Journal of Radioanalytical Chemistry, Vol. 14 (1973) 401— 413

DETERMINATION AND GEOCHEMICAL SIGNIFICANCE OF TRACE ELEMENTS IN IRAQI CRUDE OILS USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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(Received October 12, 1972)

The trace-element composition of crude oil was studied using instrumental neutron activation techniques and a large-volume high-resolution Ge(Li) detector. A total of 29 elements were determined in oils representing the various producing formations of the Iraqi oil fields. These were: Al, Ar, As, Au, Br, Ca, Cl, Co, Cr, Cu, Eu, Fe, Ga, Hg, K, La, Mn, Mo, Na, Ni, Re, S, Sb, Sc, Se, Sm, V, W and Zn. The significance of these trace elements in the geochemical investigation of crude oil is discussed.

Introduction

Oil is built up primarily from hydrogen, carbon and sulfur, but many other elements are present in trace quantities. The determination of these trace elements has contributed significantly to the geochemical investigations of oil.[1-4]

Trace elements that are found in crude oils appear in two distinct forms: as metallo-organic complexes (e.g. V and Ni), or as solid and liquid suspensions. V and Ni are introduced into oil during its formation as porphyrins and other high molecular weight complexes. During oil migration these heavy molecules are retarded and the V and Ni concentrations decrease along the course of migration. The concentration gradients of these two elements can therefore be used in the study of the history of formation, migration and accumulation of oils.[3]

The elements that are present as solid and liquid suspensions are most likely introduced into oil during migration and/or from the reservoir rocks. The study of their concentrations may throw light on the geochemical nature of the reservoir and/or path of migration.[4]

The trace-element composition of oil is also important as regards refining and processing. Certain elements, e.g. V, Ni, Cu, Fe and As, are catalytic poisons in the cracking process and adversely affect the quality of the end-products. Others, e.g. S, Br and Pb, can be a source of air pollution on burning of oil.[5] Trace elements have also been used successfully for oil characterization in identifying the source of oils polluting water-ways.[6]

Several methods are available for the trace-element analysis of oil, including emission spectroscopy, atomic absorption, X-ray fluorescence, polarography and colorimetry.[5] All these methods suffer from limited sensitivity, or need chemical treatment, which constitutes a potential source of contamination. Instrumental neutron activation analysis techniques have been developed by Bryan et al.[6] and Shah et al.[7,8] Both groups used Ge(Li) detector systems and determined a total of 22 and 23 elements, respectively, in various samples of oils from different origins.

The instrumental neutron activation technique is well suited to the trace-element determination of oil because the carbon and hydrogen matrix does not produce any interfering activity on neutron irradiation. The method is sensitive, multi-elemental and does not require any pre- or post-irradiation treatment, eliminating major sources of contamination.

In this study, the trace-element composition of crude oils from all the producing formations of the Iraqi oil fields is determined using instrumental neutron activation analysis. A total of 29 elements were measured. These were: Al, Ar, As, Au, Br, Ca, Cl, Co, Cr, Cu, Eu, Fe, Ga, Hg, K, La, Mn, Mo, Na, Ni, Re, S, Sb, Sc, Se, Sm, V, W and Zn. The geochemical significance of some of these elements is discussed briefly. (See Refs[3,4] for more detailed discussions.)

Experimental

Apparatus

The samples were irradiated in the IRT-2000 nuclear reactor of the Nuclear Research Institute, Baghdad. For the short-lived nuclides, a rapid pneumatic system was used to place the samples at the reactor core and withdraw them in times less than 0.2 sec. For the longer-lived nuclides, the irradiation was carried out in a vertical channel at a thermal flux of $2.8 \cdot 10^{12}$ $n \cdot cm^{-2} \cdot sec^{-1}$.

The counting system consisted of a 30 cm^3 Ge(Li) detector and the associated electronics, and a 2048-channel pulse-height analyzer model ND 2200. The system resolution was 3.0 keV for the 1333 KeV ^{60}Co line.

Procedure

Oil samples from the well-heads and bottom-holes of all the producing Iraqi oil wells were delivered to this laboratory in clean 1 l polyethylene bottles. Each was shaken, and about 1 g sample taken. The samples were placed in clean high-purity polyethylene vials which had previously been washed with conc. HNO_3 and distilled water. The vials were heat-sealed and sent for irradiation.

