Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Separation of Acidic Compound Types Isolated from High-Boiling Petroleum Distillates

J. F. McKay[a]; D. M. Jewell[ab]; D. R. Latham[a]
[a] DEPARTMENT OF THE INTERIOR LARAMIE, LARAMIE ENERGY RESEARCH CENTER BUREAU OF MINES U.S., WYOMING [b] Gulf Research and Development Co., Pittsburgh, Pennsylvania

To cite this Article McKay, J. F. , Jewell, D. M. and Latham, D. R.(1972) 'The Separation of Acidic Compound Types Isolated from High-Boiling Petroleum Distillates', Separation Science and Technology, 7: 4, 361 — 370
To link to this Article: DOI: 10.1080/00372367208055579
URL: http://dx.doi.org/10.1080/00372367208055579

SEPARATION SCIENCE, 7(4), pp. 361–370, 1972

The Separation of Acidic Compound Types Isolated from High-Boiling Petroleum Distillates

J. F. McKAY,* D. M. JEWELL,† and D. R. LATHAM

LARAMIE ENERGY RESEARCH CENTER
BUREAU OF MINES
U.S. DEPARTMENT OF THE INTERIOR
LARAMIE, WYOMING 82070

Abstract

Two methods for separating the acid compound types of high-boiling petroleum distillates have been investigated. The first method utilized ferric chloride and ion-exchange resins, and the second method used gel permeation chromatography. Each method was found to have merits, and the two methods can be used to complement each other. The major compound types of a Wilmington 400–500°C acid concentrate have been separated and identified using these methods. Data from the separation schemes will aid in the characterization of the acidic materials.

INTRODUCTION

Acidic compounds are an important group of the nonhydrocarbon compounds in petroleum. Considerable research time and effort have been expended in the study of these materials. Early work in this area is described in detail by Lochte and Littmann (*1*). More recently Seifert and Howells (*2*) extracted whole crude oils with sodium hydroxide–alcohol–water and separated the resulting acids by ion-exchange and

---

* To whom correspondence should be addressed.

† Present address: Gulf Research and Development Co., Pittsburgh, Pennsylvania.

silica gel chromatography. Snyder (*3*) used a series of adsorption chromatographic separations on silica gel, alumina, and charcoal to obtain fractions enriched in acid compounds.

As a part of American Petroleum Institute Research Project 60, we are currently involved in the characterization of the compound types present in petroleum distillates boiling about 400°C (750°F). A separation scheme was developed that divides these distillates into acid, base, neutral-nitrogen, saturate, and aromatic concentrates (*4*). The acid concentrate was isolated by ion-exchange chromatography using nonaqueous solvents. Compounds of many types and acid strengths are present in this concentrate, and thus additional characterization is required. Two methods were investigated to further separate these acid concentrates. One method used a combination of ferric chloride supported on kaolin and an anion-exchange resin to separate the concentrates. The other method utilized gel permeation chromatography (GPC). This paper discusses the merits of the two separation methods and suggests how they may be used in a complementary manner for the separation of acid concentrates into acidic compound types.

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded using a Perkin-Elmer Model 521 infrared spectrophotometer.* Molecular weights were obtained using a Mechrolab Model 301A vapor-phase osmometer. A description of the GPC apparatus was previously reported (*5*).

Reagents

The ferric chloride–kaolin substrate was prepared as described in an earlier publication (*6*). Sodium hydroxide was used to generate the hydroxide form of the Amberlyst A-29 anion resin (Rohm and Haas), and sodium carbonate was used to generate the carbonate form of the A-29 resin. The polystyrene gel (Waters Associates, Poragel A-1) used for gel permeation chromatography was preswollen in methylene chloride (*5*).

Preparation of the Distillate

The acid concentrate used in this investigation was obtained from a 400–500°C distillate from Wilmington, California, crude oil. The dis-

---

* Reference to specific brand names or models of equipment is made for information only and does not imply endorsement by the Bureau of Mines.

tillate was prepared in an inclined-plane still at reduced pressure (7). The temperature did not exceed 225°C during the residence time (30 sec or less) of the oil on the gold-plated surface of the still.

Preparation of the Acid Concentrate

A sample of 400–500°C distillate was placed on Amberlyst A-29 anion resin (hydroxide form). The column was eluted with pentane to remove nonreactive compounds. The material which was adsorbed on the resin was then desorbed using methanol saturated with carbon dioxide. This material represented about 4.5% of the distillate and was defined as the acid concentrate.

