.

Neutralize with hydrochloric acid to methyl orange and add enough water to spring all of the hydrocarbon out of solution. Draw off the alcoholic water phase into a beaker and boil out the methyl alcohol. The separated aqueous solution can then be submitted to the standard sulfate analysis by the barium chloride precipitation method.

"WATER REACTION" TEST FOR AVIATION FUELS

This test is designed to detect the presence of traces of surface-active materials which could contribute to difficulties in jet fuel, such as by their tendency to emulsify water, to adhere to tubing walls and jet surfaces, etc. It consists simply in shaking up a sample of the fuel with water and determining whether or not there is a clean break between the two phases after the mixture has been allowed to settle.

The test is made according to Military Specification F-5624C and is a modification of the previous "Water Tolerance Test of Aircraft Fuels" Specification VV-L-791, the modification including the optional use of a buffer solution instead of distilled water and some additional precautions in the manner of handling the sample while under test.

A rating of "1" means that the interface between the two liquids after settling is "clear and clean." A rating of "1-b" means that there are a few small bubbles around the periphery of the interface but no shreds, lace and/or film at the interface. Ratings "2," "3" and "4" are for progressively increasing amounts of scum and/or lace. Jet fuels are usually required to have a 1-b rating or better and a reciprocating engine fuel a rating of 2 or better.

Briefly, the method is as follows: 20 ml. of distilled or buffered water is placed in a scrupulously clean 100 ml. glass-stoppered cylinder and 80 ml. of the fuel is added. The cylinder is shaken for two minutes and then allowed to stand for five minutes on a vibration-free table. Details of the method and the prescription for the buffer are given in the Military Specification cited above.

