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Use of Trace Metals To Identify Illinois Crude Oils

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ABSTRACT

The purpose of this study was to analyze the trace metal constituents of Illinois crude oils and determine if their range in concentration might provide a means of identifying the oils. Samples of crude oils were obtained from eight fields and trace metals were analyzed by spectrochemical methods.

Essentially uniform concentration of vanadium and nickel were found within a single oil reservoir, whether the samples were collected from different wells or at different times from the same well.

The trace concentration of vanadium and nickel ranged from 0.1 to 5 parts per million, and there was a marked reduction in their concentration as the geologic age of the oil producing zones increased from Pennsylvanian to Devonian. Thus, significant differences in the concentration of vanadium and nickel were obtained.

The ratio of vanadium to nickel concentrations was about 0.4 to 0.5 for practically all samples and therefore could not be used for identification. A correlation of the trace copper concentration and a qualitative analysis of all trace elements also failed to provide a means of identification.

INTRODUCTION

The presence in petroleum of trace concentrations of a considerable number of metals had been known for many years. In an early investigation, Hackford (1922) reported the presence of silicon, vanadium, nickel, tin, lead, calcium, magnesium, iron, aluminum, sodium, titanium, and gold in a Mexican crude oil from the Isthmus of Tehuantepec. A number of other workers (Shirey, 1931; Gulyaeva et al., 1941; Goldschmidt et al., 1948; Katchenkov, 1949; Dodd et al., 1952; Jones et al., 1952;Scott et al., 1954; and Bonham, 1956) have found most of these same elements in samples of petroleum from many parts of the world.

In a recent detailed analysis of 29 crude oils collected from several points over the western half of the United States, Erickson et al. (1954) reported the presence of 31 trace elements including all of those listed above except gold. They also investigated a number of asphalts and petroliferous rocks and reported that metals such as vanadium, nickel, copper, cobalt, molybdenum, lead, manganese, and arsenic were consistently present in all three types of bituminous material. Earlier, Goldschmidt et al. (1948) found nickel, copper, chromium, vanadium, molybdenum, and tin in a great variety of nonbituminous as well as bituminous deposits.

Because trace metals are found in many sediments associated with bituminous rocks, geologists have been intrigued by the implications with regard to the genesis and accumulation of petroleum. According to Goldschmidt et al.

(1948) and Katchenkov (1949), the enrichment of petroleum with trace metals reflects the geochemical conditions in which the petroleum source beds originated and is not the result of reactions since the time of burial. Therefore, one should expect to find the same assemblage of trace elements in the source beds as in the hydrocarbons.

Among the variety of metal constituents that are found in petroleum, vanadium and nickel have received most attention because they are consistently found in the highest concentrations. This is no doubt the reason why they were the first metals to be reported in early analyses of petroleum (Guthrie, 1923; DeGolyer, 1924; Dunstan, 1924; Ramsay, 1924).

More recently, investigators have attempted to interpret the significance of the ratio of the V to Ni concentrations. Katchenkov (1949) reported that the V to Ni ratio for Russian oils was highest for Devonian samples and that it decreased, although not regularly, to the lowest values for Tertiary samples. Hodgson (1954), after studying a number of Canadian oils, noted an opposite trend wherein the V to Ni ratio decreased with geologic age for samples ranging from Cretaceous to Devonian. Scott et al. (1954) have reported a remarkably uniform V to Ni ratio for Lower Cretaceous oils of Canada and have suggested the possibility of a common source for these oils.

It has been postulated that because the metals are associated with the heavier components in crude oil there is little danger of loss of these heavy molecules from the crude oil by evaporation or by contact with groundwaters (Scott et al., 1954). Bonham (1956) has shown, however, that concentrations of vanadium and nickel are greatest near ancient shorelines and decrease basinward for Lower Pennsylvanian oils from the Seminole area, Oklahoma, and he suggests that trace metals may be removed during oil migration. Gulyaeva (1954) also supports this view, although he recognizes that oils containing different concentrations of metals may simply reflect differences in the original condition of the source beds.

In reviewing the literature, it soon becomes apparent that the absolute magnitude of the vanadium and nickel concentrations for crude oils from different producing zones varies considerably more than does the ratio of these two elements.

For example, Scott et al. (1954) found the concentration of V_2O_5 to vary from 10 to almost 400 ppm for eleven Lower Cretaceous oils of western Canada, but the V to Ni ratio was almost a constant. In a more extensive study of western Canadian oils, Hodgson (1954) reported vanadium concentrations that range from 0.04 to 83.7 ppm for Devonian crude oils, but their V to Ni ratio ranges only from 0.09 to 3.15. Similar results were also found for Mississippian, Jurassic, and Cretaceous oils.

This range in the concentration of trace metals in different crude oils suggested that trace constituents could be used to identify the oils and correlate the producing zones. Bonham (1956) investigated this aspect in his studies of a number of Pennsylvanian crude oils from Oklahoma but found the range of vanadium and nickel concentrations to be insufficient for his purposes.

Usually, Illinois crude oils are distinguishable by ordinary methods, but there are a number of oil fields in the state that have two, three, or even more pay zones open in the same producing well. This is true for most of the Pennsylvanian and Mississippian zones, which have produced more than 90 percent of the state's total oil. Occasionally it is desirable to identify the source of the production from a multiple-pay well, but sometimes this is not easily done because the physical characteristics of most Illinois oils do not differ appreciably (Rees et al., 1943). As waterflooding becomes more widespread in the multiple-pay fields, distinguishing which zone is responding to water injection is also becoming an important problem.

