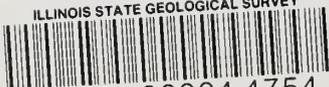


ILLINOIS STATE GEOLOGICAL SURVEY



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SPECTROCHEMICAL DETERMINATION OF COPPER, NICKEL, AND VANADIUM IN CRUDE PETROLEUM

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ABSTRACT

A procedure for analyzing crude petroleum for copper, nickel, and vanadium present as traces in Illinois crude petroleum is described. The method involves concentration of the metals in the ash from 100 grams of crude oil and converting the ash to a solution in dilute hydrochloric acid. The determination is made by spectrographic means using a rotating electrode with high voltage spark excitation. The precision of the method is of the order of 1 ppm in the range of 1 to 10 ppm.

INTRODUCTION

Recently the trace element content of crude petroleum and of products derived therefrom have attracted considerable attention. This interest has centered, on one hand, among geologists who are concerned with any facts which might shed light on questions related to petroleum geology and, on the other, among petroleum and chemical engineers in the oil refining industry who are interested in the bearing of these trace elements on design and operation problems.

The method here described for determining copper, nickel, and vanadium was designed to fit the equipment available in our laboratory and to obtain data on Illinois crude petroleum for the purpose of testing the usefulness of such data in correlating the trace metal content of crude petroleum with the geologic horizon or with the field from which the crude petroleum was obtained. The correlation aspects will be discussed elsewhere in a report by Paul A. Wither-
spoon and Kozo Nagashima.

METALS IN CRUDE PETROLEUM AND THEIR GEOCHEMISTRY

Some metals are thought to exist in petroleum as oil-soluble or dispersible compounds, such as metal chelates, probably porphyrin complexes. Because some of these metals appear in the distillates from petroleum, these compounds are presumably volatile to some degree. There is also evidence that they possess lyophylic groups.

Woodle and Chandler (1952) studied the mechanism of the distillation of vanadium in petroleum refining and concluded that this metal might exist in crude petroleum associated with a family of compounds having a broad molecular weight range. Only those on the lower end of this range were observed in the distillates. Skinner (1952) reported that all vanadium in Santa Maria Valley petroleum is present as a porphyrin complex which is stable up to 230°F. Erdman et al. (1956) demonstrated the volatility of metallo-porphyrin complexes of copper, nickel and vanadium.

Dodd, Moore, and Denekas (1952) studied the surface activity of metalliferous substances in crude petroleum and observed a selective adsorption of the complexes involving zinc, copper, nickel, titanium, calcium, magnesium, iron, and vanadium at petroleum-water interfaces. These facts have significant bearing on the behavior of trace metals as related to the geochemistry and the refining of petroleum, as well as to the methods used to analyze for the trace metals themselves.

The evidence is quite convincing that metal porphyrin complexes exist in petroleum. It seems quite likely that other organo-metal complexes may occur, or perhaps that metal ions adsorbed on macromolecules may account for a part of the trace metals found in petroleum. Crude petroleum as it comes from the well is usually a mixture of hydrocarbons, brine, and more or less solid material in the form of small suspended particles. On storage some stratification and some reaction with air is to be expected. Karchmer and Gunn (1952) described such stratification in a crude oil and separated a part of the metal contaminants from the oil by centrifugation and filtration.

Among the variety of elements which have been reported as present in petroleum samples from many places on the earth, nickel, vanadium, copper, and iron predominate.

We detected silver, aluminum, boron, barium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, sodium, nickel, lead, silicon, tin, titanium, and vanadium in the ash from 750 grams of crude petroleum from the Salem field in Illinois. (The elements underlined were present in much greater quantity than the others.) The spectral region covered was 2300 Å to 3400 Å. The ashing was carried out with 110 milliliters of concentrated sulfuric acid and 50 milligrams of purified calcium carbonate as ash collector. Strontium was ignored because of high strontium blank in the calcium carbonate.