Method I. Ferric Chloride–Anion Resin

The first method used for the separation of compound types in the acid concentrate is outlined in Fig. 1. Approximately 450 mg of the acid concentrate was placed on the ferric chloride–kaolin substrate (30 g) and eluted with pentane. Nonreactive materials (predominantly oxygen-containing compounds) were removed in the pentane eluate. Reactive material (predominantly nitrogen-containing compounds) formed coordination complexes with the ferric chloride and was held on the column. These complexes were removed by desorption with 1,2-dichloroethane and then passed through a column of A-29 anion resin (hydroxide form) where the complex was broken. The metal salt was retained by the resin, while the nitrogen compounds were recovered in the effluent.

The two fractions obtained by this procedure were separated into seven subfractions of different acidity using ion-exchange resins eluted with various solvents. As an example, the fraction containing nitrogen compounds was dissolved in pentane and placed on A-29 resin in the carbonate form. Compounds which did not react with the resin (weak acids) were washed through the column and placed on a column containing A-29 resin in the hydroxide form. Strong acids reacted with the carbonate form of the resin. Both resins were then eluted with benzene, methanol, and methanol/CO_2, in that order. Some material was found to be nonreactive with either form of the anion resin.

Method II. Gel Permeation Chromatography (GPC)

The second method used for the separation and analysis of compound types in the acid concentrate is shown in Fig. 2. Experimental details of

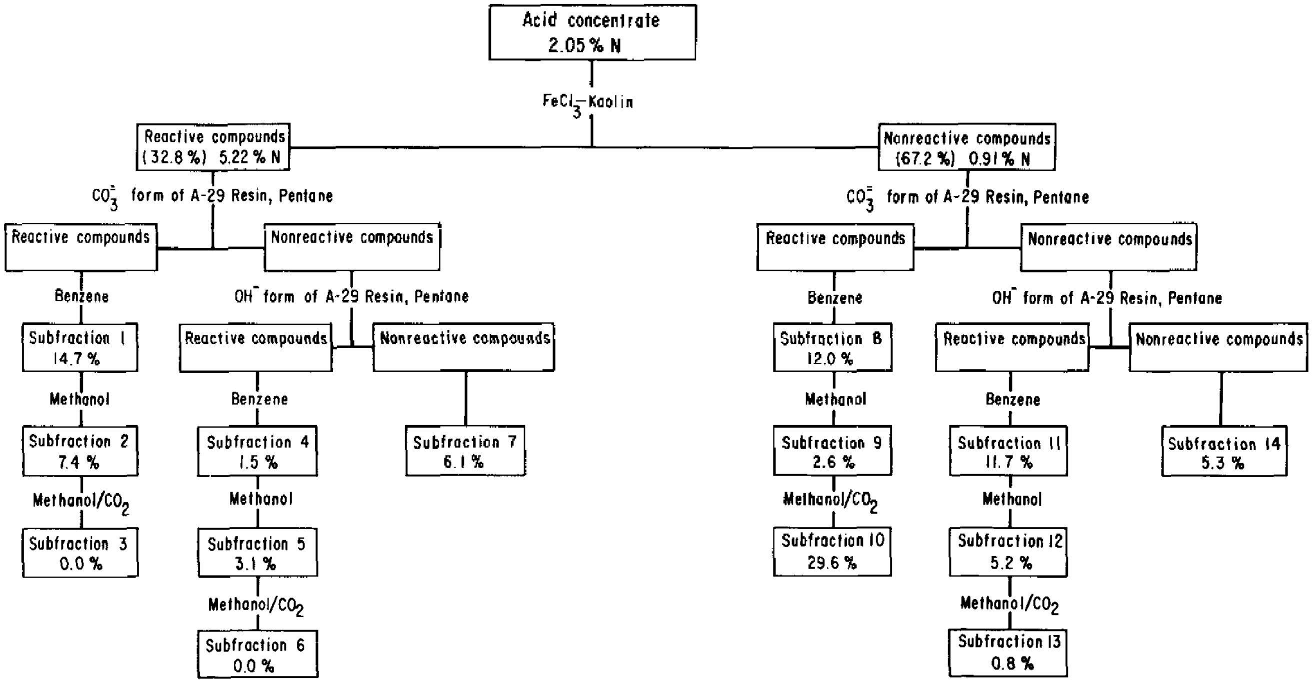

FIG. 1. The ferric chloride–anion resin separation scheme. The percentages shown are based on material recovered from the ferric chloride step. Fifteen to twenty per cent of the acid concentrate was lost during the ferric chloride step.

the GPC separation were previously described (*5*). The acid concentrate was passed through a 1.3 cm × 150 cm column which had been packed with 80 g of cross-linked polystyrene gel (Waters Associates, Poragel A-1). Methylene chloride was the solvent. The GPC subfractions were analyzed by IR spectroscopy and were combined into four fractions on the basis of the IR analysis.