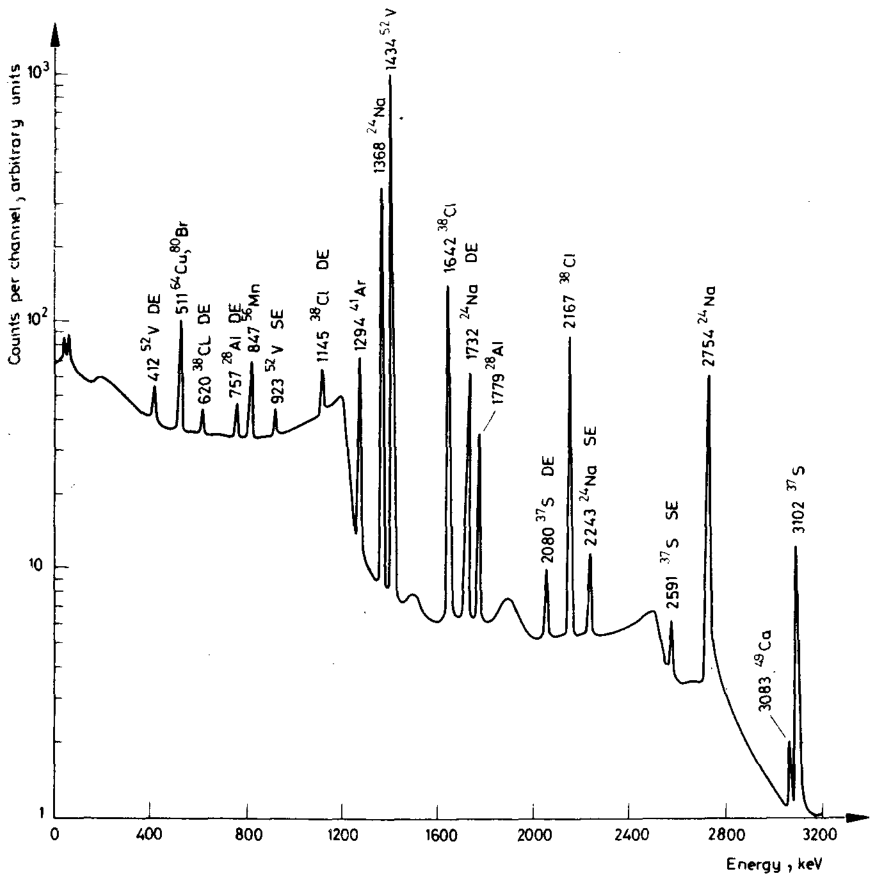

Fig. 1. Typical gamma-spectrum of neutron-activated crude oil. Irradiation time = 900 sec; decay time = 10 sec; counting time = 1000 sec. Isotopes measured: ^{28}Al, ^{52}V, ^{37}S and ^{49}Ca

The work was performed in two stages. The short-lived nuclides (^{28}Al, 2.31 m; ^{52}V, 3.76 m; ^{37}S, 5.05 m; and ^{49}Ca, 8.8 m) were determined in the first stage. The samples and the standards were irradiated using a rapid pneumatic transport system. The irradiation, delay and counting times were set at 900 sec, 10 sec and 1000 sec, respectively. A typical gamma-spectrum is shown in Fig. 1. It can be seen that ^{38}Cl, ^{56}Mn, and ^{24}Na could also be measured during this irradiation. The short time available did not allow transfer of the irradiated oil sample to an inactive container before the counting. However, the containers were cleaned thoroughly and irradiated empty under identical conditions to measure their Al, V, S and Ca contents. No V or Ca were detected, but small amounts of Al and S were measured and the necessary corrections were made.