Numerous studies of geochemical nature indicate that in crude oils from the same formation or reservoir the content of nickel and vanadium and/or the ratio of the contents of these metals tends to be constant. Some of these studies suggest that the nickel-vanadium ratio may play an important role in the explanation of the origin and migration history of petroleum. The iron and copper contents, as well as those of the less prominent elements, are apt to vary in most erratic ways in contrast with the regularity observed in the case of nickel and vanadium. This may be due to contamination from sources other than petroleum itself, for instance rocks, brine, or well equipment. Whatever the reason for the regularities which characterize the nickel-vanadium content, it has directed the attention of most workers to these two metals.

Method of Analysis

Various methods have been used for determining trace metals in petroleum, but only those employing the spectrochemical approach are considered here. The methods used have been influenced by the reasons for making the determination. If the reason had to do with catalyst poisoning in the cracking stills, for instance, the analysis would not be made on the crude petroleum, but on the charging stock. This report is concerned only with methods designed for crude oils.

Two approaches are available using the spectrographic method: 1) the oil may be arced directly; 2) some method of concentration may be employed and the determination made on the concentrate. The first is recommended by its simplicity, but is impractical in most cases for crude oils because of the extremely small amount of metal usually present.

Direct Spectrochemical Methods

Direct spectrochemical methods have proved useful in the analysis of lubricating oils, and some modifications have been applied to crude oils. Key and Hoggan (1953) used a method which employed a high voltage spark discharge and a rotating disk electrode. They reported limits of detection in parts per million for calcium 0.4, for sodium 0.2, for nickel 10, and for vanadium 2.

Meeker and Pomatti (1953) developed a method for use with lubricating oil which involved arcing a sample previously treated with graphite powder. This method was applied by Gent et al. (1955) to crude oil. Carlson and Gunn (1950) employed the electrode impregnation technique with cathode layer excitation and obtained analytical ranges of 2 to 100 ppm for some metals. Bonham (1956) ashed small amounts of crude oil in the electrode cavity and used cathode layer excitation. He reported lower limits, about 0.1 ppm, for nickel and vanadium by his method.

Concentration of Metals

Several procedures for concentrating the metals present in crude petroleum have been reported based on dry ashing, ashing with sulfuric acid, catalytic decomposition with silica (McEvoy et al., 1955), acid extraction, ion exchange resin extraction (Buchwald and Wood, 1953), and so forth.

Karchmer and Gunn (1952) presented a good review of the problems involved in sampling, ignition, combustion, and determination of the metals. Horeczy et al. (1955) have shown that wet ashing (ashing with sulfuric acid) recovers more metal than dry ashing. They added synthesized porphyrin complexes of nickel, copper, iron, and vanadium to crude oil, and after ashing by the two processes analyzed for the metals. Their results indicated essentially complete recovery for samples that were wet ashed, but significant losses from the dry-ashed samples. Gamble and Jones (1955) and Milner et al. (1952) found that wet ashing resulted in higher figures for the metals.

Barney and co-workers (1955) compared results when a variety of concentration procedures were used. These included (a) dry ashing, (b) total sulfated ashing, (c) partial sulfated ashing, (d) extraction with iodine solution, (e) extraction with a mixture of acetic acid and hydrobromic acid, (f) extraction with a mixture of acetic acid and hydriodic acid, (g) extraction with sulfuric and hydrochloric acid. Their results indicated quantitative recovery of copper, iron, lead, nickel, and vanadium by procedures (b) and (e) and (g).

We experimented with total sulfated ashing, catalytic decomposition with silica, and extraction with sulfuric acid and hydrochloric acid in an attempt to find the most satisfactory procedure for our laboratory. We examined recovery of metals by making known additions of metallo-organics to our crude

oils. From the viewpoint of recovery, all three procedures proved adequate. However, after consideration of problems of detail, we decided to adopt the total sulfate ashing procedure, described below.

Procedure for Preparation and Analysis of Oil Samples

Outline of Method

The washed and filtered sample was ashed in a Vycor beaker with appropriate amounts of concentrated sulfuric acid and nitric acid. A small amount of cobalt nitrate solution was added before ashing to serve as an internal standard for the spectrochemical analysis. The ash was dissolved in dilute hydrochloric acid. The solution was arced, using a rotating disk electrode and a porcelain boat. The excitation was by means of a high voltage spark. Analytical calibrations were made from a series of standard solutions containing varying amounts of nickel, copper, vanadium, and the constant amount of cobalt.

