

A STUDY OF METALS IN CRUDE OILS

By

Mohammad A. Bashar

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A thesis submitted to the Faculty and the Board
of Trustees of the Colorado School of Mines in partial
fulfillment of the requirements for the degree of Doctor
of Science.

Signed: Mohammad A. Bashir
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Golden, Colorado

Date Aug. 31, 1955.

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ABSTRACT
A STUDY OF METALS IN CRUDE OILS

By

Mohammad A. Bashar

The present work had the following objectives:

1. To study the metals qualitatively in crude oils locally obtained and to discuss in general their importance
2. (a) To determine the critical metals by methods commonly used
(b) To develop and improve quantitative methods
(c) To discuss and compare quantitative methods employed
3. To investigate if there exists a relationship between the metal content of crude oils and that of associated water and producing formations and to discuss the possible origin of these metals
4. To investigate if these metals could provide a better understanding of the evolution of the crude oils.

The study pursued in the above order shows that crude oils contain various metallic elements existing in diversified physical and chemical forms. Among the metals

may be mentioned iron, nickel, vanadium, copper, aluminum, sodium, calcium, magnesium, barium, tin, lead, molybdenum, gold, silver, etc. Of these metals, iron, nickel, copper and vanadium are considered harmful for the facilities using the crude oils and their products. To mention a few, the facilities susceptible to the pernicious effects of these metals are (1) cracking catalysts (2) refinery equipments (3) power turbines (4) furnaces and refractories.

In order to obtain a means of control on the product quality and to predict the extent of harmful effects to be produced it is necessary to determine these metals. In the present study iron, nickel and vanadium have been determined by (1) spectrographic (2) colorimetric (3) activated carbon methods. From a comparison of the results it has been concluded that the rotating electrode method (spectrographic method) is fast and suitable for routine analysis and the colorimetric method for accurate quantitative analysis. Besides being a quantitative procedure, the third method is an extractive process and brings out the important principle that a reagent like urea or mercaptobenzothiazole must be employed to bring about a change in the structure of complexes which then could be adsorbed by activated carbon, silica gel or similar adsorbent. Following this reasoning and adopting the technique, the author feels certain

that successful processes could be developed for purifying crude oils or extracting the metals from crude oils for commercial utilization.

Finally, it was concluded that the metals came from the original organic or plant remains from which crude oils evolved. G. W. Hodgson and co-workers¹⁸ have proposed that the age of crude oils can be correlated with V/Ni ratio. No such correlation was found in this study.

This abstract of 288 words is approved as to form and content.

I recommend its publication.

Date Aug 31, 1955

Signed James O. Ball
Prof. in charge of thesis

INTRODUCTION

Within the recent years, the petroleum industry has been increasingly concerned about metals in the crude oils. The reason for this concern arises from the realization of the harmful effects produced by these metals upon the facilities using crude oils and their products. The present work is a natural consequence of the realization of the significance of these metals.

Nine crude oil samples were obtained from local sources and analyzed qualitatively for their metal contents. The importance and significance of these metals were then discussed.

Among the metals, Fe, Ni, and V are considered harmful. These were determined by spectrographic and colorimetric methods. The author developed the activated carbon method and employed it to determine the above metals. The three methods were then compared and their advantages and disadvantages discussed.

So that the origin of these metals in crude oils

could be studied, samples of producing formations and associated water were procured and analyzed for their metal contents. From such a study and from existing knowledge, a conclusion was arrived at as to the possible origin of these metals in crude oils.

Finally, the nine crude oil samples were studied in order to verify the correlation of the age and depth of crude oils with gravity and V/Ni ratio proposed by G. W. Hodgson and his co-workers¹⁸. A conclusion was then arrived at as to the validity of such correlation on the crude oils studied.

METALS IN CRUDE OILS

A crude oil is conventionally defined as a naturally occurring substance consisting predominantly of a complex mixture of different types of hydrocarbons and having organic and inorganic impurities. The inorganic impurities are various metals existing in different forms. The occurrence of these metals in crude oils was therefore known since the very recognition and utilization of crude oils as a source of fuel and power. But, the real significance of these metals was never realized and consequently the interest in their true study is very recent.

The presence of metals is not limited to crude oils of one locality only; these metals are invariably associated with crude oils found all over the world. The metals found in crude oils are diversified in kinds and forms. A complete identification of the chemical and physical states or forms of all naturally occurring trace metals in crude oils has never been completed. Such information however, would be specially useful to the petroleum industry in as

much as it would presumably throw light on the source and origin of crude oils. It would also be useful in designing effective treating processes should the removal of these metals be deemed desirable. The various forms in which metals may exist in crude oils include true solutions, or organo-metallic substances, suspended solid particles in highly divided forms, and colloidal or emulsified dispersions of minute bodies containing metal compounds or complexes.

Small amounts of almost all metallic elements are encountered in most crude oils. Among the metallic elements identified in typical crude oils are iron, nickel, vanadium, copper, aluminum, sodium, calcium, magnesium, barium, chromium, tin, lead, molybdenum, gold, silver etc. The following are tabulations of data showing the metallic elements found in various crude oils

TABLE 1¹

Metals identified in various crude oils

Crude Oils	Metals Identified
Canadian ...	Fe, Al, Ca, Mg and traces of Ag, and Au
Ohio ...	Fe, Al, Ca, Mg, Cu, Ag, and Au
Mexican ...	Fe, Al, Ti, Mg, V, Sn, and Pb
Baku ...	Fe, Al, Ca, Mg, Cu, Ag, Au, Mn and Pb
Egyptian ...	Fe, Al, Ca, Ni, and V
Venezuelan ...	Fe, Ni, V, Ca and Mg
Iraq ...	Fe, As, Ni and V
Texas ...	Fe, Al, Ti, Ca, Mg, V and Ni
Japan ...	Fe, Ca, Mg, Ni and V

The above data are the results of qualitative analyses on ashes from various crude oils. Due to the inaccuracy of the methods (chemical) employed some metals present in very minute quantities may not have been detected.

TABLE 2
Metals found in crude oils from different horizons of the same field
(Results of the present work)

Field	Producing Horizon	Depth	Metals Found
	Mancos	... 2600 ^a ...	Fe, Ni, V, Na, Ca, Mg, Zn, Si, Pb, Ag, As, Ti, Sn, Sr
	Mancos	... 2800 ^a ...	Fe, Ni, V, Na, Ca, Mg, Zn, Si, Pb, Ag, Au, Ti, Sn, Cd, Mo, Bi, Al, Ba, Sr, Mn, Sb, Ru
Rangely, Colorado.	Mancos	... 3100 ^a ...	Fe, Ni, V, Na, Ca, Mg, Si, Pb, Ag, Sb, Sn, Sr
	Shinarump	.. 5350 ^a ...	Fe, Ni, V, Na, Ca, Mg, Zn, Pb, Ag, Sn, Ba, Ti, Sr
	Weber	... 6080 ^a ...	Fe, Ni, V, Ca, Mg, Zn, Si, Pb, Sb, Sn, Al, Ti, Ru
	Frontier	... 4677 ^b ...	Fe, Ni, V, Na, Ca, Mg, Zn, Pb, Ag, Si, B, Sb, Sn, Ba, Al
	Curtis	... 2305 ^b ...	Fe, Ni, V, Na, Ca, Mg, Zn, Si, Sn, Sb, Pb, Ag, Ba, Sr, Ti, U(?)
Grass Creek, Wyoming.	Tensleep	... 1292 ^b ...	Fe, Ni, V, Na, Ca, Mg, Si, Sn, Pb, As, Ag, La, Al, Ba, Sb, Ru, Bi, Cd, Mo, Ti, U
	Embar	... 1208 ^b ...	Fe, Ni, V, Na, Ca, Mg, Al, Zn, Ba, Sr, Pb, Ag, Sn, Sb, Si, Ru, As, Bi, Cd, Mo, Ti, U

a: Depths in feet below the surface

b: Depths in feet above sea level

The above data were produced by the present author. The method employed was spectrographic. The idea was to show any variation in the metal contents of the crude oils from the different producing horizons at different depths of the same field. The producing horizons shown above are arranged in increasing depths from the surface. The above results are not the complete or exhaustive analysis of crude oils; such analysis was not attempted by the author.

IMPORTANCE OF METALS IN CRUDE OILS

Within recent years, interest of the petroleum industry in the occurrence of trace metals in crude oils and their products has increased markedly. This interest derives from the influence of contaminant metals in refining or processing of petroleum products, or from the effects of metals on utilization or performance characteristics of the finished products or from the correlation of these metals with the geological origin of crude oils. The importance of these metals may be realized from a consideration of their effects as follows:

EFFECT ON CATALYSTS⁸

In catalytic cracking the presence of only a few pounds of such trace metals as iron, nickel, and vanadium imparted from the feed stock and accumulated on each ton of catalyst necessitates expensive catalyst replacement because their adverse effect on the catalyst activity results in poor quality of the products.