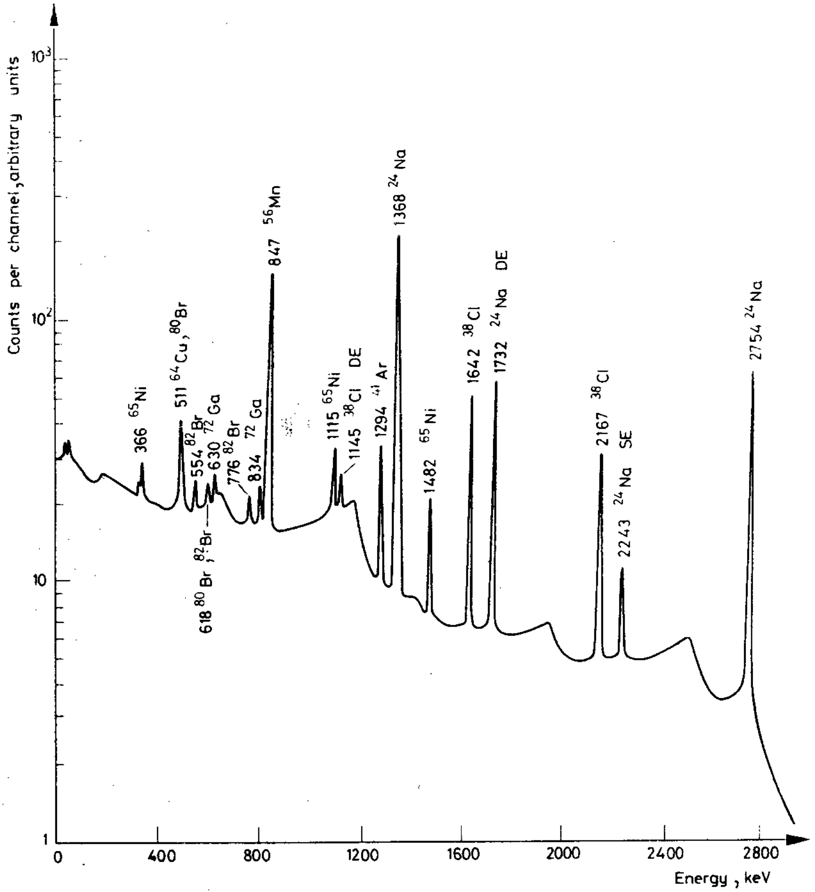

Fig. 2. Typical gamma-spectrum of neutron-activated crude oil. Irradiation time = 4 hrs; decay time = 30 min; counting time = 1000 sec. Isotopes measured: ^{38}Cl, ^{41}Ar, ^{65}Ni and ^{56}Mn

The longer-lived nuclides were all determined in the second stage using longer irradiation and counting periods. Here the sealed vials containing the samples and the standards were placed in a large polyethylene container and irradiated in a vertical channel of the reactor for four hours with an integral flux of $4 \cdot 10^{16}$ n $\cdot$ cm^{-2}. After the irradiation the samples were allowed to cool for 30 min to eliminate the Al and V interfering activities, and the samples were then quantitatively transferred to clean unirradiated containers and counted over the Ge(Li) detector for 1000 sec. At this time the following nuclides were measured: ^{38}Cl, 37.3 m; ^{41}Ar, 110 m; ^{65}Ni, 2.56 h; ^{56}Mn, 2.58 h. A typical gamma-spectrum is shown in Fig. 2. Other

