

**Physical Methods Section**

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**DETERMINATION OF 18 TRACE ELEMENTS IN PETROLEUM  
AND ITS DERIVATIVES BY NEUTRON ACTIVATION  
WITH A SMALL NUCLEAR REACTOR**

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Non-destructive neutron activation has been used to analyze 6 different samples of crude oil and heating oil, from Western Canada and Venezuela. These samples were irradiated with thermal neutrons for 2, 30 and 240 min in the SLOWPOKE reactor and the concentrations of 18 trace and minor elements (Al, As, Br, Cl, Co, Dy, Eu, Fe, I, La, Mn, Mo, Ni, Na, S, Se, Sm and V) ranging from 0.6 ppb to 2.24% have been measured. Eleven elements (As, Br, Co, Cl, Fe, Mo, Mn, Na, Ni, S and V) were determined in the fuel oil (SRM-1634) obtained from the National Bureau of Standards and were found to be in good agreement with the values certified by NBS.

**Introduction**

Environmental pollution is known to be one of the major problems confronting our society. The occurrence of many toxic elements (As, Hg, Pb etc.) in our environment has a harmful effect on human health and causes extensive property damage. The major source of these elements is the use of fossil fuels for transportation, heating and electric power generation. For example, 95 890 940 000 l of petroleum and its derivatives were consumed in 1976 in Canada.<sup>1</sup>

Petroleum, like other fossil fuels, contains small but non-negligible concentrations of trace elements and these are, at least partially, released into the environment during combustion. Although crude oil and some other petroleum derivatives have been analyzed in the past<sup>2-4</sup> by neutron activation, no systematic studies of trace element concentrations in heating oils were found in the literature. This is unfortunate, because air pollution at the local level is frequently caused by the combustion of heating oil in homes and factories. Consequently, the purpose of this work has been to analyze several crude oils and petroleum derivatives with a low power

(highest flux is  $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ ) laboratory-type nuclear reactor and to establish the detection limits which can be achieved in our experimental conditions.

The improved knowledge of concentrations of trace elements in petroleum and its derivatives will indicate the distribution of trace elements among different distillation fractions and increase the precision of the calculations of their environmental impact.

### Experimental

Oil samples were obtained in 1 l lots from refineries in the Montreal area. Each bottle was shaken and a 0.5 g sample was transferred into a clean  $1.5 \text{ cm}^3$  polyethylene vial which had been previously washed with concentrated nitric acid and distilled water. Standards, in the form of aqueous solutions, were prepared from reagent grade non-hygroscopic chemicals. The samples and the standards were heat-sealed and placed into  $7 \text{ cm}^3$  polyethylene vials and irradiated for 2, 30 and 240 min in the SLOWPOKE nuclear reactor. A thermal neutron flux of  $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$  has been used for all activations. In order to eliminate errors due to impurities in the polyethylene vials, the radioactive samples were transferred into new vials and weighed. Preliminary tests have indicated that small and variable amounts of trace elements are present in these vials. After irradiation, the samples were left to decay for 2 min, 30 min, 24 hrs and 14 days.  $\gamma$ -ray spectra were collected for 600, 2000, 4000, 20 000 and 80 000 sec with a Ge(Li) detector and a Canberra 8180 analyzer.

The Ge(Li) detector has an efficiency of 6.6% relative to a  $7.5 \times 7.5 \text{ cm}$  NaI(Tl) detector and its resolution is 1.9 keV for the 1333 keV  $^{60}\text{Co}$  line. After counting, the spectra were analyzed and peak areas calculated. From these, concentrations and detection limits were obtained.

The nuclear reactions observed, the photopeaks used and possible interferences are presented in Table 1.

### Results and discussion

Trace element compositions of the different oils analyzed are presented in Table 2. The values in this table are averages of two or more independent determinations.

As expected, the crude oils contain more elements (11 vs. 8) than their refined fractions and, generally, higher concentrations of these elements.