EFFECT ON EQUIPMENT USING PETROLEUM PRODUCTS²⁶

Among the innumerable equipment and machines using petroleum products, modern gas turbines for ship propulsion

and power generation are very critical as to the metal contents of their fuels. Vanadium, nickel, and sodium in particular are extremely harmful. The major difficulty is not in the combustion process, but in the deposition of ash and its corrosive attack on the surfaces of the combustion chamber and turbine blades.

EFFECT ON REFINERY EQUIPMENT AND REFRACTORIES

Inorganic deposition products from fuels often give rise to refinery problems in heat transfer, to equipment deterioration, and to premature failure. Metal embrittlement, metal pitting, and other costly effects on equipment are attributable to trace metals.

In many oil-fired furnaces where flame directly impinges on the refractory, the fire brick becomes coated with a thin glassy substance.²⁶ This has been attributed to actual fusion of refractory. Investigation shows that furnace temperature is not high enough to cause fusion of the refractory. The coating on the wall is rather the ash originating in the oil or a slag formed by the reaction of the ash and the refractory resulting in refractory failures. Analyses of slag and the dust from the radiant section of furnaces show high percentages of vanadium and alkali metals. It is quite evident from the analyses that the fuel-oil ash reacted with the refractory material, lowered its fusion point, and

caused premature failure. The following is a table of analyses of furnace dust and slag:

TABLE 3²⁶
Analyses of furnace slag and dust

Analysis(Wt.%)	Slag	Dust from radiant section, boiler tubes
Vanadium ...	12.5	35.3
Refractory material	80.9	7.8
Other metals including iron, nickel, tin, and zinc ...	2.3	6.9
Alkali metals ...	3.6	7.0

The foregoing discussion reveals the deleterious effects of trace metals present in petroleum products as fuels. The source of these metals is the original crude oils. The metals in crude oils are therefore important and these offer a subject for critical studies.

DETERMINATION OF METALS IN CRUDE OILS

Among the metals present in crude oils, iron, nickel, and vanadium are considered very critical. These were determined by the spectrographic and the colorimetric methods, which are commonly used.

SPECTROGRAPHIC METHOD

Outline of the method : The technique adopted is known as the "rotating electrode"^{28,15} technique. This technique was first developed by the National Spectrographic Laboratories, Inc. and used for the determination of trace metals in lubricating oils. Similar technique was adopted in the present study for the analysis of crude oils. A weighed portion of well shaken oil sample (both standard and unknown) was mixed with a solution containing the internal standard. The oil (1ml.) was then dropped on to a hot graphite disc and heated to a temperature of about 700°F to form a thin carbonaceous coating. The disc was rotated in a horizontal plane and the sample excited by a low-voltage unidirectional arc. Percentage transmission readings were obtained in the usual way by using a densitometer.

Apparatus used : The apparatus used is briefly described as follows:

Spectrograph : It is a 1.5 meter medium size grating spectrograph. Its technical details are available in Bausch and Lomb instruction pamphlet S 814 A, page 4.

The spectrograph covers a wavelength range of 3700 to 7400 A° in the first order and 1850 to 3700 A° in the second order. Most metals, including the ones considered important in the present work, have their first-order lines below 3700 A° -- the lower range of the spectrograph. Therefore, the spectral lines of these metals within the range of the spectrograph are the second-order lines of these metals. The film chosen was 35-mm. spectrum analysis no. 1, which is insensitive to the visible region and sensitive only to the ultraviolet region within which most of these metals have their wavelengths.

Spectrographic auxiliaries : These are the excitation unit, the developing equipment, and the densitometer.

Experimental work :

Preparation of internal standard solution : With a clean, dry pipette, 0.5 ml. of Uversol cobalt was measured out into a 200-ml. volumetric flask to which was then added mineral oil($d = 0.872$) upto the mark. An equal-volume

mixture of this solution with lithium naphthenate gave the required internal standard solution. One milliliter of this internal standard solution was used to every 5 grams of oil sample. The purpose of both lithium and cobalt was to make it possible to use either one as internal standard.

Preparation of emulsion calibration curve : One milliliter of the internal standard solution was evaporated on the carbon disc, and the spectrum was taken by using the filter with three steps of 6-100-25% transmissions. Lithium was used as the internal standard. Percentage transmissions were plotted against relative exposures on a log-log paper. The following table gives the data for the calibration curve.

TABLE 4
Data for the calibration curve(SA #1)
(Results of the present work)

Intd. Std.	λ	Observed as	Relative Exposure	% Tr.
			6 ...	70
L1 ...	2741.3 ...	2λ	100 ...	6.5
			25 ...	20

Selection of excitation and development conditions : The following excitation and development conditions were used in obtaining the emulsion calibration curve and followed

in all other subsequent work:

Excitation²⁸

Unit ... National Spectrographic
Laboratories "Spec-Power"

Type ... Condensed Arc

Ignition(A.C.Spark):

Capacitance ... 0.0012 mf

Resistance ... 0.0

Inductance ... 0.0

Condenser discharge/half cycle ... 2

Condenser discharge voltage ... 14,000

Power(Unidirectional Arc):

Secondary amperage ... 6

Sample ... POSITIVE

Spectrograph²⁸

Unit ... Bausch & Lomb 1.5 meter medium-sized
grating

Range ... 1850 to 3700 A° in the second order;
3700 to 7400 A° in the first order

Slit Width ... 20 microns

Collimating lens aperture ... 6 mm

Focus ... On collimating lens

Source to slit ... 34 cm.

Analytical gap ... 2 mm.

Rotation speed of platform electrode ... 10 rpm

Exposure:

Total ... 40 sec.

Pre-arc ... 0

Filter ... 6-100-25%

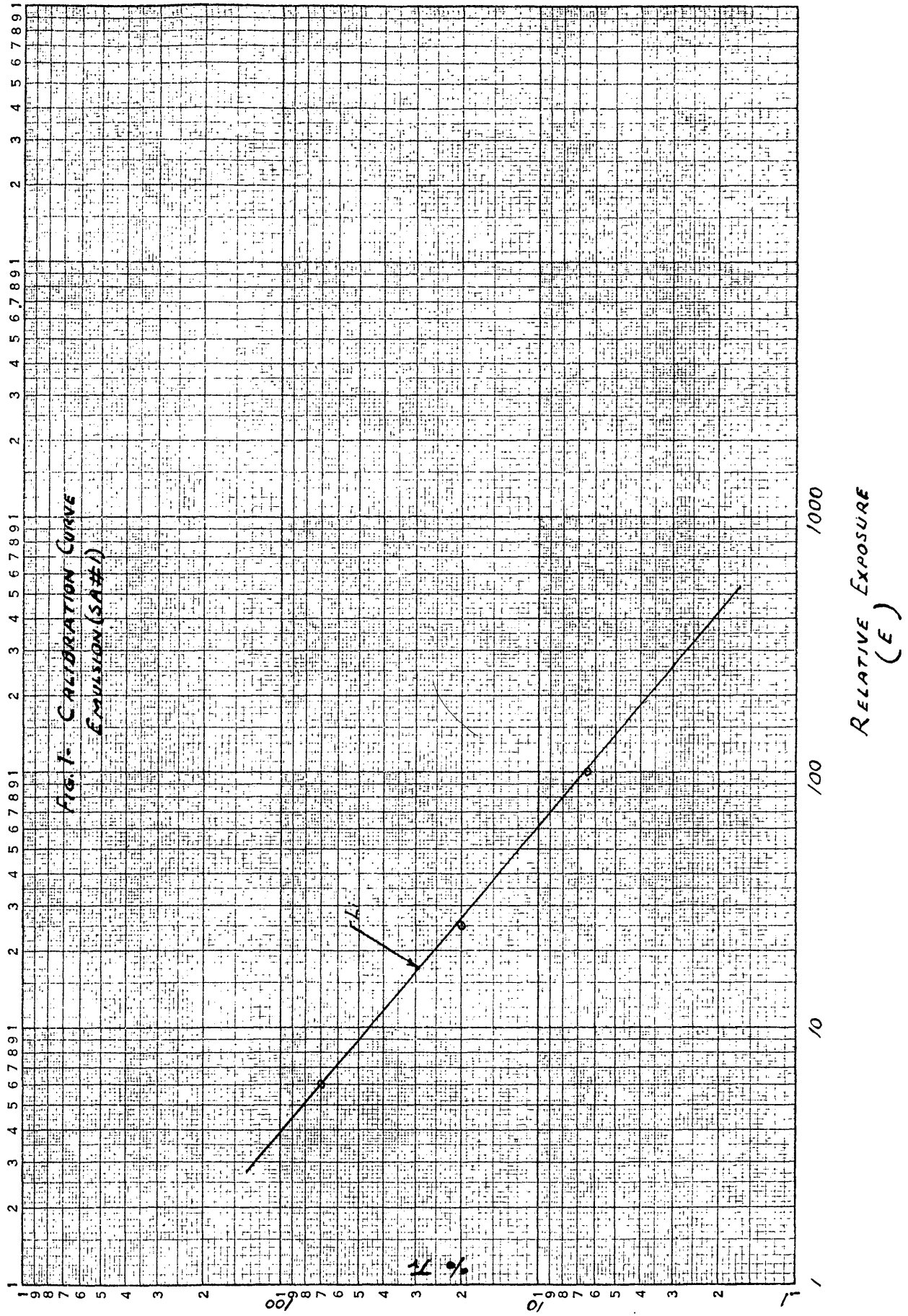
Development²⁸

Developer ... 3 min.