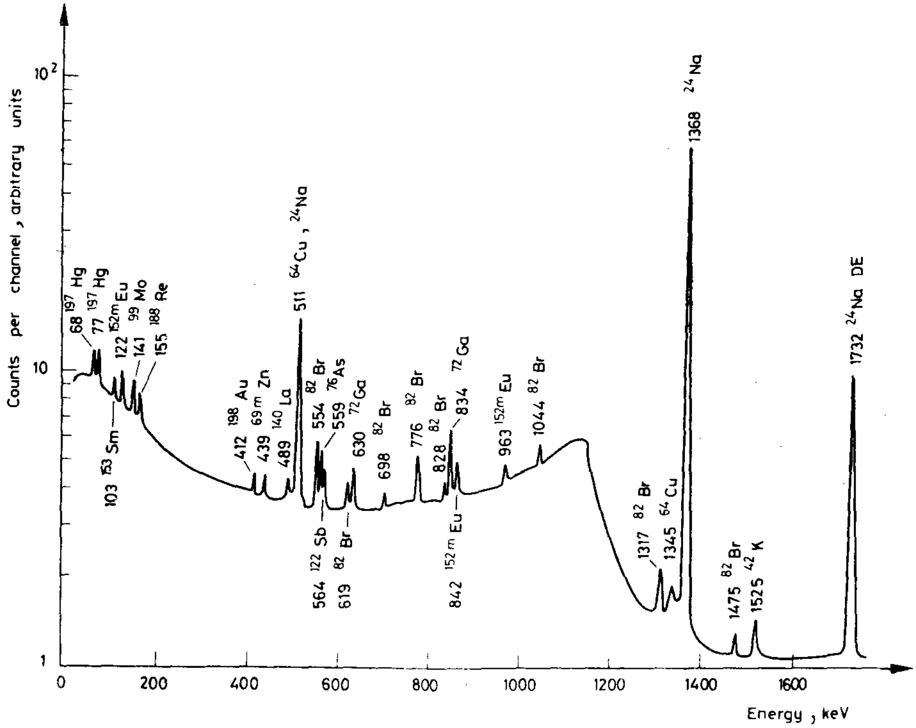

Fig. 3. Typical gamma-spectrum of neutron-activated crude oil. Irradiation time = 4 hrs; decay time = 15 hrs; counting time = 4000 sec. Isotopes measured: ^{64}Cu, ^{72}Ga, ^{24}Na, ^{188}Re, ^{76}As, ^{82}Br, ^{197}Hg, ^{99}Mo, ^{152m}Eu, ^{42}K, ^{69m}Zn, ^{140}La, ^{153}Sm, ^{198}Au and ^{122}Sb

gamma-lines (e.g. ^{24}Na lines) were also observed but they were not measured at this point. The samples were then allowed to decay for about 15 hrs and were counted again for 4000 sec. The following elements were now seen clearly: ^{64}Cu, 12.8 h; ^{72}Ga, 14.3 h; ^{24}Na, 15.0 h; ^{188}Re, 16.7 h; ^{76}As, 26.3 h; ^{82}Br, 35.9 h; ^{197}Hg, 65 h; ^{99}Mo, 66 h (see Fig. 3). In a few samples the following elements were also measured in addition to the above: ^{152m}Eu, 9.35 h; ^{42}K, 12.5 h; ^{69m}Zn, 13.8 h; ^{187}W, 24.0 h; ^{140}La, 40.3 h; ^{153}Sm, 47.1 h; ^{198}Au, 64.8 h; ^{122}Sb, 66 h.

After two weeks, the same samples were counted for the third time, for 40000 sec. The long-lived nuclides: ^{51}Cr, 27.8 d; ^{59}Fe, 45.1 d; ^{203}Hg, 46.9 d; ^{58}Co (from ^{58}Ni), 71.3 d; ^{46}Sc, 83.9 d; ^{75}Se, 121 d; ^{65}Zn, 245 d and ^{60}Co, 5.24 y were now measured. (Fig. 4).