Heating oils (or fuel oil No. 2) are considerably cleaner fuels than crude oils, and only 8 elements were determined in this matrix. The volatile elements (As, Br and I) are partially carried over during the distillation, while oil soluble compounds of some elements (Co, Na and V) tend to concentrate in the heavy fractions. Con-

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Table 1  
Nuclear reactions observed and peak energies used

Element	Reaction	Half-life	Energy, keV	Possible interferences
Al	$^{27}\text{Al}(n, \gamma)^{28}\text{Al}$	2.24 m	1778.9	$^{28}\text{Si}(n, p)^{28}\text{Al}$
As	$^{75}\text{As}(n, \gamma)^{76}\text{As}$	26.3 h	559.2	$^{76}\text{Se}(n, p)^{76}\text{As}$
Br	$^{81}\text{Br}(n, \gamma)^{82}\text{Br}$	35.4 h	554.3, 776.6	$^{85}\text{Rb}(n, \alpha)^{82}\text{Br}$
Cl	$^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$	37.2 m	1642	$^{41}\text{K}(n, \alpha)^{38}\text{Cl}$
Co	$^{59}\text{Co}(n, \gamma)^{60}\text{Co}$	5.27 y	1173.1, 1332.4	$^{60}\text{Ni}(n, p)^{60}\text{Co}$
Dy	$^{164}\text{Dy}(n, \gamma)^{165}\text{Dy}$	2.35 h	94.6, 279.5	$^{165}\text{Ho}(n, p)^{165}\text{Dy}$
Eu	$^{151}\text{Eu}(n, \gamma)^{152\text{m}}\text{Eu}$	9.3 h	121.8, 841.6	—
Fe	$^{58}\text{Fe}(n, \gamma)^{59}\text{Fe}$	44.6 d	1098.6, 1291.5	$^{59}\text{Co}(n, p)^{59}\text{Fe}$
I	$^{127}\text{I}(n, \gamma)^{128}\text{I}$	25.0 m	442.7	—
La	$^{139}\text{La}(n, \gamma)^{140}\text{La}$	40.2 h	486.8, 1595	$^{235}\text{U}(n, f)^{140}\text{La}$
Mn	$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$	2.58 h	846.9	$^{56}\text{Fe}(n, p)^{56}\text{Mn}$
Mo	$^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$	66.0 h	140.6	$^{235}\text{U}(n, f)^{99}\text{Mo}$
Na	$^{23}\text{Na}(n, \gamma)^{24}\text{Na}$	15.0 h	1368.4	$^{24}\text{Mg}(n, p)^{24}\text{Na}$
Ni	$^{58}\text{Ni}(n, p)^{58}\text{Co}$	71.3 d	810.3	$^{59}\text{Co}(n, 2n)^{58}\text{Co}$
S	$^{36}\text{S}(n, \gamma)^{37}\text{S}$	5.06 m	3102.4	$^{37}\text{Cl}(n, p)^{37}\text{S}$
Se	$^{74}\text{Se}(n, \gamma)^{75}\text{Se}$	121 d	265	—
Sm	$^{152}\text{Sm}(n, \gamma)^{153}\text{Sm}$	46.5 h	103.2	$^{153}\text{Eu}(n, p)^{153}\text{Sm}$
V	$^{51}\text{V}(n, \gamma)^{52}\text{V}$	3.75 m	1434.4	$^{52}\text{Cr}(n, p)^{52}\text{V}$

sequently, these fractions (e.g. fuel oil No. 6) contain the highest number of elements (15) which can be detected in our conditions.

In order to compare quantitatively the environmental impact of the different fossil fuels, a composite toxicity Index I has been calculated for these fuels. This index is defined, for the purpose of this study, by the following expression:

$$I = \sum_{i=1}^n \ln (C_i/\text{TLV}_i) \quad (1)$$

where  $C_i$  is the concentration (in ppb) of the element in the fuel and  $\text{TLV}_i$  is the threshold limit value (in  $\text{mg}/\text{m}^3$ ) of this element in the air as stipulated by the US Government.<sup>6</sup> A high value of this index indicates that the fuel concerned is relatively harmful to the health of the population.