With this background in mind, the primary purpose of this investigation was to analyze the trace metal constituents of Illinois crude oils and determine if their range in concentration may be useful for purposes of identification.

Acknowledgments

A number of oil companies operating in the Illinois basin very kindly permitted us to collect crude oil samples. We should like to acknowledge with thanks the assistance of: R. W. Love of The Texas Company for samples collected in the Salem Unit; R. F. Hammond of the Carter Oil Company for samples collected in the Mattoon oil field; R. A. Wilson of the Tide Water Oil Company for samples collected in the Main Consolidated oil field; and Paul Phillippi of the Forest Oil Corporation for samples collected in the Bellair, Casey, Johnson South, Siggins, and Westfield oil fields. We should also like to acknowledge the cooperation received from the field personnel of the various companies who assisted with the collection of samples.

Table 1. - Crude Oils Analyzed for Trace Metals

Oil field	Producing zone	Geologic system	No. samples analyzed
Salem Unit	Benoist	Mississippian	6
" "	Renault - Aux Vases	"	6*
" "	McClosky	"	7†
" "	Devonian	Devonian	3
Mattoon	Cypress	Mississippian	3
"	Rosiclare	"	3
"	Cypress - Rosiclare	"	3**
Main Consol.	Robinson	Pennsylvanian	6
" "	Bethel	Mississippian	1
Siggins	Siggins	Pennsylvanian	3
Bellair	Bellair	"	1
Casey	Casey	"	1
Johnson South	Upper Partlow	"	1
Westfield	"Gas" Sand	"	1
		Total	45

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* Renault and Aux Vases producing zones are separated by such a thin shale break that they are produced together; however, one of these samples was taken from a well open only in the Aux Vases sand.

† Includes one well open in the McClosky, St. Louis, and Salem zones (all Mississippian).

** Both Cypress and Rosiclare zones are open in some wells.

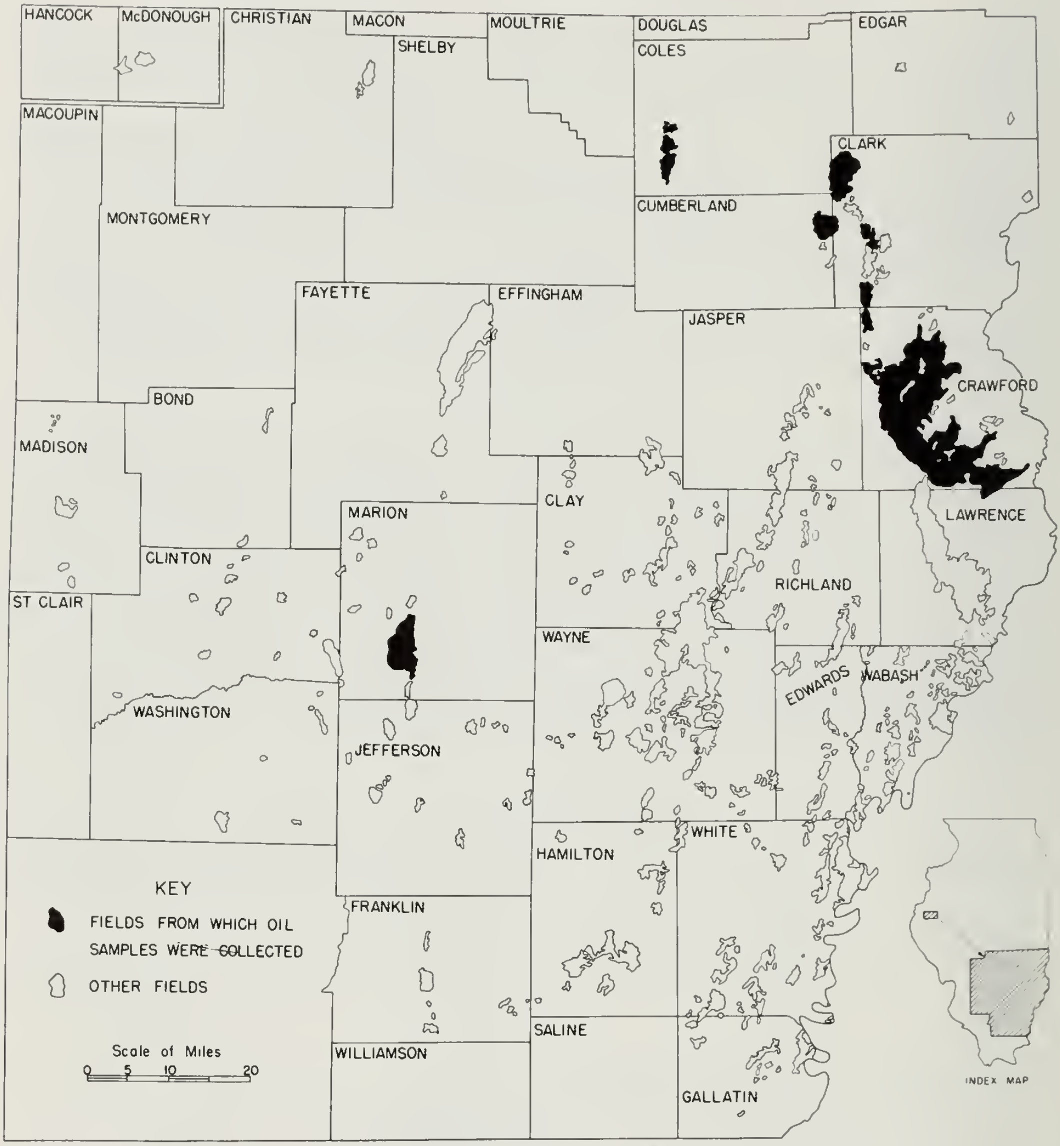

Fig. 1. - Location of oil fields in which oil samples were obtained.