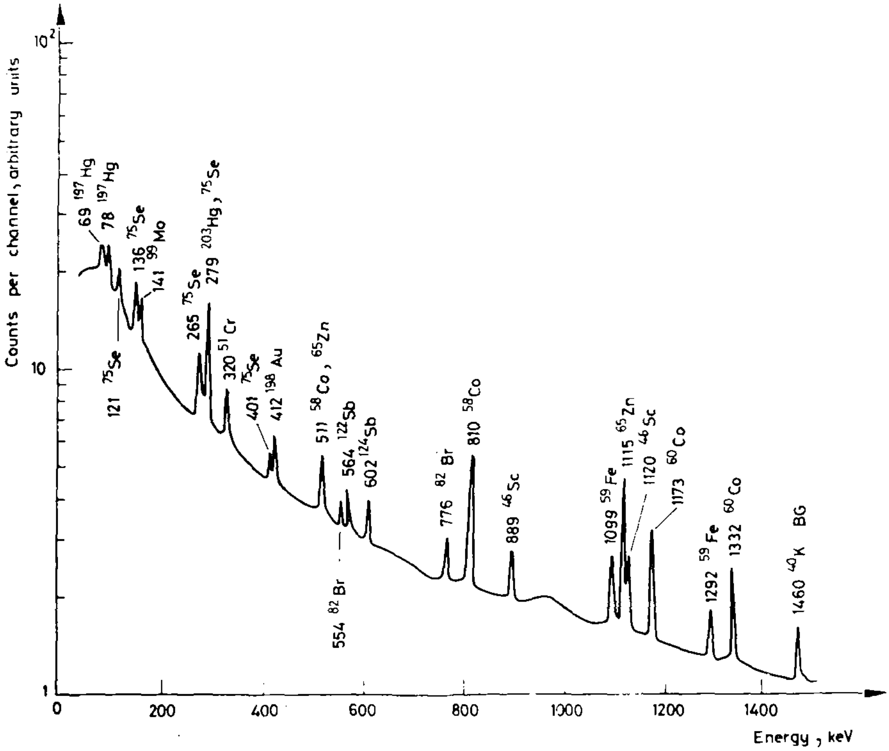

Fig. 4. Typical gamma-spectrum of neutron-activated crude oil. Irradiation time = 4 hrs; decay time = 14 d; counting time = 40000 sec. Isotopes measured: ^{51}Cr, ^{59}Fe, ^{203}Hg, ^{58}Co, ^{46}Sc, ^{75}Se, ^{65}Zn and ^{69}Co

Table 1 lists the nuclear reactions and the pertinent half-lives and photon energies used in the determinations of the various elements. Zn, Hg and Ni were each determined via two independent nuclear reactions.

The half-life of the 486.8 keV photon-producing nuclide was determined to establish which of the two following reactions gave rise to ^{140}La:

$$^{139}\mathrm{La} + \mathrm{n} \longrightarrow {}^{140}\mathrm{La} \xrightarrow[40.3\ \mathrm{h}]{\beta^-} {}^{140}\mathrm{Ce}$$

$$^{235}\mathrm{U} + \mathrm{n} \xrightarrow{\text{Fission}} \begin{matrix} ^{140}\mathrm{Ba} \\ \text{+ other fission} \\ \text{products} \end{matrix} \xrightarrow[12.8\ \mathrm{d}]{\beta^-} {}^{140}\mathrm{La} \xrightarrow[40.3\ \mathrm{h}]{\beta^-} {}^{140}\mathrm{Ce}$$

The half-life was found to be 40 hrs and no long-lived component was observed. It was thus concluded that all the ^{140}La activity was produced from ^{139}La.

For most of the elements, the photon energies used in the calculation were interference-free. However, in some cases there were serious interferences for which corrections had to be made. These are listed in Table 2.

Interferences

The positron annihilation energy (511.0 keV) was used for the determination of ^{64}Cu, 12.8 h. There were four other sources giving rise to 511 keV photons: a short-lived ^{80}Br, 17.6 m; a medium-lived ^{24}Na, 15.0 h (interference was produced from interaction of high-energy photons of ^{24}Na with surrounding materials); and two long-lived nuclides ^{58}Co, 71.3 d and ^{65}Zn, 245 d. The short-lived component was allowed to decay. The long-lived component was measured after two weeks, corrected for the decay time and substracted from the total area of 511 keV. The ^{24}Na contribution was subtracted after multiplying the 1368.4 keV peak area by a normalizing factor. This was the ratio of areas 511.0 keV/1368.4 keV calculated from the spectrum of pure ^{24}Na measured in the same counting geometry.

In measuring the 810.3 keV photon of ^{58}Co, 71.3 d, sufficient time was allowed for the interfering 810.5 keV photon of ^{72}Ga, 14.3 h to decay. The two sets of triplet peaks (554.3 keV ^{82}Br, 35.9 h; 559.2 keV ^{76}As, 26.3 h; 564.0 keV ^{122}Sb, 66 h) and (827.8 keV ^{82}Br, 35.9 h; 829.5 keV ^{188}Re, 16.7 h; 834.1 keV ^{72}Ga, 14.3 h) were resolved graphically. The doublet peaks 279.1 keV ^{203}Hg, 46.9 d and 279.6 keV ^{75}Se, 121 d could not be resolved by the detector system. To determine the area of the 279.1 keV ^{203}Hg peak, the contribution of 279.6 keV ^{75}Se was calculated by multiplying the 264.6 keV peak area by a factor and subtracting it from the total area. The ratio of 279.6 keV/264.6 keV was estimated from the spectrum of pure ^{75}Se measured in the same counting geometry.