Table 2  
Concentrations of trace elements in selected petroleum products (in ppb)

Element	Crude oils			Heating oils			Fuel oil #6
	Canada	Venezuela	Exxon	Shell	Texaco		
Al	<200	<200	<120	<120	<120	<120	21 600
As	6.8±0.7	6.8±0.7	0.64±7	0.36±0.05	0.68±0.07	0.68±0.07	37±3
Br	40±3	190±10	9.3±0.9	4.9±0.5	6.6±0.7	6.6±0.7	260±10
Cl	140±10	6 640±90	360±40	800±70	9 400±400	9 400±400	200 000±5 000
Co	29±3	48±5	<20	<20	<20	<20	70±7
Dy	<0.2	<0.2	<0.3	<0.3	<0.3	<0.3	59±0.6
Eu	<0.15	<0.15	<0.15	<0.02	<0.1	<0.1	0.62±0.05
Fe	21 000±2 000	<5 000	<10 000	<10 000	<10 000	<10 000	<10 000
I	24±1	7±0.3	3.0±0.2	1.1±0.6	4.9±0.4	4.9±0.4	70±1
La	<5	<5	<2	<2	<2	<2	570±20
Mn	<0.5	<0.5	1.2±0.1	2.5±0.2	1.6±0.2	1.6±0.2	100±10
Mo	<10	<10	<5	<5	<5	<5	170±10
Na	62±5	1 930±100	550±20	81±5	410±20	410±20	31 200±800
Ni	5 000±1 000	19 000±2 000	<1 500	<1 500	<1 500	<1 500	<1 500
S	1.23%±0.08	0.72%±0.06	0.19%±0.02	0.25%±0.02	0.3%±0.03	0.3%±0.03	2.2%±0.3
Se	<50	150±2	<50	<50	<50	<50	<50
Sm	<0.5	<0.5	<0.3	<0.3	<0.3	<0.3	144±7
V	3 730±180	72 000±3 000	<30	47±5	<60	<60	128 000±4 000

Table 3  
Interference factors due to competing nuclear reactions

X/I <sup>a</sup>	Interfering reaction	IA <sup>b</sup> , %	$\sigma$ , mb	Interference factor*	
				Calculated	Measured
Al/Si	<sup>28</sup> Si(n, p) <sup>28</sup> Al	92.2	2.0	596	500 <sup>12</sup>
As/Se	<sup>76</sup> Se(n, p) <sup>76</sup> As	9.0	0.63	369 530	
Co/Ni	<sup>60</sup> Ni(n, p) <sup>60</sup> Co	26.1	2.1	322 693	166 666 <sup>3</sup> ; 1 587 301 <sup>9</sup>
Fe/Co	<sup>59</sup> Co(n, p) <sup>59</sup> Fe	100	1.0	17	88 <sup>9</sup> ; 19 <sup>11</sup>
Mn/Fe	<sup>56</sup> Fe(n, p) <sup>56</sup> Mn	91.7	0.81	82 266	5 850 <sup>11</sup> ; 1 265 <sup>3</sup> ; 465 116 <sup>9</sup>
Ni/Co	<sup>59</sup> Co(n, 2n) <sup>58</sup> Co	100	0.15	2 094	

\*Concentration of the interfering element (in ppm) which produces an apparent concentration of the element of interest of 1 ppm.

<sup>a</sup>Element of interest and interfering element.

<sup>b</sup>Isotopic abundance.

For concentrations of the elements in coal, BERTINE and GOLDBERG's<sup>7</sup> values have been used. The I values obtained for coal, fuel oil No. 2 (Shell) and fuel oil No. 6 are 59.28, 24.35 and 48.28, respectively. Only the elements As, Cl, Mn, S and V, for which data are available for all three fuels, were used in the calculation of the index. As can be seen, the heating oil is a much cleaner fuel than either coal or fuel oil No. 6.

There are many nuclear and spectral interferences which can occur in neutron activation analysis.

In the case of petroleum products, many of the possible interferences listed in Table 1 can be neglected either because the element which can cause the nuclear interference was not detected or its concentration is lower than that of the element of interest. This applies to Br, Cl, Dy, Fe, La, Mo, Na, Ni, S, Sm and V. Possible interferences for the remaining elements must be assessed more precisely. Using the effective cross-sections for (n, p) and (n,  $\alpha$ ) reactions compiled by CALAMAND,<sup>8</sup> the importance of the nuclear interferences has been calculated and the values obtained are presented in Table 3. This table also contains experimental measurements of these interferences. The calculated values in Table 3 have been obtained using the following expression:

$$\text{Interference factor} = A_X \sigma_X M_I / k A_I \sigma_I M_X \quad (2)$$

where A is the isotopic abundance, M is the atomic mass and subscripts I and X refer to the interfering element and the element of interest, respectively. The con-

Table 4  
Detection limits in petroleum (in ppb)