CRUDE OILS INVESTIGATED

Numerous samples of crude oil were gathered in the Salem Unit oil field of Marion County, one of the largest fields in the state, which has several producing zones in the Mississippian and Devonian systems. Some of these producing zones are separated by rather short vertical distances, and therefore it was possible to determine how well the trace metal content of such closely related oils provides a basis for identification.

Another group of samples was obtained in the Mattoon oil field of Coles County, which produces from Mississippian zones. A control group of wells in

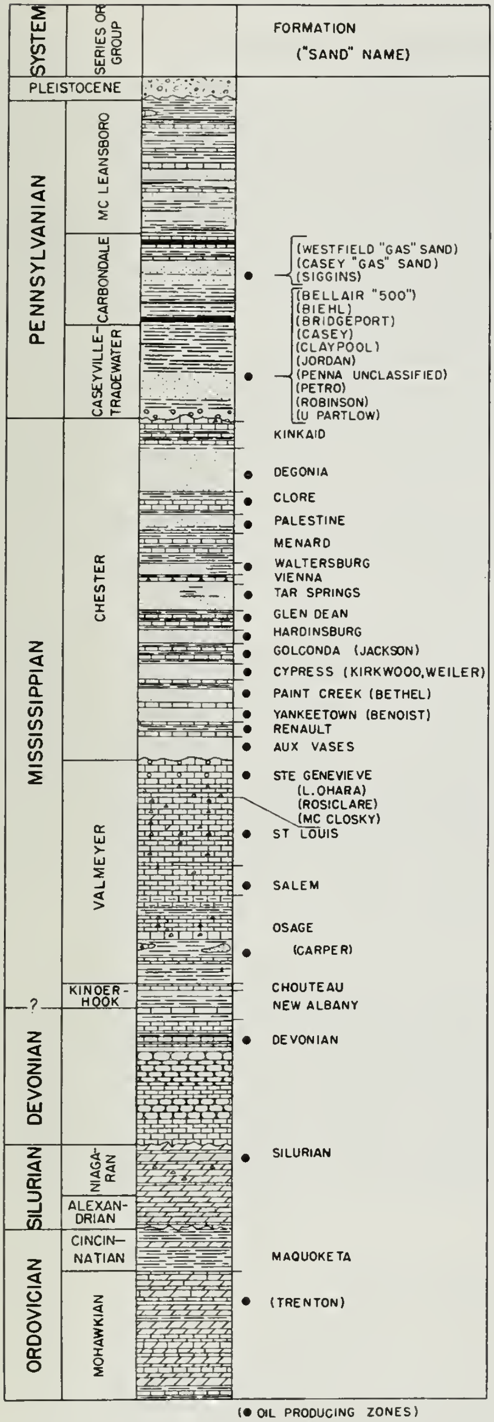

Fig. 2. - Generalized geologic column showing oil producing zones in the Illinois basin.

this field had been sampled periodically over a three-year period for other purposes, and therefore certain of these samples were analyzed to determine if trace metal contents might show any variation with time.

For comparison with the Mississippian crude oils, other samples were obtained in the Southeastern Illinois oil fields of Clark, Crawford, and Cumberland counties, which produce primarily from Pennsylvanian zones.

The number of crude oils analyzed from each field is listed by producing zone in table 1. The locations of the oil fields from which samples were obtained is shown in figure 1, and a generalized geologic column of the oil producing zones in the Illinois basin is shown in figure 2.

METHOD OF SAMPLING

Crude oil samples were collected in two-quart Mason jars by attaching a short length of small rubber hose through appropriate connections to a 1-inch gate valve normally present at the wellhead of any producing well. After the sample line was connected, the gate valve was opened so that the amount of oil and water being produced could be observed and the line purged. If the water-oil ratio was above approximately 1.0, the produced fluids were first collected in a glass separator, the water drained off, and the oil poured directly into the sample bottle.

If the water-oil ratio was less than 1.0, the produced fluids were collected directly in the sample bottle. Each sample bottle was covered with aluminum sheet foil and the metal cap screwed on. Occasionally it was necessary, depending on atmospheric temperatures, to loosen the cap and to vent any natural gas that had been released. The crude oils were stored in these containers until investigated.

SPECTROCHEMICAL METHODS OF ANALYSIS

To determine the assemblage of trace metals present in the crude oil, the following qualitative analytical procedure was adopted. Approximately 110 ml. of concentrated sulfuric acid and 50 mg. of purified calcium carbonate were added to 750 grams of crude oil that had previously been washed and filtered. This mixture was then ashed in a Vycor beaker using a procedure that was developed by Nagashima and Machin (1957). Fifteen mg. of the ash were loaded on a 1/4-inch special grade graphite electrode, arced to consumption with a D.C. arc, and the spectrum recorded on a Kodak S.A. 1 plate using a Bausch and Lomb large quartz Littrow spectrograph.

Various amounts of Spex Mix standard (Spex Industries, Inc., Queens, N. Y.) were diluted with the purified calcium carbonate, arced, and the spectrum recorded as before in order to provide a scale for a rough estimation of the relative orders of concentrations of trace elements in the crude oil. An examination for three rare earths (cerium, lanthanum, and yttrium) was performed by Juanita Witters of the Survey staff who analyzed a dilution of 1 part ash and 9 parts cupric oxide. The detection limit for Ce was 0.5 percent in the ash (or 0.5 ppm in the oil), for La 1 percent (or 1.0 ppm) and for Y 0.5 percent (or 0.5 ppm).