Preparation of Sample

From the bulk sample as delivered to the laboratory, a portion of the oil layer was transferred to a separatory funnel and shaken with an equal volume of distilled water. After standing over night the oil layer was placed in a centrifuge bottle and centrifuged for about 10 minutes to remove most of the water. The oil was then filtered through a dry filter paper.

This procedure appeared effectively to remove drops of water and coarse solids. Analysis for iron, nickel, copper, and vanadium was carried out on one sample before and after this washing procedure. Before washing, the iron content was found to be 13.7 ppm. After washing, the iron content had dropped to .2 ppm, but the other metals showed no significant change.

Internal Standard Solution

Internal standard solution was made up to concentration 0.14 mg Co/ml. (Precise adjustment of concentration of cobalt is not necessary if adequate amount is made up to last through calibration and analysis of all samples.) 2.00 ml. of this cobalt solution was added to the sulfuric acid to be used in ashing the sample. Reagent grade cobaltous nitrate was used. Sulfate or chloride would probably serve as well. In any case, the blank must be satisfactorily low in nickel, copper, and vanadium.

Ashing

One hundred grams of the crude oil was weighed into a tared Vycor beaker (800 ml.) and the mixture of 2.00 ml. Co solution and 100 ml. of concentrated sulfuric acid added, then 5 ml. concentrated nitric acid.

When the mixture was swirled in the beaker the vapors usually ignited spontaneously and were permitted to burn. After about 30 minutes the contents of the beaker were reduced to a cokelike solid. Due caution must be observed because vigorous foaming sometimes occurs near the end of the burn-down period. If foaming threatens to get out of control, it can be controlled by stir-

ring with a Vycor rod. Even if a small amount is lost over the top of the beaker, it is not fatal because of the fact that the internal standard was added beforehand.

After the burn-down the beaker was placed on a hot plate at low red heat until fuming ceased (about 2 hours). It was then placed in a muffle furnace, preheated to 550°C and held at this temperature until all carbon was consumed. A slow current of air was passed through the furnace during this heating. (Temperatures higher than 550°C tend to make the ash difficult to dissolve in hydrochloric acid.)

The residual black ash (chiefly cobalt oxide) was dissolved in 2 ml. of redistilled constant boiling HCl solution. The solution was transferred to a small beaker with a mark indicating the 10 ml. level. The Vycor beaker was rinsed out with hot dilute HCl. The rinsings were added to the main solution and the volume adjusted to 10 ml. Because the internal standard method was used the adjustment need not be precise.

In our laboratory 100-gram samples of oil were the rule. For this size sample, 10 ml. of the final solution is convenient and adequate for the spectroanalysis for copper, nickel, and vanadium in crude oil. If smaller oil samples are used, the quantities of reagents and standard may be scaled down proportionately.

The blank for copper (and lead if lead is to be determined) is not negligible, even in reagent sulfuric acid, and it changes from lot to lot. This blank was checked by two procedures: 1) the complete ashing procedure was carried out using redistilled benzene instead of crude oil; 2) 100 ml. of the sulfuric acid plus 2 ml. of the cobalt standard solution was evaporated to dryness and the residue taken up in hydrochloric acid in the usual way. Spectro determination of the metals present in the residue gave essentially the same blank by either procedure.

Standards for calibration

Standard stock solutions of copper, nickel, and vanadium, each containing one milligram of the metal per milliliter, were made up by dissolving in dilute HCl solution reagent grade nitrates of copper and nickel and ammonium metavanadate. The salts must of course have satisfactorily low metal blanks with reference to each other.

Standard solutions containing 1.00 mg., 0.400 mg., 0.100 mg., 0.040 mg., and 0.010 mg. of each element plus 0.28 mg. cobalt and 2 ml. of 18 percent (constant boiling) hydrochloric acid in 10 ml. are freshly prepared as needed from the stock solutions. These concentrations correspond to 10.0, 4.00, 1.00, 0.40 and 0.10 parts per million of the metals in the crude oil when a 100-gram sample of the oil is ashed and the ash solution adjusted to 10 milliliters as described above.

