

## TRACE IMPURITIES IN CANADIAN OIL-SANDS, COALS AND PETROLEUM PRODUCTS AND THEIR FATE DURING EXTRACTION, UP-GRADING AND COMBUSTION\*

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National energy programs for the next two decades entail increased total consumption of fossil fuels in general and, in particular of portable fuels extracted from oil sands and shales and from lower quality coals. Improved fuel-upgrading and combustion technologies are recognized to be vital for minimizing environmental degradation caused by continental and global acid-rain precipitation from fossil-fuel impurities. A further consideration, however, is the fate of those trace-element co-contaminants of acid-rain such as heavy metals, which are present at lower concentrations ( $10^{-4}$ – $10^{-7}$ ) but may also be of environmental significance when  $10^7$  to  $10^9$  tons  $\cdot$  y $^{-1}$  are utilized on several continents. In this laboratory, INAA procedures have been adapted for the determination of 25–30 trace impurities in a variety of fuels and extracts including: S, V and Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Dy, Eu, Fe, Hf, K, La, Mn, Na, Rb, Sb, Sc, Sm, Th, Ti, U. Samples were obtained of typical Canadian pumped crudes, and from several Canadian oil-sands and coal deposits (mostly bituminous and subbituminous) both in their natural states and after stages of extraction and upgrading. Also analyzed were fuels derived from them and the residues resulting from their refining and combustion. INAA of all fossil fuel extracts including light oils, viscous bitumen and such organic fluids could be performed under the same conditions as the parent substances: crude oils, oil-sands and coals, without any special sample preparation. Although no standard samples are routinely required because of the 1–2% long-term flux stability of the reactor, accuracy checks were performed periodically by reference to NBS-1632A standard coal and atomic absorption standard dilute solutions. Results obtained for the NBS coal SRM and the BAM flyash sample (1978) are also given. A wide range of trace impurities determined in the Canadian fossil fuels included some of those which are of particular significance in Canadian coals and their ashes (a STM standard ashing method). The 'inorganic' traces can also be grouped according to their fate during static combustion at 750 °C.

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### Introduction

Proposed national energy programs for North America for the period to the end of this century and beyond, place a priority on reducing oil imports and entail increased consumption of indigeneous fossil fuels in general and, in particular, of portable fuels extracted from oil sands, shales and lower quality fuels. Much research and development is underway to improve methods for extracting the hydrocarbon content both for 'mineable' and for less accessible 'in-situ' deposits.

However, there are considerable quantities of impurities of environmental importance in as-mined oil sands and coals that should, ideally, be separated out and left at the mine site. Furthermore, processes to be used for the up-grading and combustion of fuels derived from fossil fuel deposits should minimize the carry-over of such contaminants in order to lessen environmental degradation caused by continental and global acid-rain precipitation from fossil-fuel combustion. Much attention is directed to the acid-rain phenomenon but a further consideration that is the topic of this study is the fate of those trace element co-contaminants of acid-rain present at lower concentrations ( $10^{-4}$  to  $10^{-7}$ ) but which could also be of long term environmental significance when consumption of  $10^7$  to  $10^9$  tons per year of such new fuels occurs in North America and other countries possessing undeveloped coal or oil shale resources.

High quality (low ash content) coals were ignored in this study on the assumption that they will continue largely to be used for metallurgical purposes. The fossil fuel deposits and the oils derived from them which are likely to be used in thermal plants, were the major focus of this radioanalytical investigation of inorganic trace impurities of environmental importance in bitumen from oil sands and coals, compared to conventional pumped crude oils.

Among the analytical tools available to measure impurities in both solid and liquid fossil fuel materials, radioanalytical and X-ray techniques have been used<sup>1-5</sup> although some earlier work was done by emission spectrography of solids and ash<sup>6</sup>. Radioactivation methods are particularly suited to the study of a variety of fuel materials because they are readily adapted for non-destructive trace analysis for a range of trace substances in solid or liquid fractions and with little or no pre-analysis sample preparation.