Short Stop ... 15 sec.

Fixer ... 2 min.

Wash ... 5 min.



Selection of spectral lines : The following table gives the spectral lines used for the quantitative purposes

TABLE 5
Spectral lines used for
Quantitative purposes

Elements	Wavelengths(λ) (A°)	Observed as	Excitation Potential
Fe	2488.15	... 2 λ ...	3.6
Ni	3050.8	... 2 λ ...	3.6
V	3183.4	... 2 λ ...	3.8
Li	2741.3	... 2 λ ...	3.8
Co	3405.1	... 2 λ ...	4.0

Preparation of standard solutions : Difficulty was encountered in finding proper compounds which would remain in solution with oil. As far as iron, nickel, and vanadium were concerned the following procedure was found satisfactory:

1. Iron standard solution : A sample of Uversol Iron was obtained from Harshaw Scientific Company; it contains 6 % iron. With a dry clean pipette, 1.85 ml. of the Uversol Iron was measured out and dissolved in mineral oil. Then enough mineral oil was added to make the total volume 500 ml. This gave a standard solution of 250 parts per million(ppm) iron.

All other standards of lower concentrations were made by dilution with mineral oil.

2. Nickel standard solution : By trial and error, the nickel compound selected was nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. An amount of 0.2906 gram (1/1000 mole) of the compound weighed out and dissolved in 10 ml. of glacial acetic acid. To this solution was added 40 ml. of oleic acid; the whole system was then slowly heated to give a homogeneous mixture. Then 250 ml. of mineral oils was added, and the system gently heated to give a clear solution. The solution thus obtained gave a concentration of 221.1 ppm. nickel. Other standard solutions of lower strengths were made by dilution with mineral oil.
3. Vanadium standard solution : By trial and error, the compound selected was vanadium oxytrichloride (VOCl_3) having molecular weight of 173.82 and density of 1.829. An amount of 0.5531 gram of this compound was taken; to this was added 10 ml. of glacial acetic acid and then 80 ml. of oleic acid; the whole system was then gently heated to give a homogeneous mixture. Then 300 ml. of mineral oil was added. The solution thus obtained gave a con-

concentration of 582.11 ppm vanadium. The other standard solutions of lower strengths were made by dilution with mineral oil.

Preparation of working curves : Working curves for Fe, Ni, and V were made by plotting on a log-log paper concentration(ppm) against the ratio of relative exposures of the internal standards and the element spectral line chosen. The following tables give the data for working curves and the following figure gives the working curves.

TABLE 6
Working curve data for
Iron

Concentration (ppm)	% Tr		E		$\frac{E_{Fe}}{E_{L1}}$
	Fe	L1	Fe	L1	
250	2.4	2.0	310	390	0.795
200	3.8	2.3	180	330	0.545
80	5.9	2.2	108	350	0.308
40	8.4	2.0	72	390	0.184
20	14	2.1	40	370	0.108

TABLE 7
Working curve data for
Nickel

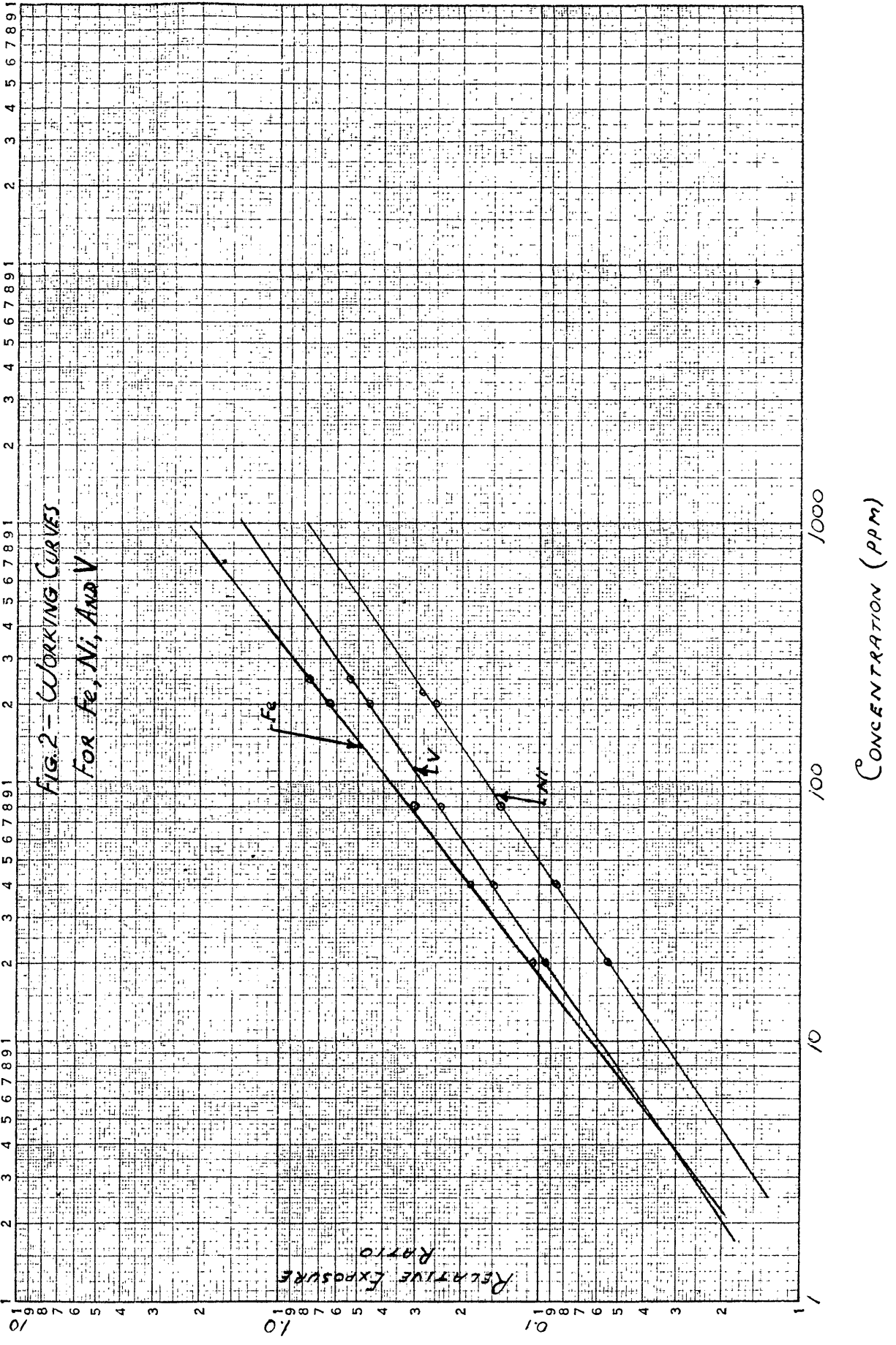
Concentration (ppm)	% Tr		E		$\frac{E_{Ni}}{E_{L1}}$
	Ni	L1	Ni	L1	
221.1	6.9	2.36	90	320	0.282
200	7.5	2.3	82	330	0.248
80	13.2	2.5	42	296	0.141
40	18.5	2.8	29	260	0.15
20	20.6	2.79	25	266	0.094

TABLE 8
Working curve data for
Vanadium

Concentration (ppm)	% Tr		E		$\frac{E_V}{E_{Li}}$
	V	Li	V	Li	
250	3.7	2.2	190	350	0.544
200	8.1	3.8	76	180	0.421
80	10.7	3.2	54	220	0.244
40	18.5	2.8	29	260	0.15
20	20.6	2.79	25	266	0.094

Wavelength of Vanadium = 3183.4 Å

Wavelength of Lithium = 2741.3 Å



Attainment of quantitative values : Nine samples of crude oils were analyzed for iron, nickel, and vanadium and their quantitative analyses were obtained by the use of the respecting working curves. The following table gives the analytical values:

TABLE 9
Analytical values of Fe, Ni, & V
Spectrographic method

Crude Oils	% Tr			L1	$\frac{E_{Fe}}{E_{L1}}$	$\frac{E_{Ni}}{E_{L1}}$	$\frac{E_V}{E_{L1}}$	ppm(wt)		
	Fe	Ni	V		Fe	Ni	V	Fe	Ni	V
Mancos (well 10)	87.5	49	85	5.5	.039	.076	.039	6.2	32	5.6
Mancos (well 255)	-	64	94	7.0	-	.074	.0466	-	31	7.4
Mancos (Buck 355)	93	92	98.5	5.4	.035	.041	.037	5.4	12.8	5.2
Shinarump	97	86	98.5	5.3	.0328	.044	.0354	4.9	14	4.9
Weber	86	80	89	5.9	.0435	.047	.0414	7.2	15.5	6.2
Frontier	84	48	98	4.2	.045	.09	.0392	7.4	41.5	5.7
Curtis	71	22	17.4	5.6	.051	.21	.269	9.0	153	90
Tensleep	70	21	16.6	5.9	.055	.22	.293	9.9	158	102
Embar	64	23	29.4	6.3	.065	.215	.169	12	157	47

Sample calculations : The following calculations are intended to illustrate how the strengths of starting standard solutions were obtained and how the lower strengths were arrived at by dilution:

250 ppm Fe standard solution

1 mg. of Uversol Iron contains 0.06 mg. Fe

Amount of Uversol Iron taken	...	= 1.8154 gm(1.85 ml.)
Amount of mineral oil($d=.872$) taken	...	= 498.15 ml.
Total volume	...	= 500 ml.
Wt. of Fe present	...	= $1.8154 \times .06 \times 1000$ = <u>108.92 mg.</u>
Wt. of mineral oil	...	= 434 gm.
Total wt.	...	= $(434 + 1.8154)$ = <u>435815.4 mg.</u>
ppm Fe	...	= $(108.92 \times 10^6) \div 435815.4$ = <u>250</u>
density of this solution(pycno- meter)	...	= .874

80 ppm Fe standard solution by dilution

1 ml. of the above solu- tion	...	= 0.2179 mg. Fe
Now, $0.2179/x$		= $80/10^6$
where x is equal to total wt. to be	...	= 2721 mg.
Therefore wt. of mineral oil to be added	...	= $2721 - 874$ = 1847 mg. = 1.847 gm.
Volume of mineral oil added	...	= $1.847/0.872$ = <u>2.12 ml.</u>
Therefore 2.12 ml. of mineral oil was added to to each milliliter of the 250 ppm Fe standard solution to give 80 ppm Fe standard.		

To check

Total wt.

1 ml. of 250 ppm
Fe standard ... = 0.874 gm.

2.12 ml. of mineral
oil ... = 1.847

2.721 gm.

= 2721 mg.

1 ml. of 250 ppm.
Fe standard ... = 0.2179 mg. Fe

Therefore ppm Fe = $0.2179 \times 10^6 \div 2721$

= 80

Accuracy

= ± 1.5 - 2.0

COLORIMETRIC METHOD

Outline of the procedure :Burning of the sample & preparation of analytical solutions:

One hundred grams of the crude oils and the standard solutions was taken in a platinum dish and gently heated until it caught fire and then allowed to burn freely to a carbonaceous residue. The carbon was then burned off by a direct flame from an ordinary bunsen burner under a very slow stream of oxygen fed into the tip of the flame. After all the carbon was burned off, the remaining residue was dissolved in 20ml. of 1:1 HCl and transferred to a 100 ml. volumetric flask and the volume was brought to the mark by adding water. This solution was used to determine the metals. It may be noted here that burning as above is as accurate as any other burning procedure e.g., wet oxidation by treatment with conc. sulfuric acid.⁹

Determination of Iron⁹

An aliquot of 20 ml. of the prepared solution was transferred to a 100 ml. volumetric flask, at the same adding an equal aliquot to a small Erlenmeyer flask. The latter was then titrated with 2 M. Na_2CO_3 ; and then at the end with 0.5 M sodium acetate until the solution was alkaline to bromophenol blue. To the portion of the solution in the volumetric flask was added

1 ml. of 10% hydroxylamine hydrochloride solution followed by 1 ml. of 0.1% orthophenanthroline solution. The amount of sodium carbonate and sodium acetate (as determined by the separate titration) was then added and the volume adjusted to the mark. Dark salmon(translucent) color indicated proper condition and successful color development. The transmittance was then measured by using the Beckman DU Spectrophotometer at 520 millimicrons and setting the instrument with reagent blank(0-phenanthroline).

Determination of Nickel⁹: An aliquot of same of the prepared solution was taken into a 100 ml. volumetric flask, and diluted with 15 ml. of water. to this then were added 0.5 grams of citric acid and 0.5 ml. of iodine solution(3.2 grams of iodine in 250 ml. of water containing 6.25 gram of KI), followed by 3 ml. of concentrated ammonium hydroxide. To the whole system then was added 0.5 ml. of dimethylglyoxime solution (1 % in alcohol) and the volume adjusted to the mark with water. Dark pink coloration indicated successful color development. The transmittance was then measured at 540 millimicrons, setting the instrument with reagent blank.

Determination of Vanadium⁹: An aliquot of 20 ml. of the

prepared solution was taken in a 100 ml. beaker. The chlorides were eliminated by evaporating with 1 ml. of concentrated sulfuric acid. Then the volume was brought to about 50 ml., which was placed in a clean electrolytic bath containing a layer of mercury deep enough to cover the lower electrode. The system was then electrolyzed at 5-6 volts and a current of 1-2 amps for 15 minutes. While the current was still flowing, first the mercury and then the electrolyte was drawn off. The electrolyte was then filtered, washed with water, and heated to boiling in a 100-ml beaker. 0.1% potassium permanganate solution was then added dropwise to the system until pink coloration persisted for several minutes. The excess permanganate was then reduced by adding 2-3 drops of 1:1 HCl and boiling. Boiling was continued until the volume of the system reduced to about 10 ml. Then, in succession were added 2.5 ml. of 2.5 M sulfuric acid, 0.8 ml. of 85% phosphoric acid, and 1.2 ml. of 0.5 M sodium tungstate solution. The whole system was gently heated to boiling, allowed to cool, and then transferred to a 100-ml volumetric flask, and the volume was adjusted to the mark. Green coloration indicated the formation of the vanadium phospho-

tungstate complex. The transmittance was then measured at 420 millimicrons, setting the instrument with reagent blank.

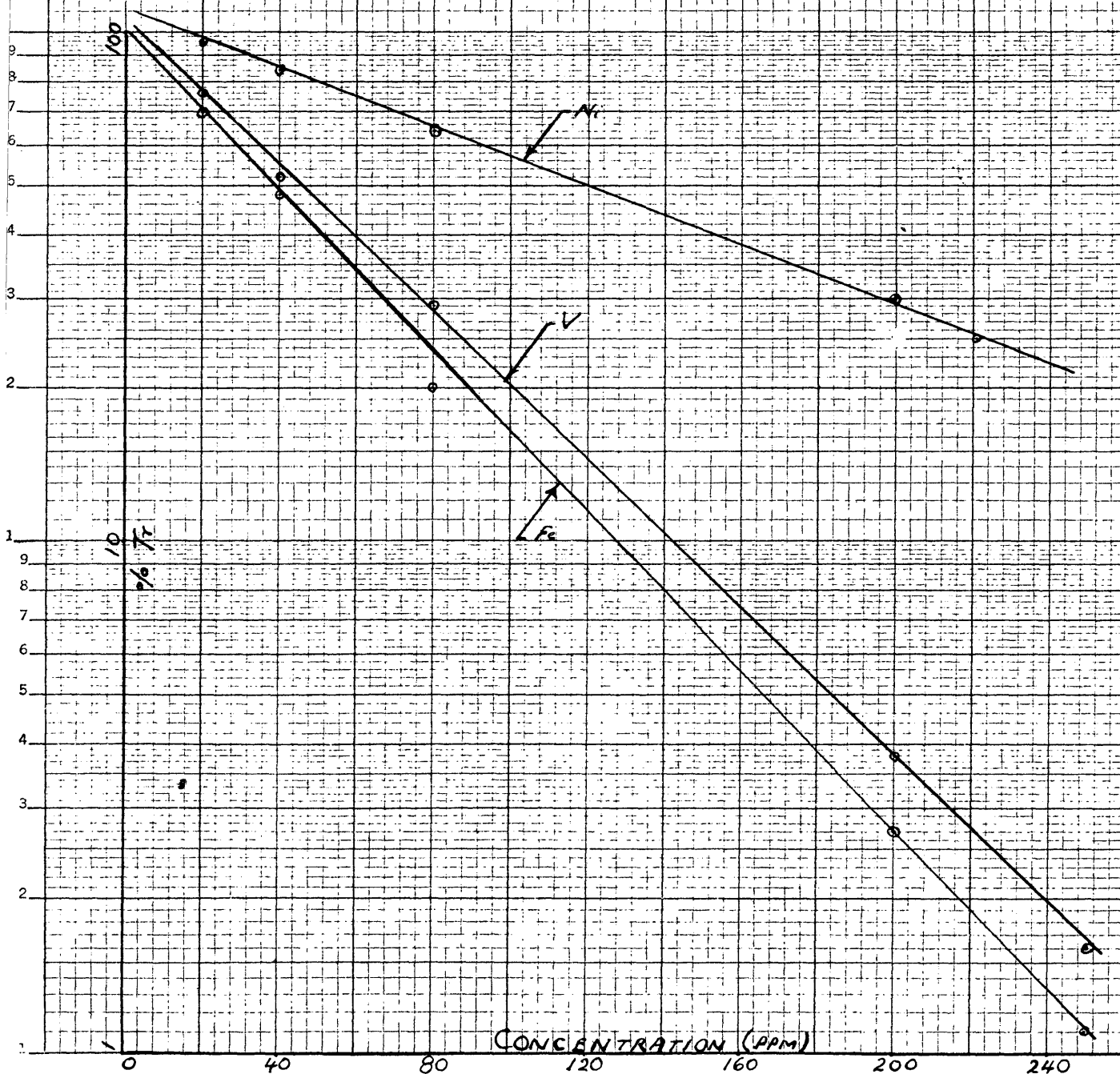
Preparation of working curves :