Apparatus, Analytical Techniques, and Data

The apparatus used in these studies was standard and included the spectrograph, etc., as listed below.

Spectrograph. - Bausch and Lomb large quartz Littrow.

Plates. - Kodak 33.

Microphotometer. - National Spectrographic Laboratory's Spec Reader (non-recording).

Electrodes. - The lower electrode was a disk 2 mm. thick by one-half inch in diameter, rotated about 10 rpm in a vertical plane on a shaft made of 3/16 inch regular grade electrode stock. (A stainless steel shaft was tried but contamination of iron and nickel was observed at times with this shaft.) The disk was made of special grade graphite electrode stock. Its lower edge dipped in the sample solution contained in a 2-ml.-capacity porcelain boat.

The upper electrode was made from 3/16 inch special grade graphite rod with the end cut flat and turned down to one-tenth inch diameter.

Excitation. - High voltage spark with source unit adjusted to give three breakdowns per half cycle. An inductance setting of 250 micro henrys was chosen because of the settings available on our source; this value resulted in the lowest background and the cleanest spark. Varying the capacitance with this inductance seemed to make no noticeable difference.

Exposure Time

A moving-plate study was made to determine a satisfactory exposure time, using a solution containing copper, nickel, vanadium, and the cobalt standard in hydrochloric acid solution under excitation conditions as described above. After the first 20 seconds the line intensities of the metals and the ratio of these intensities to those of the cobalt standard remained nearly constant up to 180 seconds exposure. This showed that the vaporization rates of copper, nickel, and vanadium were about the same as that of cobalt, so that any exposure between 20 and 180 seconds would be allowable. The exposure chosen was 150 seconds because the solution in the boat was approximately all evaporated in that time and the sensitivity was adequate for analysis of our crude oil samples. Prolonged exposure and more sample solution would probably result in increased sensitivity if it were required.

Spectrographic Technique

Approximately 2 ml. of sample concentrate or standard solution was placed in the boat and the excitation started after the disk electrode had made one revolution. The slit width was 20 microns. A rotating step sector (ratio 2.0 with four steps including the uninterrupted exposure) was used. The plates (Kodak 33) were developed in D-11 developer.

Calibration

Using the standard solutions already described, working curves were obtained for the line pairs listed in table 1. The slopes of the curves of log concentration of the element versus log intensity ratio of the element line to the cobalt line was very nearly unity over the calibration range 0.1 to 10 parts per million.

Table 1. - Line Pairs Used for Analysis

Element line Å	Internal Standard line Å	Calibration Range ppm	Detection Limit ppm
Cu 3247	Co 3044	0.1 to 10	0.05
Ni 3050	"	0.1 to 10	0.2
V 3093	"	0.1 to 10	0.1
*Fe 2631.3	Co 2632	0.1 to 10	0.1

*Although not used in this work, a normal working curve for iron was obtained.

Effect of Character of Spark Source

Repeat analyses of two samples of oil for copper, nickel, and vanadium, using in turn excitation with two, three, and four breakdowns per half cycle, did not show differences greater than normal deviation for repeat analyses using three breakdowns per half cycle.

Recovery in Ashing and Accuracy of Results

To study the recovery of the trace metals in the ashing procedure and the subsequent analysis, known amounts of metallo-organic compounds were added to a crude oil sample designated as No. 68. The samples with and without additions were then ashed and analyzed in the standard manner.