This study was undertaken not only to characterize the relative trace impurity content of 'as-mined' fossil fuel raw material, but also to follow the fate of selected components throughout the extraction and up-grading processes and the eventual fuel combustion. Several alternate procedures for extraction and up-grading of the hydrocarbon content are being used or considered and it is of interest to compare their relative efficiencies for co-extraction of trace impurities. Processes that more efficiently reduce the content of 'acid-rain' producing constituents, of toxic heavy metals or other trace impurities that accumulate in the environment and food chains may be preferred in the future, economical factors notwithstanding.

For example, a simplified flow-sheet depicting the hot water extraction process used in the present oil sands-syn-crude plants to separate bitumen and to upgrade it by carbon and sulphur removal, is shown in figure 1.

### Experimental

Samples included in this work were representative of the Canadian sources of heavy oils from the oil sands, thermal coals and pumped interprovincial crude oil obtained from industry, a power utility and government and comprised

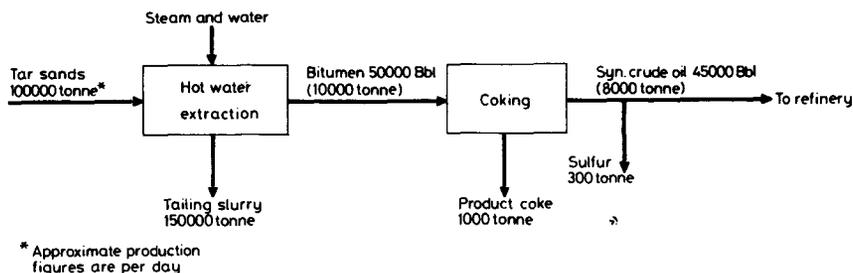


Fig. 1. Simplified flowsheet of a tar sand plant

about 30 oil sands and extracts, 120 coals and ashes (mostly Canadian bituminous and sub-bituminous, but several were of U.S. origin) and 35 conventional crude oil refined products and residues. The samples taken for multi-elemental trace analysis consisted of raw 'as-mined' mineral, cleaned, pulverized and homogeneous material and the liquid and solid products obtained from them by up-grading and refining processes and by thermal combustion done in laboratory simulations of industrial scale combustion (static combustion to 750°C in clean crucibles). Samples were removed at various stages of oil sands and coal mining and refining operations at the SUNCOR and Syncrude oil sands' plants, Alberta and at the Luscar Alberta and Cape Breton Development Corp., Nova Scotia coal mines and for special mills.

Instrumental neutron activation analysis techniques employing the University SLOWPOKE reactor (UTSR), neutron flux  $10^{11}$  to  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  and, to a lesser extent, the McMaster nuclear reactor (MNR) of  $2 \times 10^{13}$  flux, were adapted to permit the determination of S, V, halogens, rare earths, chalcophile elements: Al, Ba, Ca, Na, K, Rb, Sc and Ti, as well as As, Sb, Co, Cr, Fe, Hf, Mn, Th and U. Masses of the various solid and liquid fuel materials in the range 50-200 mg were weighed into clean polyvials, sealed, irradiated for 5 m and 16 h periods and

subjected to gamma spectrometry at times from 5 min, 3 h, 3-5 d and up to 3-4 weeks after activation. High flux MNR irradiations were for 50 h duration of 20-50 mg solid fuel, ash or fuel residue after sealing in high purity quartz tubes. Corrections were made as necessary, for contributions from impurities in the polyvials or quartz tubes themselves. An attractive aspect of using the Canadian SLOWPOKE nuclear reactor for these studies was that INAA of the associated fossil fuel extracts including synthetic crude oil, viscous bitumen and various oils and low boiling organic liquids can be performed under the same conditions as the parent substances: oil sands, crude oils and coals without any special sample preparation, ashing or other concentration.