REFERENCES

- (1) "Salts in Petroleum" (1946) and "Impurities in Petroleum" (1955), published by Petrolite Corporation.
- (2) Roberts, Stenzel and Eberz, *Petrol. Engineer* **10**, No. 4, 35; No. 5, 37; No. 6, 42; No. 7, 144; No. 8, 65 (1939).
- (3) Samuelson, *Petrol. Engineer* **26**, Dec., C-31 (1954).
- (4) R. E. Phelan, Paper No. 336-G presented to Petroleum Branch of the A.I.M.M.E. at Los Angeles, Oct. 1-2, 1953.
- (5) See for example, *Ind. Eng. Chem.* **20**, 83 (1928).
- (6) Lochte, *Ind. Eng. Chem.* **44**, 2597 (1952).
- (7) Sauer, Melpolder, and Brown, *Ind. Eng. Chem.* **44**, 2606 (1952).
- (8) Ball, Whisman, and Wenger, *Ind. Eng. Chem.* **43**, 2577 (1951).
- (9) Deal, Weiss, and White, *Anal. Chem.* **25**, 426 (1953).
- (10) Richter, Caesar, Meisel, and Offenhauer, *Ind. Eng. Chem.* **44**, 2601 (1952).
- (11) Viland, *Petrol. Refiner* **37**, No. 3 (March) 197 (1958).
- (12) Mills, Boedeker, and Oblad, *J. Am. Chem. Soc.* **72**, 1554 (1950).
- (13) Jones and Hardy, *Ind. Eng. Chem.* **44**, 2615 (1952).
- (14) Woodle and Chandler, *Ind. Eng. Chem.* **44**, 2591 (1952).
- (15) Mills, *Ind. Eng. Chem.* **42**, 182 (1950).
- (16) Abraham, "Asphalt and Allied Substances," D. Van Nostrand, N. Y. (1945).
- (17) Gallo, Carlson, and Biribauer, *Ind. Eng. Chem.* **44**, 2610 (1952).
- (18) Buchanan, Bruggink, and Lowry, *Refining Engineer* **30**, No. 2 (Feb.) C-19 (1958).
- (19) Duval, Malin, and Kalichevsky, *Petrol. Refiner* **34**, No. 9 (Sept.) 142 (1955).
- (20) Hanna and Johnson, *Anal. Chem.* **22**, 555 (1950).
- (21) Griswold and Kasch, *Ind. Eng. Chem.* **34**, 804 (1942).
- (22) Stenzel and Waterman, Tech. Paper 57-3, Western Petrol. Ref. Assoc. Meeting Houston, Texas, Feb. 7-8, 1957.
- (23) Blair, *Ind. Eng. Chem. Anal. Ed.* **10**, 207 (1938).
- (24) Horne and Christianson, U. S. Bur. Mines Rep. Inv. 3517 (1940).
- (25) Neilson, Hume, and Lincoln, *Ind. Eng. Chem. Anal. Ed.* **14**, 464 (1942).
- (26) Dickey and Sorg, *Am. Pet. Inst. Proc.* **28**, III, 57 (1948).
- (27) "Standard Methods of Water Analysis," Am. Pub. Health Assn. (1933).
- (28) Bureau of Mines Technical Paper 432 (1928).
- (29) "Applied Inorganic Analysis," Hillebrand and Lundell (1929).
- (30) Roberts, *Ind. Eng. Chem.* **10**, 518 (1938).
- (31) Karchmer and Gunn, *Anal. Chem.* **24**, 1733 (1952).
- (32) Lake, McCutchan, Van Meter, and Neel, *Anal. Chem.* **23**, 1634 (1951).
- (33) Carlson and Gunn, *Anal. Chem.* **22**, 1118 (1950).
- (34) Milner, Glass, Kirchner, and Yurick, *Anal. Chem.* **24**, 1728 (1952).
- (35) Horeczy, Hill, Walters, Schutze, and Bonner, *Anal. Chem.* **27**, 1899 (1955).
- (36) Jay and Dickson, *Petrol. Process* **9**, 374 (1954).
- (37) Griffing, Rozek, Snyder, and Henderson, *Anal. Chem.* **29**, 190 (1957).
- (38) Davis, Jones, and Neilson, *Oil and Gas J.*, **37**, No. 2, 62 (1938).
- (39) Lykken, Porter, Ruliffson, and Tuemmler, *Ind. Eng. Chem., Anal. Ed.* **16**, 219 (1944).
- (40) A.S.T.M. Method D664-51, "Neutralization Value by Electrometric Titration."
- (41) Mohler and Jacob, *Anal. Chem.* **29**, 1369 (1957).
- (42) Schmauch and Grubb, *Anal. Chem.* **26**, 308 (1954).
- (43) Wankat and Gatsis, *Anal. Chem.* **25**, 1631 (1953).
- (44) Noble, *Anal. Chem.* **27**, 1413 (1955).
- (45) Bond and Harriz, *Anal. Chem.* **29**, 177 (1957).
- (46) Wittmann, *Angew. Chem.* **60**, 33 (1948).
- (47) Fritz, *Anal. Chem.* **22**, 1028 (1950).
- (48) Moore, *Anal. Chem.* **23**, 1639 (1951).
- (49) Brant, *Petrol. Refiner* **36**, No. 9 (Sept.) 226 (1957).

SODIUM HYDROXIDE

Densities and Concentrations
at 60/60°F

Caustic Soda (NaOH)