The quantitative analytical procedure used has been discussed in detail by Nagashima and Machin (1957) and is merely summarized here. A 100-gram sample of crude oil was washed, filtered, and ashed in a Vycor beaker with 100 ml. of concentrated sulfuric acid and 5 ml. of nitric acid. A small amount of cobalt nitrate solution (containing 0.28 mg. Co) was added before ashing to serve as an internal standard for the spectrochemical analysis. The ash was dissolved in dilute hydrochloric acid and the volume adjusted to 10 ml. The solution was arced in a porcelain boat with a rotating disk electrode; the excitation was furnished by a high voltage spark.

Quantitative determinations were made for only three trace metals: copper, nickel, and vanadium. Therefore, analytical calibrations were made from a series of standard solutions containing varying amounts of copper, nickel, and vanadium and the constant amount of cobalt. The spectra were recorded on Kodak 33 plates and the Cu 3247, Ni 3050, and V 3093 lines were compared with the Co 3044 line as the internal standard. The calibration range was from 0.1 to 10 ppm for each element, and the precision of the analytical results was evaluated by performing 10 duplicate ashing and spectrographic procedures on each element. The coefficients of variation obtained in these duplicate determinations were ± 12 percent for copper, ± 9 percent for nickel, and ± 11 percent for vanadium.

EXPERIMENTAL RESULTS

Qualitative Analysis of Trace Metals

To determine the assemblage of trace metals present in the crude oils of the Salem Unit, eight samples were analyzed qualitatively by the procedure outlined above. The oil samples were obtained from two different wells producing from each of the four zones listed in table 1, and the results are given in table 2.

Table 2. - Qualitative Analysis of Trace Metals in Crude Oils of Salem Unit*

Element	Benoist		Renault - Aux Vases		McClosky		Devonian	
	1	2	3	4	5	6	7	8
Ag	1	1	1	1	1	1	1	1
Al	3	3	3	3	3	3	3	2
As	3	3	3	3	3	2	-	-
B	1	1	-†	-†	1	1	1	1
Ba	+	+	+	+	?	?	?	?
Ce	-	-	-			-		
Co	1	2	1	1	1	1	1	1
Cr	1	1	1	1	1	1	1	1
Cu	3	3	4	3	4	3	3	3
Fe	3	3	4	3	4	4	4	2
La	-	-	-			-		
Mg	+	+	+	+	+	+	+	+
Mn	+	+	+	+	+	+	+	+
Mo	1	1	1	1	1	1	-	-
Na	3	3	3	4	3	3	3	3
Ni	4	4	4	4	4	4	4	4
Pb	2	2	2	2	2	2	2	1
Si	+	+	+	+	+	+	+	+
Sn	1	1	1	1	1	1	1	1
Ti	+	+	+	+	+	+	+	+
V	4	4	4	4	4	4	4	4
Y	-	-	-			-		

* Numbers indicate relative orders of concentration detected.
+ = element detected but concentration not certain.
- = element not detected. Except for calcium and strontium, elements other than those listed were not found. Calcium and strontium were ignored because a calcium carbonate blank containing strontium was used as an ash collector.
† Sometimes boron may be lost in the ashing procedure.

It will be noted that the most prominent trace metals present are the same as have been reported by numerous other investigators. In particular, the nickel and vanadium are consistently present in the highest concentrations, and on the basis of the literature, this appears to be the general case over the world. The relatively high concentration indicated for iron and sodium may not be reliable because of the possibility of contamination, which could easily occur because mixtures of oil and brine are produced through metallic tubing.

The aluminum and silicon concentrations may also be the result of contamination in the oil, possibly due to the suspension of minute particles of rock materials in the hydrocarbons. The concentrations indicated for arsenic also are subject to some doubt because of the ease with which arsenous compounds will volatilize during the ashing procedure. For these reasons, it was decided that the subsequent quantitative investigations should be confined to an analysis of vanadium, nickel, and copper.

Table 3. - Vanadium, Nickel, and Copper Concentrations in Crude Oils of Salem Unit

Sample no.	Lease and well no.	Location Sec.-T.-R.	Depth to top of pay		Trace metals			
			Total ft.	Subsea ft.	V ppm	Ni ppm	Cu ppm	V/Ni ratio
			Benoist*					
1	Foster 1	7-1N-2E	1790	1252	0.88	2.3	1.8	0.38
2	Salem St. Bank 5	20-2N-2E	1736	1204	0.88	1.9	0.50	0.46
3	C. Loyd 21	28-2N-2E	1795	1309	1.4	3.0	0.10	0.46
4	K. Wayman 18	31-2N-2E	1727	1224	0.96	2.0	0.24	0.48
5	W. Sands 3	33-2N-2E	1805		0.80	2.0	0.39	0.40
6	G. Mercer 2	34-2N-2E	1899	1343	0.74	1.5	0.96	0.49
			Range		0.74-1.4	1.5-3.0		0.38-0.49
			Renault-Aux Vases*					
7	Salem St. Bank 2B	20-2N-2E	1788	1256	0.80	1.9	2.4	0.42
8	J. Shanafelt 22	20-2N-2E	1811	1278	1.0	2.2	0.56	0.46
9	E. Brooks 5	29-2N-2E	1786	1246	1.1	2.7	0.36	0.41
10	A. Dempsey 9	31-2N-2E	1781	1298	1.2	2.1	2.1	0.57
11	E. Farthing 7B	32-2N-2E	1790	1266	0.88	1.9	0.88	0.46
			Range		0.80-1.2	1.9-2.7		0.41-0.57
12	Foster 13[†]	8-1N-2E	1877	1335	0.64	1.2	1.8	0.53
			McClosky*					
13	C. Bundy 18	6-1N-2E	1915	1397	0.53	1.0	3.2	0.53
14	W. Chitwood 21	16-2N-2E	2011	1474	0.53	1.0	10-20	0.53
15	W. Chitwood 24	16-2N-2E	1998	1490	0.75	1.5	0.21	0.50
16	J. Young 14	29-2N-2E	2026	1497	0.67	1.1	0.13	0.61
17	E. Farthing 6A	32-2N-2E	1894	1410	0.61	1.0	3.3	0.61
18	City Centralia 49	33-2N-2E	2043	1522	0.57	1.3	10-20	0.44
			Range		0.53-0.75	1.0-1.5		0.44-0.61
			McClosky**					
19	J. Young 12	29-2N-2E	1939	1407	0.80	1.1	0.46	0.73
			Devonian*					
20	M. Young Heirs 39	20-2N-2E	3363		0.30	0.62	0.1	0.48
21	J. Chapman 22	28-2N-2E	3440	2925	0.34	0.47	6.6	0.72
22	O. Hopkins 9	32-2N-2E	3303	2813	0.35	0.56	1.0	0.62
			Range		0.30-0.35	0.47-0.62		0.48-0.72