Standard solutions of iron, nickel, and vanadium were prepared under the spectrographic method. These solutions were used here to make the respective working curves. The above outline was followed, and the working curves were prepared. The following table gives the data for and the figure the working curves on semi log paper.

TABLE 10
Working curve data for
Fe, Ni, V

Concentration (ppm)	% Transmittance		
	Fe	Ni	V
250	1.1	-	1.6
200	2.7	25.0	3.8
80	20.0	64.0	29.0
40	48.0	84.0	52.0
20	70.0	95.0	76.0

FIG. 3 - WORKING CURVES FOR Fe, Ni AND V



Attainment of the quantitative values :

The nine samples of crude oil were taken for analysis. The above procedure was followed in burning the samples, in obtaining the analytical solutions, and in determining the quantity of Fe, Ni, and V by the use of their respective working curves. The following table gives the analytical values.

TABLE 11
Quantitative values of Iron, Nickel,
Vanadium by the colorimetric method

Crude Oils	% Tr			ppm		
	Fe	Ni	V	Fe	Ni	V
Mancos (well 10)	88	87	94	6	35	5
Mancos (well 255)	96	90	92	1	30	7
Mancos (Buck 355)	90	102	93	5	12	6
Shinarump	90.5	100	94	4.3	16	5
Weber	87	99	90	6.9	17	8
Frontier	87	84	92	7	40	7
Curtis	84	39	23	9	152	91
Tensleep	80	37	19.5	12	160	101
Embar	82	38	46	10	156	48.0

AN IMPROVED QUANTITATIVE METHOD

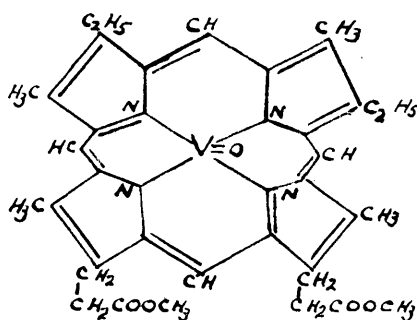
DEVELOPMENT

The rotating electrode and the colorimetric methods are both associated with evaporation of samples. This evaporation causes loss of mineral content. It was therefore desired to develop a rapid quantitative method using spectrographic technique but avoiding any evaporation loss of the mineral content.

To avoid any ashing and evaporation step it is necessary to extract and isolate the metal contents from the crude oils by some means and to determine them quantitatively. It is known that the metals exist in the crude oils in different physical and chemical forms, which are selective towards a single extractive agent or adsorbent. The present paper deals with only iron, nickel, and vanadium and an attempt was made to develop a process for extracting these metals.

Activated carbon and silica gel(used as is)have been found inadequate to adsorb these three metals. This

is probably due to the fact that these metals exist in complex forms having such structural arrangements as keep them concealed and protected in the very interior without at all exposing them to the influence of the carbon or the silica gel. Investigations carried on the form of vanadium complexes tentatively gave the following structural arrangement²⁷ in the light of which the above reasoning appears to be true.



Provisional structure of
Vanadium-Porphyrin complex

In order to extract these metals, therefore, one has to pay special attention to the physical and chemical forms in which these metals exist. To be successful a process must bring about a structural rearrangement, so that the metals can be adsorbed on the carbon or the silica gel. With this idea in mind the author devoted much of his studies to finding a reagent that would presumably form a super complex with these metal complexes and thus bring about the

desired change so that these could be adsorbed on the carbon. In the course of tedious experimentations some reagents were actually tried and found effective as follows:

Reagent		Effective for
Mercaptobenzothiazole	...	Iron and Nickel
Dimethylglyoxime	...	Nickel
Sulphuretted Hydrogen	...	Nickel and Vanadium
Hydrochloric acid	...	Nickel and Vanadium
Urea	...	Iron, Nickel and Vanadium

Urea was selected as the desired reagent and several experimentations were carried on it. Standard solutions of iron, nickel, and vanadium were individually and collectively treated with urea for half an hour and then with activated carbon for another half an hour. The system was then filtered to dryness in a gooch crucible under moderate suction and the filtrate was spectrographically tested for iron, nickel, and vanadium. A crude oil already known to contain iron, nickel, and vanadium was similarly treated and tested. On each test, the result indicated success, and within the limits of his experimentations and observations, the author had ample evidences to state that it is a satisfactory process for extracting and isolating the iron, nickel, and vanadium complexes simultaneously.

All these metals(iron, nickel, and vanadium) would now be adsorbed on the carbon and would consequently remain with the residue on the filter paper. These could now be carefully removed and analyzed spectrographically for their quantitative values. The whole procedure, therefore, is an analytical method besides being a process of extraction and isolation.

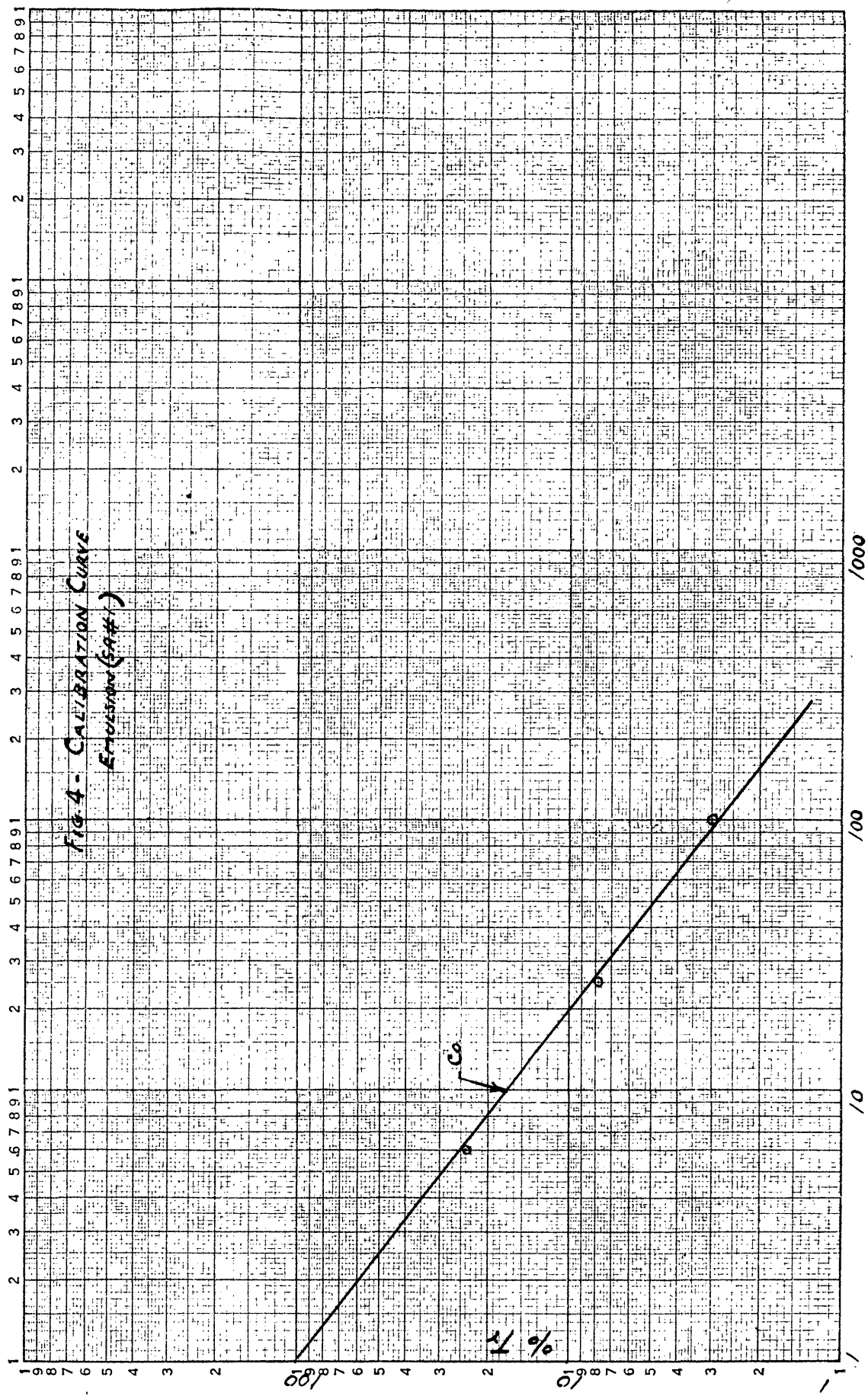
EMULSION CALIBRATION CURVE

Cobalt but not Lithium has been found to be extracted by urea and activated carbon. It remains in the residue and hence may be used as the internal standard in quantitative determinations. An emulsion calibration curve using cobalt was made as follows:

Three milliliter of the uversol cobalt solution prepared by the procedure described under the spectrographic method was taken in a small beaker and treated with urea and activated carbon for one hour. It was then filtered in a gooch crucible under moderate suction. The residue was used to obtain the spectrum of cobalt with a 3-step filter as previously mentioned. The following table gives the data for emulsion calibration curve

TABLE 12
Data for calibration curve(SA # 1)

Internal Standard	Relative Exposure(E)	% Tr
Cobalt	6	24
	100	3
	25	8

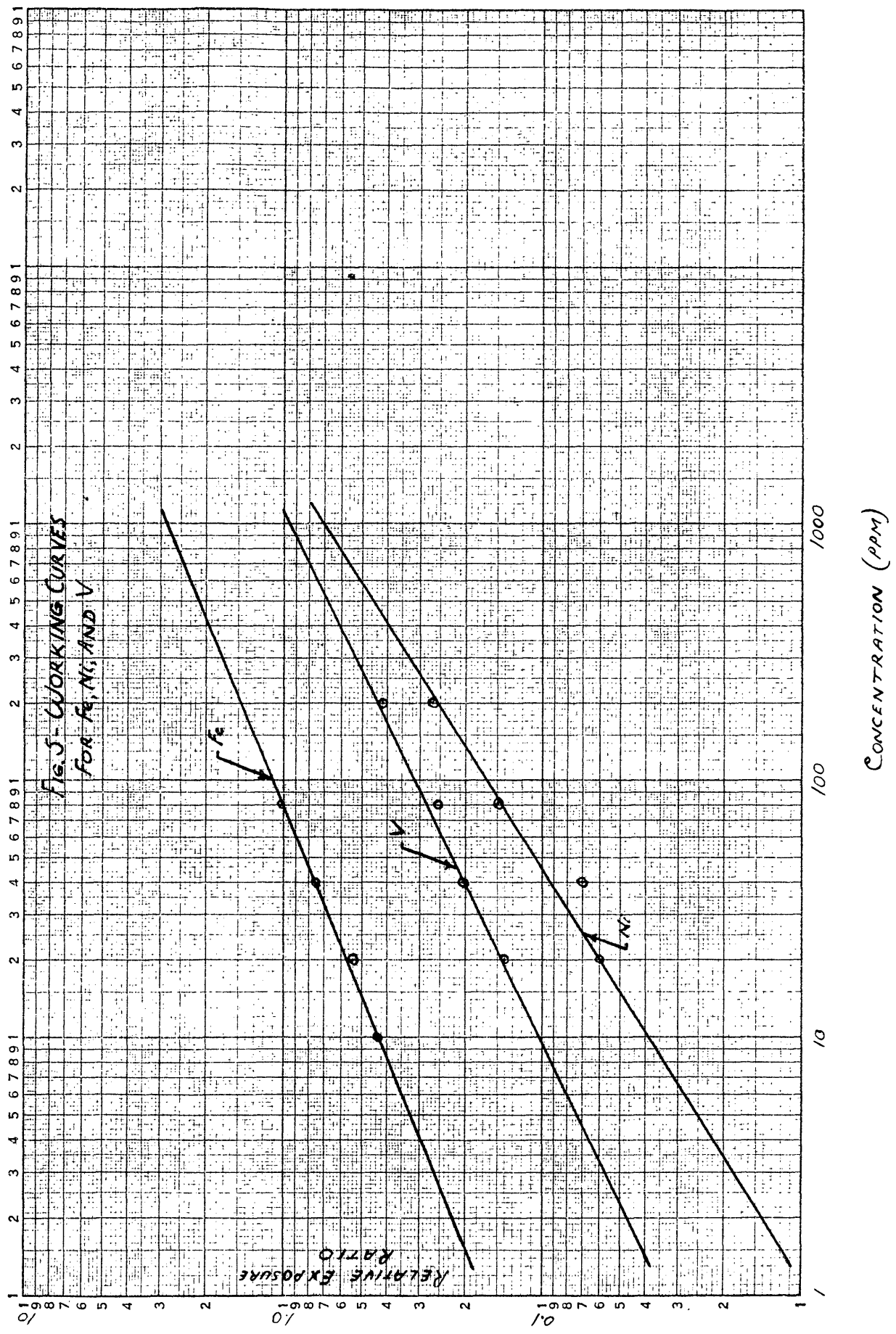


WORKING CURVES

Standard solutions of iron, nickel, and vanadium were prepared following the procedures described under the spectrographic method. 25 ml. of each of the standard solutions was mixed thoroughly with a 3 ml. of cobalt (uversol) solution, contacted with 0.2 gram of urea for half an hour, and then with 0.1 gram of activated carbon for another half an hour with frequent stirring. The system was then filtered in a gooch crucible under moderate suction. The residues contained the known amounts of the respective elements and were used for obtaining the spectra of known concentrations. The spectrographic carbon rod drilled to a fixed depth was used as the lower electrode, the upper electrode being also the spectrographic carbon properly shaped. The crater of the lower electrode was filled with an aliquot portion (5.8 mg.) of the residue obtained as above. The details were the same as described under the spectrographic method. The following is a tabulation of data for the different working curves:

TABLE 13
Working curve data for Fe, Ni, and V

Concentration (ppm)	% Tr				E				$\frac{E_{Fe}}{E_{Co}}$	$\frac{E_{Ni}}{E_{Co}}$	$\frac{E_V}{E_{Co}}$
	Fe	Ni	V	Co	Fe	Ni	V	Co			
200	-	19	13.8	8.6	-	8.55	12.7	31.6	-	.27	.435
80	6.4	31	20.5	8.5	34	4.5	7.63	32.0	1.06	.141	.24
40	8.0	54	24	8.4	25	2.2	6.36	30.0	.758	.069	.212
20	11	61	31	8.6	17	1.9	4.43	31.6	.538	.06	.14
10	13.2	-	-	8.5	13.5	-	-	32	.422	-	-



ATTAINMENT OF ANALYTICAL VALUES

Nine crude oil samples were treated in the same way as the standards. The procedure described under the working curves was followed, and the crude oils analysed for iron, nickel, and vanadium. The following tables give the data of quantitative values.