Gamma-ray analysis was performed for short-lived nuclides (viz. half-lives up to 40 min) at the SLOWPOKE site using a Ge(Li) detector (resolution 1.9 keV at 1333 keV) coupled to a Canberra 8180 analyzer, and for all other nuclides, using a Ge(Li) detector (efficiency 8%; resolution 2.3 keV at 1333 keV) in conjunction with a Tracor-Northern TN-11 data reduction system. The largest contribution to analytic error in these measurements was the statistical fluctuations in net gamma photopeak results.

Although no analytical standard samples or  $k_0$  flux monitors are routinely required in NAA determinations done with a SLOWPOKE because of its inherent 1-2% short or long-term flux stability, accuracy checks were done periodically during this study by reference to the NBS-1632A standard coal and aliquots of atomic absorption standard dilute solutions (table 1.); the precision and accuracy among the elements reported ranged from 2-15% in general for many but were as high as 20-35% especially in the case of S in oil sand and coal and traces of Au and W. However S could be determined with a precision of 10-20% in bitumens and derived oils.

Table 1  
Analytical precision and accuracy: NBS coal 1632A

ELEMENT	CONCENTRATION (ppm)	
	this work (INAA)	NBS, and (others)
S %	1.5 ± 0.7	(1.64)
Cl	770 ± 24	(800 ± 70)
Al	2.9 ± 0.12	(3.07)
Ca	2160 ± 130	(2400)
Mn	27.3 ± 1.4	28 ± 2
Na	799 ± 15	(850)
V	43 ± 1	44 ± 3
As	8.7 ± 0.2	9.3 ± 1
Ti	1580 ± 80	(1750)
Fe %	1.10 ± 0.3	1.11 ± .02
Ba	126 ± 11	122 ± 11
Sb	0.52 ± .03	0.58 ± .02
Sc	5.9 ± 0.2	(6.3)
Sr	79 ± 9	84 ± 9
Cr	34 ± 3.6	34.4 ± 1.5
Br	40 ± 2.3	43.3
Dy	2.0 ± 0.1	2.2 ± 0.3
La	21 ± 1	(18)
Th	4.3	4.5 ± 0.1
U	1.31 ± 0.09	1.28 ± 0.02

Since some of the samples analyzed contained from 1 to 15 ppm of U and Th, possible interference in the determination of other trace elements such as Ba and La which are both neutron activation and fission products was considered. However a search for other possible high yield fission products in the gamma spectra indicated negligible fission contributions.

#### *Sample homogeneity*

In order to establish whether sample inhomogeneities could cause large variations in trace element content, a series of samples were obtained across exposed faces of both oil sands and coal deposits being mined. The trace content of a set of these 'grab' samples and well pulverized and mixed samples were compared with respect to the reproducibility in the concentrations of each of about twenty elements (an example is provided in table 2). It was observed that concentration variations were not greater than the analytical error for each element, demonstrating that variations in composition across a mining site were small and therefore, that any single 'grab' sample could be taken as representative.

Lump coal was less homogeneous than powdered coal and there was evidence of physical separation of some mineral mass after coarse grinding. Therefore, only coals pulverized to less than 100 mesh size were obtained from most deposits and used for the trace analyses reported here.

#### *Syncrude from oil sands*

Samples from the 'as-mined' oil-sands (or, tar-sands) and the various process streams leading to product syncrude oil (fig. 1) were compared for trace impurity content (table 3) and it can be seen that (i) impurities found ranged from a few