The contribution of 778.5 keV of ^{99}Mo to the 776.6 keV peak of ^{82}Br was found to be negligible.

Results and discussion

The trace-element composition of oil representing the various producing formations of the Iraqi oil fields are presented in Table 3. The concentrations vary widely among the different fields, and for certain elements even within the same reservoir. The trace-element concentrations range from less than 1 ppb, e.g. Re, Eu and Sm, to more than 100 ppm, e.g. V and Ca. Sulfur is present in concentrations up to 5% and more.

The range of concentration variation among the different fields is relatively small for some elements (less than 10-fold for As, Co and Zn), but extremely wide for others

Table 1

Nuclear reactions, half-lives and photon energies used in the study

Element	Reaction	Half-life	Photon measured, keV
Al	$^{27}Al(n,\gamma)^{28}Al$	2.31 m	1778.9
V	$^{51}V(n,\gamma)^{52}V$	3.76 m	1434.4
S	$^{36}S(n,\gamma)^{37}S$	5.05 m	3102.4
Ca	$^{48}Ca(n,\gamma)^{49}Ca$	8.8 m	3083
Cl	$^{37}Cl(n,\gamma)^{38}Cl$	37.3 m	1642.0
Ar	$^{40}Ar(n,\gamma)^{41}Ar$	110 m	1293.6
Ni	$^{64}Ni(n,\gamma)^{65}Ni$	2.56 h	1481.7
Mn	$^{55}Mn(n,\gamma)^{56}Mn$	2.58 h	846.9
Eu	$^{151}Eu(n,\gamma)^{152m}Eu$	9.35 h	121.8
K	$^{41}K(n,\gamma)^{42}K$	12,5 h	1524.7
Cu	$^{63}Cu(n,\gamma)^{64}Cu$	12,8 h	511.0
Zn	$^{68}Zn(n,\gamma)^{69m}Zn$	13.8 h	438.7
Ga	$^{71}Ga(n,\gamma)^{72}Ga$	14.3 h	834.1
Na	$^{23}Na(n,\gamma)^{24}Na$	15.0 h	1368.4
Re	$^{187}Re(n,\gamma)^{188}Re$	16.7 h	155.1
W	$^{186}W(n,\gamma)^{187}W$	24.0 h	685.7
As	$^{75}As(n,\gamma)^{76}As$	26.3 h	559.2
Br	$^{81}Br(n,\gamma)^{82}Br$	35.9 h	776.6
La	$^{139}La(n,\gamma)^{140}La$	40.3 h	486.8
Sm	$^{152}Sm(n,\gamma)^{153}Sm$	47.1 h	103.2
Au	$^{197}Au(n,\gamma)^{198}Au$	64.8 h	411.8
Hg	$^{196}Hg(n,\gamma)^{197}Hg$	65 h	77.6
Mo	$^{98}Mo(n,\gamma)^{99}Mo$	66 h	140.6
Sb	$^{121}Sb(n,\gamma)^{122}Sb$	66 h	564.0

(Table 1. cont.)

Element	Reaction	Half-life	Photon measured, keV
Cr	$^{50}\mathrm{Cr}(n, \gamma)^{51}\mathrm{Cr}$	27.8 d	320.0
Fe	$^{58}\mathrm{Fe}(n, \gamma)^{59}\mathrm{Fe}$	45.1 d	1098.6
Hg	$^{202}\mathrm{Hg}(n, \gamma)^{203}\mathrm{Hg}$	46.9 d	279.1
Ni	$^{58}\mathrm{Ni}(n, p)^{58}\mathrm{Co}$	73.1 d	810.3
Sc	$^{45}\mathrm{Sc}(n, \gamma)^{46}\mathrm{Sc}$	83.9 d	889.4
Se	$^{74}\mathrm{Se}(n, \gamma)^{75}\mathrm{Se}$	121 d	264.6
Zn	$^{64}\mathrm{Zn}(n, \gamma)^{65}\mathrm{Zn}$	245 d	1115.5
Co	$^{59}\mathrm{Co}(n, \gamma)^{60}\mathrm{Co}$	5.24 y	1172.1