Known weights of metallo-organic solutions containing nominally 6 percent nickel, 3 percent vanadium and 8 percent copper were diluted with redistilled benzene. (These metallo-organic solutions were prepared by the Nuodex Products Co., Elizabeth, N. J., and were purchased from the National Spectrographic Sales Corp., Cleveland, Ohio.) The final concentrations (based on the nominal figures given) were 0.05₆ mg./5 ml. of copper, 0.05₂ mg./5 ml. of nickel, and 0.05₅ mg./5 ml. of vanadium. These solutions were added to 100-gram samples of No. 68 crude oil. The amounts added were 5 ml., 10 ml.,

Table 2. - Tests of Recovery (by known additions)

Element and Trial	Milliliters of solution of metallo-organic added to 100 grams of No. 68 crude oil									
	0		5		10		20		40	
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
Copper										
1	0	0.24	0.56	0.88	1.1	1.4	2.2	2.4	4.4	4.2
2					1.1	1.8	2.2	2.6	4.4	2.9
Nickel										
1	0	2.0	0.52	2.5	1.04	3.2	2.08	4.4	4.16	6.4
2					1.04	3.1	2.08	4.3	4.16	5.9
Vanadium										
1	0	0.96	0.55	1.6	1.1	1.9	2.2	3.0	4.4	4.7
2					1.1	2.3	2.2	3.5	4.4	5.0

20 ml., and 40 ml. One sample was used with 5 ml. additions, and two samples each for the larger additions, that is, seven samples in all. These samples were ashed and analyzed.

The results are set forth in table 2. The agreement between "added" and "found" (ppm added, and ppm added + ppm originally present in the crude) seems satisfactory. The presumption is that the two varieties behave similarly in the ashing procedure. If this is so, the recovery of the metals by the ashing procedure may be considered good and the analytical results given by our method are close to the true values.

Precision of Analytical Results

Duplicate ashing and spectrographic procedures were carried out on seven Illinois crude oils. The results are given in table 3. The coefficients of variation were computed from the data of tables 2 and 3 by means of the expression:

$$V = 100\sqrt{\frac{\sum (d/m)^2}{2n}}$$

Wherein V = coefficient of variation.

m = the mean of duplicate analyses.

d = the difference between duplicate analyses.

n = the number of pairs of duplicate analyses.

The coefficients of variation obtained were: for copper \pm 12 percent; for nickel \pm 9 percent; and for vanadium \pm 11 percent.

Comparison with Results Obtained Using Another Method

Samples 65, 67, 68, and 70 had previously been analyzed by J. Witters in our laboratory using a procedure that involved adding to the crude oil a mineral oil solution (containing 30 percent calcium sulfonate to increase the amount of ash so that it could be collected) before wet ashing with sulfuric acid.

The ash was diluted with 9 parts calcium sulfate and 90 parts lithium carbonate plus 1 percent indium oxide (for the internal standard). This mixture was loaded into a high-purity graphite electrode crater and arced to exhaustion against a high-purity graphite counter electrode. The excitation was by means of the D. C. arc. Table 4 lists the results obtained by Witters and those obtained by the present method.

Table 3. - Duplicate Analyses of Samples
Metals in ppm

Sample No.	Element and trial						Description of sample		
	Copper		Nickel		Vanadium		Oil field	Name of formation	Geologic age
	1	2	1	2	1	2			
65	0.21	0.21	1.6	1.5	0.74	0.76	Salem	McClosky	Mississippian
67	0.38	0.34	3.0	2.5	1.2	0.96	Salem	Renault-Aux Vases	"
70	0.09	0.07	0.65	0.54	0.35	0.25	Salem	Devonian Lime	Devonian
78	0.30	0.31	3.7	3.5	1.4	1.4	Casey	Casey	Pennsylvanian
79	0.39	0.42	3.8	3.5	1.3	1.4	Johnson South	Upper Partlow	"
82	0.10	0.11	3.8	3.5	1.5	1.5	Westfield	Gas Sand field	"
84	2.4	2.5	3.2	2.6	1.1	1.3	Siggins	Siggins	"

Table 4. - Comparison With Other Spectrographic Analyses
Metals in ppm

Sample No.	Cu		Ni		V	
	A	B	A	B	A	B
65	0.21	0.16	1.5	1.3	0.75	0.71
67	0.36	0.34	2.7	2.3	1.1	1.0
68	0.24	0.23	2.0	2.0	0.96	1.1
70	0.08	0.078	0.59	0.77	0.32	0.33

A - Analysis by the present method. Results of 65, 67 and 70 are the mean of the duplicate analyses shown in table 3.

B - Analyses by J. Witters using a different procedure.

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