RESULTS AND DISCUSSION

Method I

The first method utilized ferric chloride to separate nitrogen compounds from oxygen-containing compounds. These two fractions were further separated into subfractions of different acidity using anion-exchange resins.

Figure 1 shows that one-third of the material recovered from the ferric chloride treatment had reacted with ferric chloride. This fraction contained 5.22 wt-% nitrogen, whereas the original acid concentrate contained only 2.05 wt-% nitrogen. Two-thirds of the recovered material did not react with ferric chloride. Subsequent analysis indicated that the

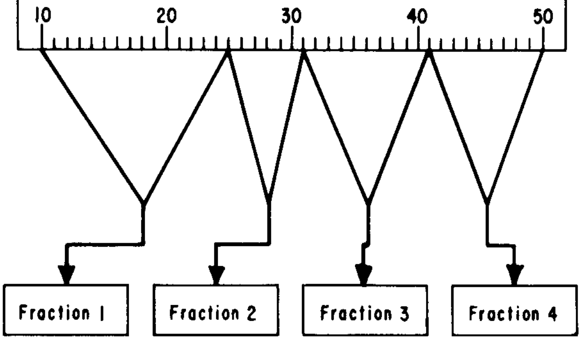

FIG. 2. The gel permeation chromatography separation scheme.

unreactive material is composed predominantly of oxygen-containing compounds, although it contains 0.91 wt-% nitrogen. Eighty to eighty-five percent of the total acid concentrate was recovered from the ferric chloride treatment.

Analysis of each of the 14 subfractions by IR spectroscopy (methylene chloride solvent) showed that carbazoles and amides had been concentrated in Subfractions 1, 2, 4, and 5, with very small amounts in Subfractions 8 and 12. Materials having N—H absorption of the pyrrolic type (carbazoles) were identified by the IR absorption band at 3460 cm^{-1} and amides of the quinolone type by adsorption at 1655 cm^{-1}. That all of the carbazoles and amides did not react with the ferric chloride is evidenced by the 3460 cm^{-1} absorption in Subfraction 8 and 1655 cm^{-1} absorption in Subfraction 12. Amides probably account for most of the 0.91 wt-% nitrogen found in the predominantly nonnitrogen fraction.

Phenolic compounds were concentrated in Subfractions 8, 9, and 11 as shown by IR absorption at 3590 cm^{-1}. Carboxylic acids were found in Subfractions 8, 9, and 10, as shown by the absorption at 1710 cm^{-1} due to the carbonyl band of acid dimers; an absorption band observed at 1735 cm^{-1} indicated the presence of acid monomers.

Although the acid concentrate was originally obtained by anion-exchange resins, a significant quantity of material was found to be nonreactive to the ion-exchange resins after the ferric chloride treatment, as evidenced by Subfractions 7 and 14. These subfractions were nearly colorless oils. They may contain entrained compounds such as hydrocarbons and/or other compounds which are essentially nonacidic by themselves but which are capable of being associated with other acidic materials; this weak association may be broken by the ferric chloride treatment or the anion-resin treatment. The IR spectra of these two subfractions indicated that OH and NH compounds were not present; but a carbonyl band was observed at 1730 cm^{-1}, possibly indicating the presence of ketones or esters.

Method II

The second method involved the use of GPC in which compounds are separated according to differences in effective molecular volume. GPC did not separate nitrogen compounds from oxygen-containing compounds nor did it separate compound types having different acidities. The weight percent of each fraction based on material recovered from two runs is shown in Table 1.

Fraction 1 represented a very small percentage of the acid concentrate, as shown in Table 1. The material found in Fraction 1 was not identifiable by IR analysis because functional group absorption was not observed. This high-molecular-weight material was more associated in methylene chloride solvent (mol wt 1860) than in tetrahydrofuran (mol wt 785). Since the compound types in the high-molecular-weight material are presently unknown, the mechanism of bonding is also unknown.

Fraction 2 was formed by combining GPC Subfractions 25 to 31 which showed carboxylic acid carbonyl absorption at 1710 and 1735 cm^{-1}. As shown in Table 1, these compounds accounted for approximately two-thirds of the acid concentrate. The carboxylic acids are thought to be separated from other compound types because they form dimers in methylene chloride solvent (*5*). Infrared absorption bands due to phenols, carbazoles, and amides were not observed in this fraction. Although phenols and carbazoles have low extinction coefficients relative to the carbonyl absorption of carboxylic acids (~150 vs. 500 to 1500) and may be difficult to detect in the presence of carboxylic acid absorption, it is unlikely that the carboxylic acid fraction is contaminated by more than 10% by weight of these compounds. Because the separation of the carboxylic acids from the other compound types is not a baseline separation, a small amount of contamination of Fraction 2 by the components of Fraction 3 is to be expected.