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* Samples 1 through 19 from Mississippian producing zones.

† Aux Vases only.

** McClosky, St. Louis, and Salem zones (all Mississippian) are open in this well.

Quantitative Analysis of Trace Metals

The concentration of vanadium, nickel, and copper in ppm as determined for the Salem Unit crude oils are listed in table 3, which also includes the location of the wells sampled and depths to the producing zone.

As mentioned, a control group of producing wells in the Mattoon oil field was sampled periodically over a three-year period. Certain of these oil samples were selected for quantitative analysis to determine whether there were any variation in the trace metal concentrations over such a time period, and the results are given in table 4.

As a significant amount of Illinois oil production comes from Pennsylvanian zones, it was of interest to compare the trace amounts of copper, nickel, and vanadium in these oils with the trace metals obtained from the Mississippian zones. The primary area of Pennsylvanian oil production is in the Southeastern Illinois oil fields of Clark, Crawford, Cumberland, and Lawrence counties (fig. 1). Table 5 shows the results of trace metal analyses on a group of crude oils collected in this area.

Table 4. - Vanadium, Nickel, and Copper Concentrations in Crude Oils of Mattoon Field

Sample no.	Lease name and well no.	Location Sec.-T.-R.	Date sampled	Trace Metals V ppm	Ni ppm	Cu ppm	V/Ni ratio
			Cypress*				
23	I. Welch 2	2-11N-7E	8-20-53	0.38	1.6	0.17	0.24
24	I. Welch 2	2-11N-7E	12-21-54	0.34	1.4	0.1	0.24
25	I. Welch 2	2-11N-7E	11-8-56	0.39	1.3	0.1	0.30
			Rosiclare*				
26	E. Jeffries 6	26-12N-7E	8-20-53	0.36	1.3	0.24	0.28
27	E. Jeffries 6	26-12N-7E	12-21-54	0.34	1.1	0.1	0.31
28	E. Jeffries 6	26-12N-7E	11-8-56	0.37	1.4	0.1	0.26
			Cypress and Rosiclare*				
29	E. Strong 1	35-12N-7E	8-20-53	0.39	1.6	0.1	0.24
30	E. Strong 1	35-12N-7E	12-21-54	0.39	1.8	0.41	0.22
31	E. Strong 1	35-12N-7E	11-8-56	0.42	1.7	0.17	0.25

* Mississippian producing zones.

DISCUSSION OF RESULTS

On the basis of the qualitative spectrochemical analyses of the Salem Unit crude oils (table 2), it is apparent that these oils have about the same assemblage of trace metals as has been reported by other investigators. All of the 22 elements listed in table 2 have been detected in the extensive studies of crude oils from the western half of the United States made by Erickson et al. (1954). It is interesting to note, however, that whereas they reported cerium, lanthanum, and yttrium in concentrations ranging from X to 0.00X ppm

Table 5. - Vanadium, Nickel, and Copper Concentrations in Crude Oils of Southeastern Illinois Oil Fields

Sample no.	Lease name and well no.	Location Sec.-T.-R.	Producing zone*	Trace metals V ppm	Ni ppm	Cu ppm	V/Ni ratio
			Main Consolidated				
32	K. Hudson 2	6-5N-12W	Bethel	0.8	1.5	0.32	0.53
33	N. Lindsey 7	16-5N-11W	Robinson 2	1.9	5.1	0.13	0.37
34	M. Birch	14-6N-13W	Robinson 1, 2, 3	1.7	3.1	0.22	0.55
35	S. Reinoehl 5	21-6N-13W	Robinson 2	1.2	2.4	0.1	0.50
36	Meserve	9-7N-12W	Robinson 4	2.1	4.7	0.12	0.45
37	Ikemire 5	15-7N-13W	Robinson 2	1.4	2.6	0.22	0.54
38	Clark	18-7N-13W	Robinson 2	1.4	2.2	0.1	0.64
			Siggins				
39	T. Emrich W-11	7-10N-11E	Siggins	1.0	2.3	0.80	0.43
40	Stockbrine A-1	11-10N-10E	Siggins	1.1	2.7	2.1	0.51
41	F. Walker 7	13-10N-10E	Siggins	1.2	2.9	2.4	0.41
			Bellair				
42	S. Smith M-11	11-8N-14W	Bellair 500	1.9	4.3	0.30	0.44
			Casey				
43	McCory J-15	14-10N-14W	Casey	1.4	3.6	0.30	0.39
			Johnson South				
44	McFarling H-15	27-9N-14W	U. Partlow	1.4	3.6	0.51	0.39
			Westfield				
45	B. Mounds G-15	30-11N-14W	"Gas" Sand	1.5	3.6	0.1	0.43