| Degrees Baume | Specific Gravity | Weight % | Grams per Liter | Pounds per Gallon | Normality |
|---------------|------------------|----------|-----------------|-------------------|-----------|
| 1.0 | 1.007 | 0.60 | 6.04 | 0.05 | 0.15 |
| 2.0 | 1.014 | 1.22 | 12.35 | 0.10 | 0.31 |
| 3.0 | 1.021 | 1.86 | 18.97 | 0.16 | 0.47 |
| 4.0 | 1.028 | 2.50 | 25.68 | 0.21 | 0.64 |
| 5.0 | 1.036 | 3.15 | 32.61 | 0.27 | 0.81 |
| 6.0 | 1.043 | 3.81 | 39.70 | 0.33 | 0.99 |
| 7.0 | 1.051 | 4.50 | 47.25 | 0.39 | 1.18 |
| 8.0 | 1.058 | 5.18 | 54.75 | 0.46 | 1.37 |
| 9.0 | 1.066 | 5.88 | 62.62 | 0.52 | 1.56 |
| 10.0 | 1.074 | 6.60 | 70.82 | 0.59 | 1.77 |
| 11.0 | 1.082 | 7.31 | 79.02 | 0.66 | 1.97 |
| 12.0 | 1.090 | 8.05 | 87.67 | 0.73 | 2.19 |
| 13.0 | 1.098 | 8.79 | 96.43 | 0.80 | 2.41 |
| 14.0 | 1.107 | 9.54 | 105.51 | 0.88 | 2.64 |
| 15.0 | 1.115 | 10.30 | 114.74 | 0.96 | 2.86 |
| 16.0 | 1.124 | 11.09 | 124.54 | 1.04 | 3.11 |
| 17.0 | 1.133 | 11.88 | 134.48 | 1.12 | 3.36 |
| 18.0 | 1.142 | 12.69 | 144.79 | 1.21 | 3.62 |
| 19.0 | 1.151 | 13.51 | 155.36 | 1.30 | 3.88 |
| 20.0 | 1.160 | 14.33 | 166.08 | 1.39 | 4.15 |
| 21.0 | 1.169 | 15.17 | 177.17 | 1.48 | 4.42 |
| 22.0 | 1.179 | 16.02 | 188.70 | 1.57 | 4.71 |
| 23.0 | 1.189 | 16.89 | 200.64 | 1.67 | 5.01 |
| 24.0 | 1.198 | 17.78 | 212.81 | 1.78 | 5.32 |
| 25.0 | 1.208 | 18.68 | 225.45 | 1.88 | 5.63 |
| 26.0 | 1.218 | 19.61 | 238.63 | 1.99 | 5.96 |
| 27.0 | 1.229 | 20.55 | 252.33 | 2.11 | 6.31 |
| 28.0 | 1.239 | 21.50 | 266.15 | 2.22 | 6.65 |
| 29.0 | 1.250 | 22.47 | 280.62 | 2.34 | 7.01 |
| 30.0 | 1.261 | 23.46 | 295.57 | 2.47 | 7.38 |
| 31.0 | 1.272 | 24.46 | 310.84 | 2.59 | 7.77 |
| 32.0 | 1.283 | 25.50 | 326.67 | 2.73 | 8.17 |
| 33.0 | 1.295 | 26.52 | 343.13 | 2.86 | 8.57 |
| 34.0 | 1.306 | 27.61 | 360.26 | 3.01 | 9.00 |
| 35.0 | 1.318 | 28.71 | 378.06 | 3.15 | 9.45 |
| 36.0 | 1.330 | 29.86 | 396.78 | 3.31 | 9.91 |
| 37.0 | 1.342 | 31.00 | 415.78 | 3.47 | 10.39 |
| 38.0 | 1.355 | 32.21 | 436.05 | 3.64 | 10.90 |
| 39.0 | 1.368 | 33.42 | 456.78 | 3.81 | 11.41 |
| 40.0 | 1.381 | 34.67 | 478.36 | 3.99 | 11.95 |
| 41.0 | 1.394 | 36.00 | 501.50 | 4.19 | 12.53 |
| 42.0 | 1.408 | 37.31 | 524.85 | 4.38 | 13.12 |
| 43.0 | 1.422 | 38.70 | 549.81 | 4.59 | 13.74 |
| 44.0 | 1.435 | 40.00 | 573.28 | 4.78 | 14.33 |
| 45.0 | 1.450 | 41.61 | 602.80 | 5.03 | 15.07 |
| 46.0 | 1.464 | 43.00 | 628.76 | 5.25 | 15.71 |
| 47.0 | 1.480 | 44.68 | 660.66 | 5.51 | 16.51 |
| 48.0 | 1.495 | 46.27 | 691.11 | 5.77 | 17.28 |
| 49.0 | 1.511 | 48.00 | 724.72 | 6.05 | 18.11 |
| 50.0 | 1.526 | 49.60 | 756.21 | 6.31 | 18.90 |
| 51.0 | 1.543 | 51.32 | 791.14 | 6.60 | 19.77 |
| 52.0 | 1.559 | 53.10 | 827.08 | 6.90 | 20.67 |