Table 2

Interfering nuclides encountered in the determinations

Nuclide of interest			Interfering nuclide		
Nuclide	Photon energy, keV	Half-life	Nuclide	Photon energy, keV	Half-life
$^{64}\mathrm{Cu}$	511.0	12.8 h	$^{80}\mathrm{Br}$	511.0	17.6 m
			$^{24}\mathrm{Na}$	511.0	15.0 h
			$^{58}\mathrm{Co}$	511.0	71.3 d
			$^{65}\mathrm{Zn}$	511.0	245 d
$^{76}\mathrm{As}$	559.2	26.3 h	$^{82}\mathrm{Br}$	554.3	35.9 h
			$^{122}\mathrm{Sb}$	564.0	66 h
$^{122}\mathrm{Sb}$	564.0	66 h	$^{76}\mathrm{As}$	559.2	26.3 h
$^{82}\mathrm{Br}$	776.6	35.9 h	$^{99}\mathrm{Mo}$	778.5	66 h
$^{58}\mathrm{Co}$	810.3	71.3 d	$^{72}\mathrm{Ga}$	810.5	14.3 h
$^{72}\mathrm{Ga}$	834.1	14.3 h	$^{82}\mathrm{Br}$	827.8	35.9 h
			$^{188}\mathrm{Re}$	829.5	16.7 h
$^{203}\mathrm{Hg}$	279.1	46.9 d	$^{75}\mathrm{Se}$	279.6	121 d

Table 3

Trace-element com-

Oil Field	Level	Concentrations, ppm								
		V	Ni	Br	Cl	Na	K	Ca	Al	Mn
Ain Zalah	First	70	18	0.11	4.6	5.6	-	<30	-	1.8
	Second	109	26	0.25	1.2	0.21	<0.2	<30	<1	0.04
Butma		35	19	0.11	4.1	0.78	<0.1	<30	5.1	0.02
Kirkuk										
(Khurmala)	First	27	18	0.07	4.1	0.70	-	<30	3.4	0.50
(Avanah)	First	26	15	0.05	2.1	0.13	<0.3	<30	-	0.06
(Baba)	First	25	17	0.04	2.5	0.19	-	<30	-	0.10
	Second	47	23	0.27	12.9	0.11	<0.8	140	7.3	0.02
Bai Hassan	First	26	17	0.10	4.2	0.75	-	<30	<1	0.17
	Second	48	15	0.25	8.9	1.1	0.8	<30	<1	0.19
Jambur		9	14	<0.01	1.7	0.47	<0.4	<30	8.5	0.02
Zubair	Second	57	19	0.20	34	0.46	0.3	136	<1	0.04
	Third	15	9	0.41	77	7.5	<0.1	<30	-	0.17
	Fourth	1.6	<0.7	-	-	0.92	<0.1	<30	8	0.25
Rumaila		25	14	0.50	204	0.39	<0.2	<30	10	58

[a] Concentrations in ppb.

[b] Concentrations %.

(more than 1400-fold for Hg). Within the same field some elements maintain a constant value among the different wells producing from the same formation (e.g. V and Ni in the first level of the Kirkuk field), while the concentrations of others (e.g. Na, Ca, Mn and Cl) vary noticeably even within the same formation.

In the Kirkuk oil field, the V and Ni concentrations in oil are remarkably uniform within the first level which is of Tertiary age (25-27 ppm V and 15-18 ppm Ni), but clearly different from those of the second level which is Cretaceous (47 ppm V and 23 ppm Ni). The decrease in the V and Ni concentrations from the Cretaceous level through to the overlying Tertiary level indicates that there is a vertical migration of oil. V and Ni concentrations decrease along tha path of migration. (For a detailed discussion of the relationship between the concentrations of these two elements and the direction of oil movement, see Ref.[3])

The Br concentration follows the pattern of V and Ni concentration variation. In general the lower the V and Ni content, the lower the Br content, and vice versa. (Details of the correlation between Br concentration and oil migration are being prepared for publication.)