Table 2  
Coal homogeneity

ELEMENT	CONCENTRATION (ppm)			
	65 Mesh	150 Mesh	200 Mesh	Mean
Al (%)	1.29	1.37	1.36	1.34 ± 3%
Ba	121	162	164	149 ± 13%
Br	16.3	16.4	15.4	16 ± 3%
Ca (%)	0.78	1.02	1.04	0.94 ± 12%
Cl	1131	1064	1059	1085 ± 3%
Co	2.94	4.30	4.16	3.80 ± 15%
Dy	0.787	0.926	0.925	0.879 ± 7%
I	2.25	3.25	2.58	2.69 ± 14%
Mn	29.0	36.0	34.9	33.3 ± 9%
Na	397	440	452	430 ± 5%
Sr	152	142	153	149 ± 3%
Ti	584	646	644	624 ± 4%
U	0.827	0.913	0.842	0.861 ± 4%
V	19.1	19.9	20.3	19.8 ± 2%

parts per  $10^9$  to several parts per  $10^3$  in the case of S, Al, Ca, Fe: (ii) many impurities are partially eliminated by the extraction and up-grading processes however S, V and some As and halogens are co-extracted with the oil fraction deposit in the residual coke from bitumen up-grading (iii) the coke, which can be utilized as a local fuel material at an oil sands plant, contains greatly

Table 3  
Fate of impurities during oil sands extraction and up-grading; comparison of syncrude  
and pumped crude oils

ELEMENT	CONCENTRATION (ppm)			Pumped* Crude
	SUNCOR Oil sand	Bitumen	Synthetic Crude	
S	8000	33000-44000	800-2100	1000-4000
Cl	35	7-31	5-6	3.8-371
Al	9100	310-1600	3	0.5-20
Mn	12	2.4-14	0.1	0.1-2.5
Na	310	30-120	7	3-5.5
V	34	145-200	0.002-0.007	0.02-6
As	0.9	0.2-0.6	< 0.02	1.5
Ti	610	32-130	< 0.6	7-19
Fe	550	100-600	< 10	0.7
Ba	210	5-12	< 0.9	6
Sc	0.5	0.04-0.3	< 0.002	0.1
Cr	7.9	1.8-3	< 0.2	0.09
Br	0.2	0.1-0.2	0.02-0.03	0.1-0.8
La	6.7	0.5-1.6	< 0.02	-
U	0.5	0.08-0.3	< 0.1	-

elevated concentrations of impurities including As, S, V, Ti, Mn, traces of U and Th, a fraction of which (varying from 15 to 98%) are released during coke combustion, and (iv) the product 'syncrude' oil derived from oil sand has lower concentrations in most impurities than conventional crude oil pumped from nearby

geological formations. However it should be noted that the syncrude oil being compared to pumped crude oil has undergone a stage of upgrading both to increase the C/H ratio and for S and V removal.

Reserve portions of the 'as-mined' oil sand were extracted in the laboratory with toluene and the derived bitumen—corresponding to about 10-15% by weight—was centrifuged to remove any extracted or entrained mineral grains and subjected to INAA for comparison with the industrial bitumen extract: the hot-water extract was of slightly higher purity than that obtained in the laboratory by toluene extraction, possibly explain as incomplete separation of clay fines. A sample extracted with steam in a laboratory simulation of an *in-situ* recovery process <sup>7</sup> was of higher purity than that produced by the hot water process.

Comparison of results obtained in this study (table 3) with those of Filby <sup>8</sup> for 13 of the same elements measured indicated good agreement for most elements particularly since the samples compared were taken at times at least 5 years apart.

In table 3 trace element concentrations (on a wt/wt basis) are compared; however for the purpose of tracking the 'carry-over' of individual trace elements, an extraction efficiency, or a 'retention factor' is more useful. An indirect procedure was used for calculating retention factors for the trace elements across each processing step: assuming that certain elements exhibiting maximum retention (or the greatest increase in concentration in a product compared to the impure raw material) are assigned retention factor values of unity (corresponding to 100 % retention in the product stream). On this basis the concentration data of table 3 corresponds to > 90% retention of oil sand sulphur and vanadium content and about 5 - 10% of halogens, As, Sb and Co; > 90% retention of the bitumen content of chalcophile elements (Ca, Na, K, Fe, Mn, Ba, Ti) by the coke, 80-90% of V and Al;

60-80% of V and Al; 60-80% of Cr, Th, U and rare earths; 40-50% of As and Sb; and from 10-30% of S and halogens.