SULFURIC ACID

Densities and Concentrations
at 60/60°F

| Degrees Baume | Specific Gravity | H ₂ SO ₄ Wt. % | lbs. H ₂ SO ₄ per gal. | Degrees Baume | Specific Gravity | Wt. % H ₂ SO ₄ | lbs. H ₂ SO ₄ per gal. |
|---------------|------------------|--------------------------------------|--|---------------|------------------|--------------------------------------|--|
| 0 | 1.0000 | 0.00 | 0 | 36 | 1.3303 | 42.63 | 4.73 |
| 2 | 1.0140 | 2.08 | .18 | 38 | 1.3551 | 45.35 | 5.12 |
| 4 | 1.0284 | 4.21 | .36 | 40 | 1.3810 | 48.10 | 5.54 |
| 6 | 1.0432 | 6.37 | .55 | 42 | 1.4078 | 50.87 | 5.97 |
| 8 | 1.0584 | 8.55 | .75 | 44 | 1.4356 | 53.66 | 6.42 |
| 10 | 1.0741 | 10.77 | .96 | 46 | 1.4646 | 56.48 | 6.90 |
| 12 | 1.0902 | 13.01 | 1.18 | 48 | 1.4948 | 59.32 | 7.39 |
| 14 | 1.1069 | 15.25 | 1.41 | 50 | 1.5263 | 62.18 | 7.91 |
| 16 | 1.1240 | 17.53 | 1.64 | 52 | 1.5591 | 65.13 | 8.47 |
| 18 | 1.1417 | 19.89 | 1.89 | 54 | 1.5934 | 68.13 | 9.05 |
| 20 | 1.1600 | 22.25 | 2.15 | 56 | 1.6292 | 71.17 | 9.67 |
| 22 | 1.1789 | 24.61 | 2.42 | 58 | 1.6667 | 74.36 | 10.3 |
| 24 | 1.1983 | 27.03 | 2.70 | 60 | 1.7059 | 77.67 | 11.0 |
| 26 | 1.2185 | 29.53 | 3.00 | 62 | 1.7470 | 81.30 | 11.8 |
| 28 | 1.2393 | 32.05 | 3.31 | 64 | 1.7901 | 85.66 | 12.8 |
| 30 | 1.2609 | 34.63 | 3.64 | 65 | 1.8125 | 88.65 | 13.4 |
| 32 | 1.2832 | 37.26 | 3.99 | 66 | 1.8354 | 93.19 | 14.3 |
| 34 | 1.3063 | 39.92 | 4.35 | | | | |

OLEUM TABLE

| Free SO ₂ % | H ₂ SO ₄ % | Free SO ₂ % | H ₂ SO ₄ % | Free SO ₂ % | H ₂ SO ₄ % |
|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|----------------------------------|
| 0 | 100.00 | 34 | 107.65 | 68 | 115.30 |
| 2 | 100.45 | 36 | 108.10 | 70 | 115.75 |
| 4 | 100.90 | 38 | 108.55 | 72 | 116.20 |
| 6 | 101.35 | 40 | 109.00 | 74 | 116.65 |
| 8 | 101.80 | 42 | 109.45 | 76 | 117.10 |
| 10 | 102.25 | 44 | 109.90 | 78 | 117.55 |
| 12 | 102.70 | 46 | 110.35 | 80 | 118.00 |
| 14 | 103.15 | 48 | 110.80 | 82 | 118.45 |
| 16 | 103.60 | 50 | 111.25 | 84 | 118.90 |
| 18 | 104.05 | 52 | 111.70 | 86 | 119.35 |
| 20 | 104.50 | 54 | 112.15 | 88 | 119.80 |
| 22 | 104.95 | 56 | 112.60 | 90 | 120.25 |
| 24 | 105.40 | 58 | 113.05 | 92 | 120.70 |
| 26 | 105.85 | 60 | 113.50 | 94 | 121.15 |
| 28 | 106.30 | 62 | 113.95 | 96 | 121.60 |
| 30 | 106.75 | 64 | 114.40 | 98 | 122.05 |
| 32 | 107.20 | 66 | 114.85 | 100 | 122.50 |

CONVERSION FACTORS FOR CONCENTRATION OF SALTS IN CRUDE OILS (1 barrel = 42 U.S. Gallons)

| Mg. per liter | Pounds per 1000 Bbls. | Grains per U. S. Gallon | Grains per B. I. Gallon |
|---------------|-----------------------|-------------------------|-------------------------|
| 1 | .350 | .0584 | .0701 |
| 2.85 | 1 | .167 | .200 |
| 17.1 | 6.00 | 1 | 1.20 |
| 14.3 | 5.00 | .833 | 1 |

Note: Mg./liter is equivalent to grams/kiloliter.

Mg./liter can be converted to parts per million (ppm.) by dividing mg./l. by the specific gravity of the oil.

Ppm. is also equivalent to grams/metric ton.

Notes

Notes