TABLE 14

Data for analysis of Fe, Ni, and V
Activated carbon method

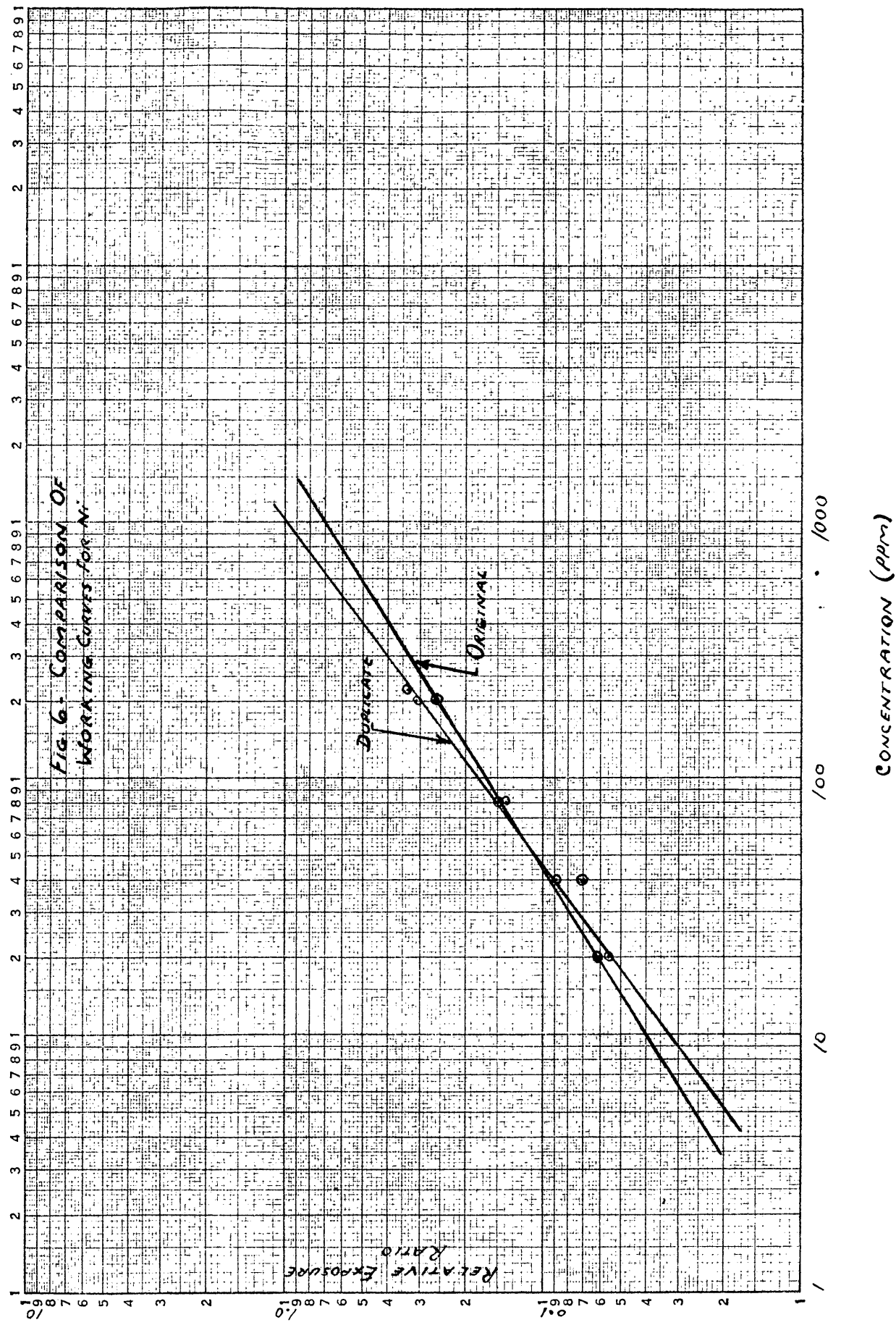
Crude Oils	% Tr				$\frac{E_{Fe}}{E_{Co}}$	$\frac{E_{Ni}}{E_{Co}}$	$\frac{E_V}{E_{Co}}$	ppm (wt)		
	Fe	Ni	V	Co				Fe	Ni	V
Mancos (well 10)	16.5	50	52	8.9	.334	.08	.071	5.8	31	4.9
Mancos (well 255)	23	50	45	8.7	.210	.08	.09	1.95	31	8.0
Mancos (Buck 355)	17	82	54	8.7	.31	.041	.07	4.8	11	5.0
Shinarump	18.5	72	54	8.8	.30	.049	.07	4.4	14.8	5.0
Weber	15	71	48	8.7	.36	.05	.082	6.8	15	6.6
Frontier	14.5	43	54	8.6	.38	.094	.07	8.0	41	5.0
Curtis	13.6	22.5	28.5	8.5	.41	.21	.27	9.2	150	86.0
Tensleep	13	21.9	28	8.5	.43	.220	.29	11.9	155	50.0
Embar	12.8	22.0	23	8.6	.45	.218	.21	10.6	160	100

REPRODUCIBILITY OF ANALYTICAL VALUES

In order to ascertain the reproducibility of results the whole procedure was repeated on nickel standard solutions; the working curve for nickel was prepared and compared with the original curve. This time, samples from two opposite spots on the carbon residue were used to provide enough data for knowing whether there was any segregation of metal on the carbon residue. The following is a tabulation of such data:

TABLE 15
Duplicate working curve data
for Nickel

Concentration (ppm)	% Tr		$\frac{E_{Ni}}{E_{Co}}$
	Ni	Co	
221.1			
a.	20.5	9.0	0.33
b.	21.0	8.5	0.31
200			
a.	17.2	7.8	0.34
b.	17.4	7.9	0.34
80.0			
a.	35	8.2	0.15
b.	35	8.4	0.16
40.0			
a.	54	9.0	0.09
b.	54.2	8.7	0.07
20.0			
a.	74	8.5	0.058
b.	73.6	8.3	0.07



In the above table, (a) and (b) represent the two opposite spots in the carbon residue. The data indicate that there was not much segregation of metal. The above data were plotted together with those originally obtained and the two working curves were graphically compared. Figure 6, gives such comparison. It can be seen from Fig. 6 that the data were not wholly reproduced. The deviation ranged from 0-15% within the working limit. On average, the result could be reproduced within 10 percent. Some crude oil samples were worked again; their nickel values were obtained on the basis of the new working curve and compared with the original values. The following table gives such comparison:

TABLE 16
Duplicate analytical values
of Nickel

Crude Oils	% Tr		$\frac{E_{Ni}}{E_{Co}}$	ppm Ni		Percent Deviation
	Ni	Co		Duplicate	Original	
Mancos (well 10)	60	8.9	.0825	33.0	31.0	6.45
Mancos (well 255)	63	8.6	.078	30.0	31.0	3.23
Frontier	52	8.4	.094	41.2	41.0	0.49
Tensleep	30	8.8	.215	154.0	155.0	0.645

From the above data, it could be safely said that results were reproducible within 10 percent.

DISCUSSION AND COMPARISON OF THE ANALYTICAL
METHODS

Analysis of the various crude oils for the determination of their metal contents is necessary in order to predict deleterious effects, to design an effective process for metal removal, and to provide a means of control of the product quality. Several methods have been employed for such determinations, among which the colorimetric and the spectrographic methods are commonly used. The colorimetric method employs an ashing procedure which is associated with volatilization loss and is not suitable for rapid determination. The rotating electrode method (as employed previously) is quick, sensitive, and suitable for rapid determination, but it is not accurate because of the loss of mineral matters during evaporation. In view of the above fact, it was desired to develop a rapid quantitative method using spectrographic technique but avoiding any evaporation loss of the mineral matters. The author worked out such a method, called the "activated carbon method". The following is a comparative discussion of these three methods:

ACTIVATED CARBON METHOD

This procedure, besides being a quantitative method may be successfully used as a commercial means of removing the metals from crude oils by simply establishing contact with reagents like urea and activated carbon (as tried by the author). As a quantitative method, it is fast and time saving, though not quite as rapid as the rotating electrode method. However, it has the definite advantage that it is free from the volatilization loss inherent in the spectrographic and the colorimetric methods. This is the desired improvement sought for. However, it will involve handling losses which may, of course be, minimized by efficient analytical skill. The success of the method will depend on the complete removal of these metals and their uniform distribution in the carbon residue. This method could be made rapid and accurate by experience and skill.

SPECTROGRAPHIC METHOD

The spectrographic method using the rotating electrode technique is a fast, convenient, and time-saving method. It is best suited for rapid determination and regular routine work. But it is not accurate because some metals are lost at the temperature of evaporation. Also, the author has encountered difficulty in controlling the

amounts to be evaporated on the carbon disc (particularly with heavy oils). The difficulty lies in the fact that some thick and viscous crude oils leave a great residue after the evaporation of a fraction of a milliliter, whereas some others would leave hardly any residue after the evaporation of the same amount. On the other hand, if the amount to be evaporated were cut down to a small value, the intensity of the spectral lines would be too faint for quantitative work. In spite of the above difficulties it is fast, time-saving, fairly accurate, and very convenient method.

COLORIMETRIC METHOD

This method, being principally a chemical method, is slow and very time consuming. In the course of his work, the author found this method very accurate and sensitive to trace elements. Because of its inherent slowness it will not qualify as a method for routine analysis, but for accurate determination it is the method to be employed. The following table gives a comparative picture of the analytical values by the three different methods:

TABLE 17
Comparison of analytical
values by the three methods

Crude Oils	°API	Spectrographic			Colorimetric			Activated Carbon		
		Fe	Ni	V	Fe	Ni	V	Fe	Ni	V
Mancos (well 10)	43.1	6.2	32	5.6	6.0	35	5	5.8	31	4.9
Mancos (well 255)	42.3	-	31	7.4	1.0	30	7	1.95	31	8.0
Mancos (Buck 355)	41.7	5.4	12.8	5.2	5.0	12	6	4.8	11	5.0
Shinarump	37.5	4.9	14.0	4.9	4.3	16	5	4.4	14.8	5.0
Weber	33.6	7.2	15.5	6.2	6.9	17	8	6.8	15	6.6
Frontier	42.7	7.4	41.5	5.7	7.0	40	7	8.0	41	5.0
Curtis	22.7	9.0	153	90	9.0	152	91	9.2	150	86.0
Tensleep	23.1	9.9	158	102	10.0	160	101	10.6	160	100
Embar	22.3	12	157	47	12	156	48	11.9	155	50

The values are in ppm(wt)