Engineering estimates for a full scale oil sands' plant input indicate that, per  $10^5$  tonne.d<sup>-1</sup> of oil sands processed (of which from 8-14% is extractable oil) the following quantities of trace elements are involved: (in kg.d<sup>-1</sup>) As:100; Sb:20; U:100; Th:700; S:700; Cr:2,000; Ba:22,000 and Ti:  $1.7 \times 10^5$  and of this, the quantities remaining with the product syncrude oil (a feedstock for refineries) are: As: < 0.2 ; Sb: n.d.; U: <1; Th: n.d.; S: 55; Cr: 2; Ba: < 7 and Ti: < 5 kg.d<sup>-1</sup>.

Comparison of oil refinery feed stock, the low boiling products, kerosenes, heating oils, gasolines, residual oils and bottom ends (table 4) indicate that the majority of the trace impurities in petroleum feed stocks appear to be in low volatility - higher molecular weight fractions except for vanadium and sulfur. This indicates that the most probable fate of trace impurities in petroleum feed stocks depends on the uses to which the heavy and residual oils are put and whether or not they are combusted as thermal plant fuels without any further processing to reduce metal and inorganics content.

### *Coal*

Apart from its use in metallurgical and coking processes most of the coal produced is burnt as a heat source and trace impurities in it can be volatilized or emitted as airborne particulate or it can be entrained in residual ash. The thermal coals analyzed ranged from 7 to 33 % ash by weight. Among the trace elements found in typical Canadian bituminous and sub-bituminous thermal coals from Alberta, Saskatchewan, New Brunswick and Nova Scotia (table 5), a number can be recognized as so-called chalcophiles, elements commonly associated with rocks and minerals, viz. Al, Ba, Ca, Na, K, Rb, Sc and Ti and their concentrations

Table 4  
Impurities in petroleum products

ELEMENTS	CONCENTRATION (ppm)					
	Crude	Bunker	Fuel Oil	Sec. Tops	Cat. feed	Pitch
S (%)	0.36	1.20	2.4	24	0.67	1.49
V	5.9	29	260	3.3	411	43
Al	0.53	18	55	1.21	1.42	16.5
Ca	-	1-2	98	13	10	166
Cl	27	15.2	5.7	2.8	11.7	98
Cu	0.34	-	68	0.42	1.75	37
Mn	0.07	0.087	0.33	0.24	0.19	1.03
Ti	7.6	22	91	1.1	3.0	42
Ba	-	-	13	1.25	4.15	50
Br	0.15	0.16	0.76	0.05	0.12	0.46
I	0.70	0.67	0.84	0.064	0.20	2.44

tend to be highest among the trace components (except for Rb and Sc) ranging from about 0.01 to 1%.

Concentrations of Al, Mg, Ti and Ce were strongly correlated ( $r > 0.85$ ) with coal ash content suggesting that they are mostly associated with the mineral phase; Sr, Cs, Ta and other rare earths were less strongly correlated with ash.

From table 5 it can be seen that there is a wide variation in trace element content according to the source (note: it has already been stated that variations within one mine area are small by comparison). In general, sub-bituminous coals had lower impurity concentrations than bituminous; Mn is higher in western Canadian coal than in eastern; conversely Cl was much reduced in western coals; similar findings were reported by the Ill. State Geol. Survey<sup>9</sup>. The range in As and K vary approximately by a factor of  $10^3$  among the different Canadian sources. Owing to the wide range of observed concentrations, median values have been given and for example, there were few high values for Br, K and Sb so that the median values are much less than the highest results.

A few U.S. thermal coals obtained from N.Y. state power stations and from Pennsylvania were compared with the range of Canadian thermal coals and few significant differences were noted among the 32 trace elements determined.