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* Sample 32 is Mississippian; samples 33 through 45 are all Pennsylvanian in age.

for many of their oils, a special analysis with a lower detection limit of 0.5 ppm for yttrium and 1.0 ppm for lanthanum and cerium failed to find these rare earths. Erickson et al. also reported zinc in concentrations ranging from 0.X to 0.0X ppm, but this element was not found in these Illinois oils at a lower detection limit of 0.1 ppm.

On the other hand, the ashing procedure used in this investigation made it possible to detect arsenic in all of the Mississippian samples, whereas Erickson et al. (1954) did not find this element in their crude oils, probably because they used an open flame method of ashing that could easily volatilize the arsenous compounds. They recognized that arsenic very probably should be present, and the fact that they report arsenic in their asphalt samples suggests that this metal is closely associated with the asphaltic fractions of crude oil. As the Devonian oil from the Salem Unit is low in asphalt content, this may provide an explanation for the failure to detect arsenic in this oil. Either arsenic is not present, or the concentration was below the 0.05 ppm detection limit used in this study.

It will be noted from the semiquantitative data in table 2 that the elements and their concentrations are almost the same for all of the Mississippian crude oils so that it is impossible to distinguish among the Benoist, Renault-Aux Vases, and McClosky oils on this basis. On the other hand, the Devonian samples may be distinguished from Mississippian oils because the Devonian characteristically lack arsenic and molybdenum. This is not particularly useful information, however, because the color of Devonian oil in the Salem field is distinctly different from all the Mississippian oils. Although only eight samples of crude oil from the Salem Unit were analyzed, the results do not suggest that this type of qualitative analysis will be helpful in distinguishing between different crudes. For this reason, attention was directed to the quantitative analyses of copper, nickel, and vanadium, the metals found to be consistently present in the highest concentrations.

An examination of the trace element concentrations listed in table 3 will reveal that the Benoist, McClosky, and Devonian crude oils each have characteristic amounts of nickel and vanadium. The Benoist oil, with one exception, has a vanadium content of about 0.8 ppm and a nickel content of about 2 ppm, whereas the McClosky oil has about 0.6 ppm V and 1 ppm Ni, and the Devonian oil has only 0.3 ppm V and 0.6 ppm Ni. Although these differences are not large they are greater than the experimental error (±10%), particularly in the case of the Ni concentrations.

The location of the wells from which these various samples were obtained over the Salem oil field is shown in figure 3. The outline indicated for the field is the productive limit of the Benoist formation. The productive area of each of the other oil zones is less than that of the Benoist, although all producing zones are on an asymmetrical anticline whose axis is located approximately as shown. In the case of the Benoist, McClosky, and Devonian oils, the apparent uniformity in the vanadium and nickel concentrations, regardless of structural position, is an important consideration and is interpreted as an indication that these trace metals are uniformly distributed in any given reservoir in this field.

In the case of the Renault-Aux Vases samples, the variation in vanadium and nickel concentrations is somewhat greater than for the other formations. This is probably due to the fact that the oil in either zone has its own characteristic concentration of these two elements, and various mixtures were being produced at the several wells sampled. It will be noted on figure 3 (Renault-Aux Vases) that sample 12 from the Aux Vases alone was obtained at the south end of the field and it has substantially lower concentrations of vanadium and nickel. If the results obtained with this single sample are indicative of the Aux Vases oil in general, the Renault oil apparently has vanadium and nickel concentrations enough higher than the Aux Vases to allow the two crude oils to be easily distinguished. This point could be investigated further by analyzing a representative group of individual samples from each producing zone.

Inasmuch as several investigators have used the V to Ni ratios in their work, these ratios are included in table 3. It will be noted that, for any group