RELATIONSHIP OF THE METALS IN CRUDE OILS WITH THOSE
OF PRODUCING FORMATIONS AND ASSOCIATED WATERS

METALS IN PRODUCING FORMATIONS

In order to study whether any relation exists between the metals in crude oils and those in producing formations, nine samples of such formations were obtained. These were procured from the same depths as the nine crude oils under investigation. The rock samples were pulverized in an agate mortar and then mixed with carbon powder. These were then analyzed spectrographically for their metal contents. The following is a table of such analysis:

TABLE 18
Analysis of Producing formations

Formations	Metals Identified
Mancos(well 10)	Fe, Ca, Mg, Al, Si, Na, Zn, Au
Mancos(well 255)	Fe, V, Ca, Mg, Al, Si, Na, Zn, Ag
Mancos(Buck 355)	Fe, V, Ca, Mg, Al, Si, Na, Zn, Pb, Ag
Shinarump	Fe, Ni, V, Ca, Mg, Al, Si, Na, Ba, Zn, Pb, Ag, Mn
Weber	Fe, Ni, V, Ca, Mg, Al, Si, Na, Zn, Pb(?), Mn
Frontier	Fe, V, Ca, Mg, Al, Si, Na, Ba, Zn, Pb
Curtis	Fe, V, Ca, Mg, Al, Si, Na, Ba, Zn, Pb, Ag
Tensleep	Fe, V, Ca, Mg, Al, Si, Na, Pb, Ag, Mn
Embar	Fe, Ni, V, Ca, Mg, Al, Si, Na, Ba, Pb

The above table reveals the fact that the metals in the rocks are mostly iron, calcium, aluminum, and magnesium. Nickel and vanadium are completely absent in most rocks and are very barely present in a few. Comparison of Table 18 with Tables 1 and 2 makes it clear that the metals in crude oils are not the same as those in their reservoir rocks. If the metals in crude oils originated solely from the rocks, the same metals would probably have been present in the reservoir rocks. The relatively high concentrations of some unusual metals in crude oils for example, nickel and vanadium indicate that this could not have been the case and that their concentration could have been brought about only by some agency connected with the actual formation of oils¹.

METALS IN ASSOCIATED WATERS

In order to study the metals in the associated waters, only four samples could be locally obtained. 100 ml. of each was evaporated in a platinum dish and the residue analyzed spectrographically for their metal content. The following is a table of such analysis:

TABLE 19

Analysis of water samples

Water Sample	Metals Identified
Frontier ...	Fe, V, Na, Ca, Mg, Al, Si, B
Curtis ...	Fe, V, Na, Ca, Mg, Zn, Al, Si, B
Tensleep ...	V, Na, Ca, Mg, Al, Si, B, Ag, Th(?), Sr
Embar ...	Fe, Ni, V, Na, Ca, Mg, Zn, Al, Si, B, Sr

T 819 c. 2
Comparison of Table 19 with Tables 1 and 2 indicates that the metals in the crude oils are not the same as those in the water. Most of the metals in the waters are sodium, calcium, and magnesium. Iron, nickel, and vanadium are almost absent. These waters, therefore, could not possibly bring about high concentration of some of these metals in the crude oils.

It is generally agreed, and the author holds the view, that crude oils originated from either animal or plant remains.¹ It is therefore logical to assume that these organisms were largely the medium of concentration of these unusual metallic elements in the crude oils. In support of this view it has been observed that vanadium occurs in small quantities in some marine animals and plants. It has also been observed that some of these animals or organisms absorb vanadium as a substitute for copper and phosphorous in their blood where vanadium is in high concentration¹. It is therefore probable that oils containing vanadium are connected in their origin with marine animals and organisms which are capable of concentrating vanadium.

Certain plants also use vanadium as a substitute for phosphorous¹, and fertile soils have been found to contain nickel in minute quantities, which indicate that small quantities of nickel are beneficial to plants¹.

Moreover, nickel, among other elements, has been detected in the ash obtained from sea weeds. These facts merely bring to light that crude oils originated from some animals, organisms, and/or plants which have brought about the concentration of elements like iron, nickel, and vanadium in the crude oils.

THE ROLE OF METALS IN PROVIDING UNDERSTANDING
OF THE EVOLUTION OF CRUDE OILS

G. W. Hodgson and co-workers¹⁸ proposed that a correlation exists between the age and depth of crude oils with gravity and V/Ni ratio. These workers generalized their observations in this respect as follows:

1. The heavier the crude, the higher is the metal concentration.
2. The older the crude, the lighter it becomes.
3. The lighter and older the oil, the smaller is the V/Ni ratio. This has been explained by the fact that vanadium complexes are less stable than nickel ones and hence the ratio becomes smaller as the crude oil becomes older.

The above generalizations are believed to be the result of progressive evolution or change of the original crude oils with passage of time. While it is generally believed that the original crude oil is undergoing a progressive change, it is not certain whether the above gene-

realizations are true. To verify the above generalizations, therefore, the author carried out some investigation in this respect on the nine crude oil samples locally obtained. The following data give the result of such investigation:

TABLE 20
Data for density and V/N₁ ratio

Field	Crude Oils	Depth	Deg. API	V/N ₁
	Mancos (well 10)	2600 ^a	43.1	0.143
	Mancos (well 255)	2800 ^a	42.3	0.233
Rangely, Colorado.	Mancos (Buck 355)	3100 ^a	41.7	0.500
	Shinarump	5350 ^a	37.5	0.312
	Weber	6080 ^a	33.6	0.470
	Frontier	4677 ^b	42.7	0.175
Grass	Curtis	2305 ^b	22.7	0.499
Creek, Wyoming.	Tensleep	1292 ^b	23.1	0.631
	Embar	1208 ^b	22.3	0.308

a : Depths are in ft below the surface

b : Depths are in ft above sea level

The V and N₁ values were taken from Table 11 under the colorimetric method and their ratios were calculated.

The crude oils shown above are in an order of increasing depths and age. The above table reveals that the

foregoing generalizations are not true as far as these crude oils are concerned. Since it is necessary to obtain numerous data to arrive at a generalization and since the author had only a handful of samples, it is not possible to make a general statement contrary to the above generalizations. The author therefore concludes by merely stating that the above generalizations are not true within the limits of the present investigation.

CONCLUSION

In the light of the present study it is concluded that it is important to examine critically the metals in crude oils. The importance arises from the realization of the harmful effects produced by the metals on the facilities using crude oils and their products. Moreover, the analysis of the crude oils shows the presence of almost all metallic elements; it is quite likely that some crude oils could furnish a source of some rare metals for commercial extraction.

In order to purify crude oils from the harmful metals or to extract the metals for commercial utilization, it would be essential to know the physical and chemical forms in which these metals exist in crude oils. Only then would it be possible to develop a successful treating or extracting process. While developing the "activated carbon method", the author had to try several reagents before selecting urea for extracting iron, nickel, and vanadium. This simply points to the truth of the above statement.

Within the limits of the author's experimentations and observations there was ample evidence to indicate that the activated carbon method was successful in extracting iron, nickel, and vanadium. However, it is important to point out that these complexes exist or may exist in more than one forms and being limited in his observations, the author does not feel justified in concluding that this method would be effective for all iron, nickel, and vanadium complexes in all crude oils.

This method brings out the important principle that a reagent like urea or mercaptobenzothiazole has to be employed to bring about some change in the structure of these complexes which would then be adsorbed by activated carbon, silica gel, or a similar adsorbent. It is therefore concluded that following the above reasoning and adopting the technique, it would be possible to develop treating or extracting methods which could be used to purify the crude oils from these metals or to extract them for commercial utilization.

Urea was not found to be effective for some elements like sodium, potassium, calcium, and lithium. The action of urea is not clearly understood. However, from the above behaviour it appears that the action of urea is selective to some elements. This fact indicates the possibility of using urea in separating the metals into groups. Further studies in this respect would be interesting.

Among the different methods used in the present work, the spectrographic method using the rotating electrode technique is the fastest and very convenient for routine work. The colorimetric method has been found to be very sensitive, delicate, and accurate for microdeterminations. The activated carbon method though free from evaporation losses is not independent of other difficulties mentioned under discussion. Though much faster than the colorimetric method, it does not seem to have any special advantage over the rotating electrode method as regards fastness, accuracy, and working convenience. It is therefore concluded that the rotating electrode method (spectrographic) is suitable for rapid determination and routine analysis, that the colorimetric method is particularly suitable for accurate determination.

Study of metals in reservoir rocks and associated waters does not reveal any correlation with those in crude oils. In the absence of further evidence and being limited in his work, the author subscribes to the conclusion previously arrived at, that the metals came from the original organic and plant remains from which crude oils evolved. The generalization proposed by G. W. Hodgson and his co-workers¹⁸ as to the correlation of the age of crude oils with gravity and V/Ni ratio was studied. Such a study made by the author did not reveal the proposed correlation.

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