The concentrations of the elements Na, K, Ca, Al, Mn and Cl bear no relation to the path of oil migration. Even within the same reservoir the concentrations position of Iraqi oils

(unless otherwise indicated)

Sc[a]	Cr	Fe	Co[a]	Cu[a]	Zn	Ga[a]	As[a]	Mo	Re[a]	Hg	Ar	S[b]
<1	1.5	53	120	190	0.7	22	17	0.73	7.6	71.7	0.09	3.6
<1	0.08	<3	80	50	0.7	43	28	0.10	8.3	-	0.14	5.0
-	-	-	180	8	<0.5	45	9	0.21	10.6	-	-	2.2
<1	0.53	<10	70	5	1.7	124	10	0.12	8.8	27	1.0	1.8
<1	<0.1	<10	80	30	1.5	124	6	0.10	-	0.06	1.0	2.1
<1	0.15	<10	100	-	1	76	14	0.08	3.4	0.05	0.46	2.9
<1	<0.1	<10	50	40	1	71	7	0.25	6.0	0.06	0.08	2.7
<1	0.48	7.3	140	40	1.8	69	11	0.15	8.1	34	<0.01	3.9
<1	<0.1	<5	40	9	0.2	75	11	0.29	15.0	66	1.25	5.0
<1	<0.1	<5	190	40	1.5	-	9	-	-	-	0.73	-
<1	<0.1	<5	70	58	1	41	19	0.05	10.9	-	1.0	6.9
7	<0.1	<5	<2	45	0.7	3	<4	-	-	0.08	0.19	3.1
<1	<0.1	9.6	-	10	-	-	<4	<0.005	<0.2	-	-	2.1
<1	<0.35	<10	<40	6	-	9	<4	0.17	-	-	0.90	4.2

of these elements may vary widely. It was noted that an increase in Cl content was always accompanied by an increase in the concentration of one or more of the other above-mentioned cations. This suggests that the elements are most likely present as chloride salts. Generally, for the lower wells, i.e. closer to the water surface, higher concentrations of these elements were measured, but this was not true in all cases.

The concentration of Sc, Cr, Fe, Co, Cu, Zn, Ga and As did not vary appreciably within the same reservoir, and the differences between the average concentrations of the different reservoirs were also small. The average concentration of Ga in the upper level of the Kirkuk field was higher than in the other fields. The heavier oils of the Ain Zalah field contained more As than the lighter oils of the southern fields (Rumaila and Zubair).

Mo and Re were measured in almost all the samples and generally the higher the Mo content, the higher the Re, and vice versa. More Mo and Re were found in the heavier oils of Ain Zalah, the second level of Bai Hassan and the second level of Zubair.

The concentrations of mercury varied from about 0.05 ppm (Avanah and Baba domes of the Kirkuk field) to 71.7 ppm (first level of the Ain Zalah field). Oils from the

Bai Hassan field, the Khurmala dome of the Kirkuk field and the first level of Ain Zalah contained much higher concentrations of mercury (in general three orders of magnitude greater than the rest of the oils). The source of this mercury is being investigated.

Samples from Ain Zalah fields contained measurable amounts of Sb, La, Eu, Sm and Au. These elements were not detected in any other field. A few samples from the different fields contained W, while a few others contained Se. The highest W concentration was 49 ppb in the Butma field. Se was of the order of 1 ppm when measured. The Ar concentration varied from 0.1 to 1 ppm.

Conclusions

In this study, a total of 29 trace elements are determined in oil samples from all the producing Iraqi fields, using instrumental neutron activation analysis.

The concentrations of V, Ni and Br decrease along the path of oil migration, and can be used as indicators of such movements. The results of the study provide evidence for vertical migration in the northern Iraqi oil fields.

Na, K, Ca, Al, Mn and Cl are most likely present as chloride salts in solid or liquid suspensions in oil. Ar, Sc, Cr, Fe, Co, Cu, Zn, Ga, As, Mo and Re are generally present in all oils in low concentrations. The concentration of Hg varied from an average value of 0.06 ppm in most oils to remarkably high concentrations (more than 70 ppm) in certain fields. Se, Sb, La, Eu, Sm, W and Au were measured in a few samples.

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The authors are greatly indebted to Mr. Gaddo of the Iraqi Petroleum Company for providing samples and for some useful discussions. Our colleagues at the Activation Analysis Laboratory and the Reactor Department provided helpful assistance.

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