Fraction 3 was found by IR analysis to contain phenols, carbazoles, and amides. These materials represented about one-third of the acid concentrate. Only trace amounts of carboxylic acid were detected in the fraction. Fraction 4, which represented 1% or less of the acid concentrate, was a highly fluorescent aromatic material.

TABLE 1

GPC Separation of Acid Concentrate

	Percent by weight of recovered acid concentrate			
Run	Fraction 1 (high mol wt material)	Fraction 2 (carboxylic acids)	Fraction 3 (nitrogen compounds, phenols)	Fraction 4 (fluorescent aromatic material)
1	2.8	62.2	34.3	0.7
2	3.1	64.1	31.7	1.1

The gel permeation method of separating compound types was quite reproducible. Recovery of material passed through the column exceeded 98%.

Evaluation of the Two Separation Methods

A comparison of the two separation methods shows that each method has important advantages and disadvantages. In several respects the methods appear to be complementary. Table 2 shows some of the factors that determine the usefulness of each method.

The ferric chloride–anion resin method (Method 1) is especially useful for obtaining concentrates of nitrogen compounds and weakly acidic phenols. Materials isolated by this method are definable by relative acidity, and the fractions are suitable for studies which require rather pure compound types. This method requires a large amount of time to carry out the separation, a large number of fractions is obtained, and a considerable amount of material is lost during the separation.

The GPC method (Method II) is a very fast separation method which requires only about 4 hr for one run. Carboxylic acid concentrates relatively free from other compound types may be quickly obtained by this method. The separation is reproducible, and essentially all of the acid concentrate can be recovered from the column, thus the subsequent

TABLE 2

Comparison of Two Separation Methods

	Method I (ferric chloride and anion resin)	Method II (GPC)
Time required for separation	Days	Hours
Compound types isolated	Nitrogen compounds, weak phenols, entrained materials	Carboxylic acids, heavy mol wt materials, fluorescent aromatic materials
Percent of material lost during separation	15–20	Less than 2
Relative acidity of compound types	May be determined	May not be determined

analyses are carried out on the total sample. Chemical artifacts are probably not produced by this separation method. Phenols are not separated from amides and carbazoles, and the fractions are complex.

The two methods complement each other. For example, carboxylic acids are readily isolated by the GPC method but are more difficult to isolate by Method I. Carboxylic acids are apparently adsorbed on kaolin and account for the material lost during the ferric chloride separation step. Although phenols cannot be isolated for further study by the GPC method, weakly acidic phenols may be isolated by the ferric chloride–anion resin method. Efforts are currently being made to use a combination of the two methods for the isolation of all phenolic materials. Carboxylic acids are first removed using the GPC method, and then phenols and nitrogen compounds are separated using the ferric chloride method. Some materials may be more easily detected in the acid concentrate by one method than by the other. The heavy molecular weight material isolated by the GPC method was not observed to be a discrete material by the ferric chloride method.

Data from the separation schemes themselves aided in the characterization of the acidic material. For example, compound types isolated by the ferric chloride–anion resin scheme may be classified as weak acids or strong acids, depending on where they were found in the separation scheme. GPC indicated that some components of the acid concentrate exist in solution as associated molecules while other components are not associated. This behavior was related to specific functional groups present in the molecules.

Acknowledgment

This investigation was performed as a part of the work of American Petroleum Institute Research Project 60 on the Characterization of the Heavy Ends of Petroleum, carried out by the Bureau of Mines at Laramie, Wyoming. Work was done under cooperative agreements between the Bureau of Mines, U.S. Department of the Interior; the American Petroleum Institute; and the University of Wyoming.

REFERENCES

1. H. L. Lochte and E. R. Littmann, *Petroleum Acids and Bases*, Chemical Publishing Co., New York, 1955.
2. W. K. Seifert and W. G. Howells, *Anal. Chem.*, *41*, 554 (1969).
3. L. R. Snyder, *Acc. Chem. Res.*, *3*(9), 290 (1970).

4. D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, *Amer. Chem. Soc., Div. Petrol. Chem. Preprints*, *16*, September 1971.
5. T. E. Cogswell, J. F. McKay, and D. R. Latham, *Amer. Chem. Soc., Div. Petrol. Chem. Preprints*, *15*(3), A133 (1970); *Anal. Chem.*, *43*, 645 (1971).
6. D. M. Jewell and R. E. Snyder, *J. Chromatogr.*, *38*, 351 (1968).
7. W. E. Haines, *Proc. Amer. Petrol. Inst.*, *42*, *VIII*, 51 (1962).

Received by editor November 4, 1971