Element	Crude oil	Heating oil	Fuel oil #6
Al	200 c	120 a	500 e
As	1.6 c	0.2 c	6 c
Br	5 c	1 c	20 c
Cl	40 f	20 b	1 500 f
Co	20 d	20 d	20 d
Dy	0.2 f	0.05 b	0.4 f
Eu	0.15 c	0.02 c	0.2 f
Fe	10 000 d	10 000 d	10 000 d
I	2 f	1.3 b	10 f
La	5 c	2 c	9 c
Mn	0.5 f	0.15 b	1.7 f
Mo	10 c	5 c	50 c
Na	20 c	20 c	40 c
Ni	1 500 d	1 500 d	1 500 d
S	100 000 e	10 000 e	200 000 e
Se	50 d	50 d	50 d
Sm	0.5 c	0.3 c	1.3 c
V	80 e	30 a	900 e

## Conditions:

Code	a	b	c	d	e	f
tir, min	240	240	240	240	2	30
td	2 m	30 m	24 h	14 d	2 m	30 m
tc, sec	600	2000	20 k	80 k	600	2000

stant  $k$  (equal to 0.21 in our case) is the ratio of the fission neutron flux to the thermal neutron flux. This ratio has been measured experimentally using Si and Ni as the neutron flux monitors.

In the matrices analyzed, we have calculated the possible interelement interferences. The corrections were negligible, except in the case of Si and Al. Unfortunately, the concentration of Si in oil is difficult to measure with neutron activation and no data were found in the literature on this subject. Nevertheless, it can be safely assumed that this concentration is much lower than 4600 ppm of Si which must be present in order to produce the photopeak equivalent to 21.6 ppm of Al found in fuel oil No. 6.

The second main purpose of this study is to establish the detection limits which can be achieved using SLOWPOKE as the neutron source. The detection limits

Table 5  
Trace element composition of the fuel oil (SRM-1634)

Element	Concentration	NBS value <sup>1 4</sup>	'PACE <sup>1 5</sup>
As (ppb)	63 ± 3	95*	—
Br (ppb)	41 ± 4	—	39.1 ± 5.3
Cl (ppm)	8.4 ± 0.5	—	7.8 ± 0.5
Co (ppb)	310 ± 15	—	301.0 ± 14.0
Fe (ppm)	14.2 ± 1.5	13.5 ± 1	12.5 ± 2.2
Mn (ppb)	110 ± 10	120*	—
Mo (ppb)	870 ± 80	—	—
Na (ppm)	13.2 ± 1.5	—	11.2 ± 0.7
Ni (ppm)	37 ± 2	36 ± 4	37.4 ± 1.5
S (%)	2.3 ± 0.3	2.14 ± 0.02	2.05 ± 0.4
V (ppm)	318 ± 15	320 ± 15	312 ± 16.4

\*Suggested value.

were calculated using CURRIE's<sup>1 3</sup> "well-known blank" expression and are listed in Table 4. As can be seen from this table, fuel oil is a very convenient matrix for neutron activation analysis and five elements (As, Dy, Eu, Mn and Sm) can be determined with sensitivity better than 1 ppb. Ten other elements (Al, Br, Cl, Co, I, La, Na, Mo, Se and V) have detection limits varying between 1 ppb and 1 ppm, and only three elements which were observed (Fe, Ni and S) are detectable above the 1 ppm level.

In order to verify the accuracy and precision of the method used, the fuel oil Standard Reference Material 1634, which was obtained from the US National Bureau of Standards, was analyzed using the procedure described. The results obtained are presented in Table 5. Good agreement was obtained between the concentrations of 11 elements determined in this study and the values certified or suggested by NBS. Only in the case of As, a substantially lower concentration was measured. This may be due to the diffusion of As into the polyethylene vials during and after irradiation or, more probably, to a relative instability of natural arsenic compounds (arsine) in fuel oil as observed by POWERS et al.<sup>1 6</sup> and attributed to a combination of oxydation and adsorption. This problem is currently being investigated.

### Conclusion

Non-destructive neutron activation with the SLOWPOKE reactor makes possible the determination of 11 elements in crude oil, of 8 and 14 elements in heating oils No. 2 and 6, respectively. The method is simple, accurate, sensitive (detection limits range from 0.05 ppb to 2000 ppm) and does not involve any pre-concentration or chemical separations. Interferences from fast neutron reactions are minimal and can be corrected.

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