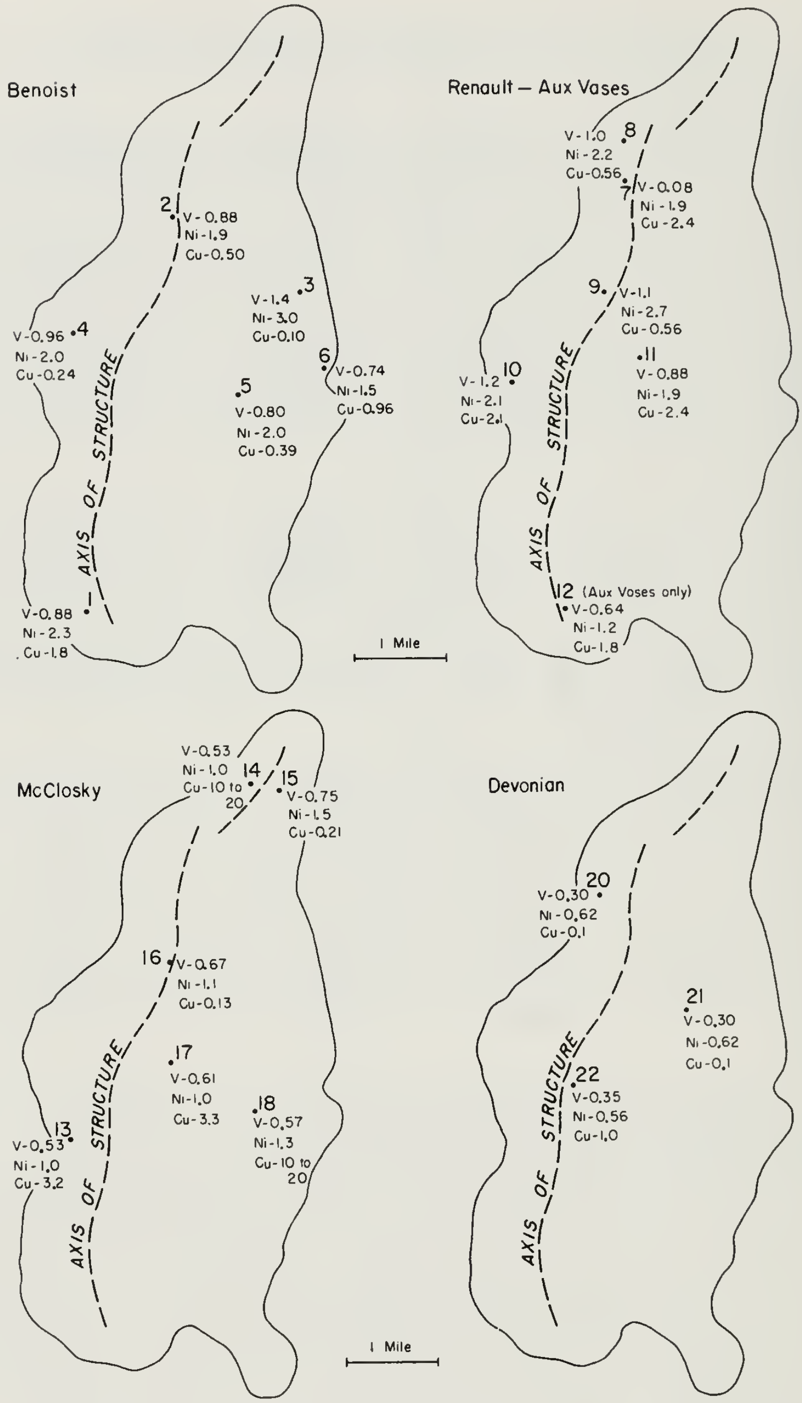

Fig. 3. - Salem Unit oil field showing pay zones and well locations from which oil samples were obtained.

of samples from a particular zone, the variation in the magnitude of the ratios within the group is about the same as the variation between groups of samples from different zones. Thus, these ratios could not be used as a means of distinguishing between the crude oils produced from the Salem Unit. The degree of variation in this ratio probably is a reflection of the errors inherent in the analytical procedure used.

It also will be noted in table 3 that there is a wide variation in the copper concentrations, and a similar variation has been noted in the results of other investigators (Erickson et al.; Bonham, 1956). It does not seem reasonable that vanadium and nickel would be uniformly distributed in a crude oil and copper not. One possible explanation for the erratic results obtained for copper is that contamination takes place as the crude oil passes through the production equipment. In any event, the large variations in the copper concentrations prevent this trace metal from being used as a means of identification.

The trace metal concentrations in the crude oils of the Mattoon field (table 4) reveal some interesting facts. Over the three-year sampling period, there was no apparent variation in the trace metal concentration with time. Thus, one is again led to the conclusion that, if the trace elements are uniformly distributed throughout a reservoir, the concentrations analyzed for any oil sample will always be the same, regardless of where or when the sample is obtained. Secondly, the vanadium and nickel concentrations for the Mattoon oils are significantly different from those of the Salem Unit. This also is evident from the fact that the V to Ni ratio for the Mattoon samples is about half that obtained for the Salem crude oils. The Cypress and Rosiclare formations also have essentially the same vanadium and nickel concentrations (table 4) and therefore these data cannot be used to separate these two crudes. Undoubtedly, similar situations may occur in other multiple-pay fields, especially if all the oil came originally from a common source.

From the results shown in table 5, it is apparent that the concentrations of vanadium and nickel are considerably higher in the Pennsylvanian oils than in either the Mississippian or Devonian samples collected in the Mattoon and Salem fields (fig. 4). It will also be noted that the single Mississippian Bethel oil (Sample No. 32) obtained beneath the Robinson producing area of the Main Consolidated field has vanadium and nickel concentrations comparable to those of the Benoist oils in the Salem Unit (table 3) and, therefore, substantially less than those of the overlying Pennsylvanian oils.

Some petroleum geologists have postulated that the Pennsylvanian oils of the southeastern Illinois oil fields came from Mississippian source beds, and if this is the case, one would anticipate a similarity in the trace metal concentrations of at least some Mississippian and Pennsylvanian oils. The indicated differences in the trace metal contents mentioned above, however, casts some doubt on this hypothesis, especially as the Pennsylvanian metal concentrations are higher than those in the Mississippian oils rather than being about the same or perhaps lower (in the event that metals might have been lost during migration). This point should be pursued further by a careful sampling of closely related oil reservoirs situated in Pennsylvanian and Mississippian strata.

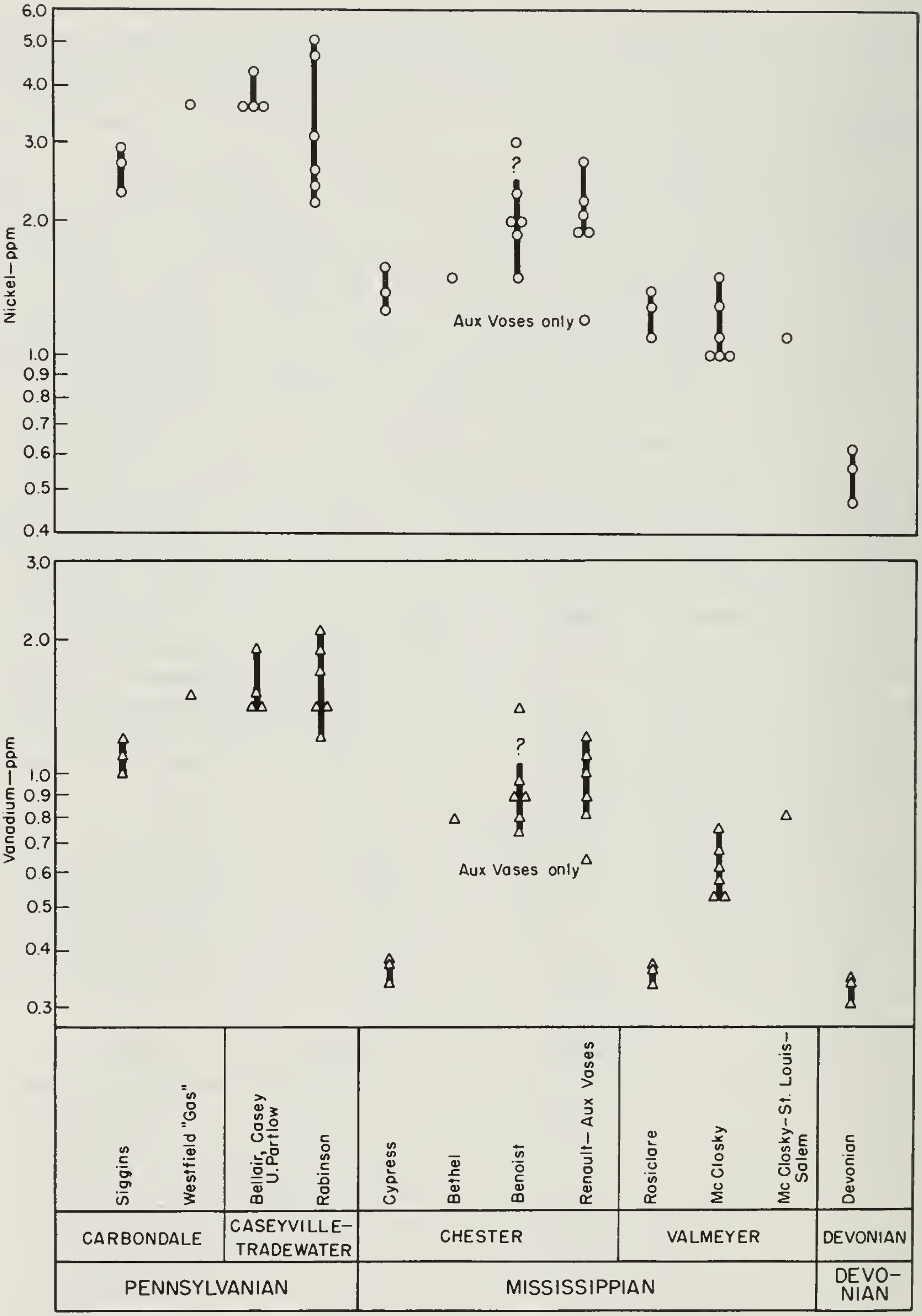

Fig. 4. - Correlation of nickel and vanadium content of Illinois crude oils with geologic age of producing zone.

It also may be noted in table 5 that there is some variation in the vanadium and nickel concentrations for the Robinson oils of the Main Consolidated field. There are several producing zones in this field all of which are rather closely related and which some operators have numbered arbitrarily Robinson 1, 2, 3, and so forth. Because of difficulties in stratigraphic correlation, the exact limits of these different pay zones are not well known. There is an indication in table 5, however, that the Robinson 2 oil might be distinguished from other Robinson oils by its relatively low vanadium and nickel content. Perhaps the Robinson 4 oil with the indicated high content of vanadium and nickel in one sample may also be distinguished from other oils of this field, but further samples of the individual Robinson pay zones should be investigated to test this hypothesis.

The rather uniform vanadium and nickel concentrations in the Siggins samples further corroborates the idea of a homogenous distribution of trace metals, as noted for the Mattoon and Salem oil fields. Such a distribution is, of course, to be expected. It is interesting to note that the vanadium and nickel metal contents in the Bellair, Casey, Johnson South, and Westfield oils are about the same and are all somewhat higher than the concentrations measured for oils from the Siggins field, which is located not too far away. As in the case of the other crude oils, the copper concentrations for these Pennsylvanian oils are not consistent and do not provide a basis for identification. Nor do the V to Ni ratios appear to have any useful correlation.

The vanadium and nickel concentrations for all samples are plotted on figure 4 to show the correlation with geologic age of the producing zones. This graph further illustrates the fact that there are significant differences between the vanadium and nickel concentrations of the various oils studied. Thus, when conventional methods of identifying crude oils fail, the trace metal concentrations of a particular oil may be sufficiently different from those of other closely associated oils that the vanadium and nickel contents can be used as a positive means of identification. It is suggested that other Illinois crude oils from different parts of the basin be investigated to demonstrate more fully the usefulness of this approach.

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Illinois State Geological Survey Circular 239
16 p., 4 figs., 5 tables, 1957

CIRCULAR 239

ILLINOIS STATE GEOLOGICAL SURVEY

URBANA

LITHOGRAPHERS 166