Some collieries engage in coal cleaning, e.g. simple procedure is the impinging of a water jet on crushed coal lumps in such a manner that some mineral matter fines are removed. A comparison of an Alberta coal before and after cleaning is shown in table 6: there is an appreciable reduction in the concentration of several of the components, which elements appear to be associated with the mineral or ash phase of the coal, viz. Al, Ca, La, Ti whereas other components including those that are readily volatilized with the organic phase of coal, viz. As, V, Cr, U are less affected by cleaning.

Table 5  
Trace elements in Canadian bituminous and sub-bituminous coals

ELEMENT	NO. OF DET.	CONCENTRATION (ppm)	MEDIAN
Al %	60	0.2 - 3.9	1.1
As	56	0.3 - 320	12
Ba	60	13 - 3900	124
Br	50	0.13 - 3550	12
Ca	59	284 - 18180	1754
Ce	55	1.8 - 52	12
Cl	60	16 - 3710	829
Co	56	0.3 - 18	2.6
Cr	59	0.16 - 35	10
Cs	56	0.02 - 4.1	0.60
Dy	60	0.2 - 2.6	0.98
Eu	52	0.04 - 0.8	0.28
Fe %	60	0.15 - 9.57	1.06
Hf	55	0.11 - 4.9	0.60
I	56	0.2 - 4.0	1.1
K	58	74 - 29000	1061
La	59	1.3 - 35	6.9
Mg	58	50 - 5000	598
Mn	60	6 - 285	80
Na	60	43 - 8361	457
Rb	31	1.3 - 30	9.4
Sb	59	0.08 - 23	0.78
Sc	60	0.5 - 8.6	2.5
Sm	60	0.3 - 16	1.2
Sn	25	8 - 267	98
Sr	55	8 - 735	89
Ta	41	0.02 - 1.2	0.15
Tb	19	0.02 - 0.5	0.25
Th	55	0.3 - 14	2.1
Ti	60	50 - 1950	542
U	60	0.1 - 4	0.84
V	59	2.4 - 87	17

Table 6  
Effect of coal cleaning

ELEMENT	CONCENTRATION (ppm)	
	Raw Coal (Luscar)	Cleaned Coal
Al (%)	1.74	0.76
As	7.9	5.6
Ca (%)	1.44	0.59
Cl	17	16
Co	3.5	2.6
Cr	12	8.8
Fe (%)	2.57	0.41
La	15	7.2
K	3370	773
Mn	176	73
Sb	0.98	0.78
Ti	780	314
Th	4.6	2.2
U	2.1	1.3
V	20	11

*Effect of coal combustion*

A number of the Canadian thermal coals which had been analyzed in powdered form were slowly burned and reduced to ash in silica crucibles in a clean muffle furnace whose temperature was increased in final stages to 750°C according to the

Table 7  
Effect of static coal ashing

Mostly volatilized (75-100%)	Cl, Br, I, Se, Hg
Partially volatilized (25-75%)	Na, K, Sb, Sc, Sr
Mostly retained in ash (10-25% volatilized)	Ba, Sn, Hf, Eu, U
Retained in ash (< 10% volatilized)	Al, Ca, Ce, Co, Cr, Cs, Dy, Fe, Mg, Mn, Ta, Ti, Th, V, Zr

ASTM recommended coal ashing procedure. The ash fraction of each coal was determined from the weights of coal and the ash produced. In table 7 are given the effect of ashing on groups of trace elements arranged from 0 to 98% of element volatilized. Notable among the low volatility elements are several of the chalcophile elements and most rare earths, whereas halogens, As, Hg, Se, Sb and alkalis tended to be volatilized to a large degree, viz. 30-100%. The fraction of these latter elements lost from coal during static combustion showed some inverse variation with ash content, or conversely with organic content of coal; coals of lower ash content tended to exhibit higher volatilities. These findings are in good agreement with work on U.S. coals<sup>9</sup>.

However, it should be noted that the relative volatility of trace elements during coal combustion is more obviously related to the fusion temperatures of the elements and their oxides than to any other parameter. Obviously trace elements

volatilized contribute to atmospheric loading while those retained in the ash may be important in evaluating the impact on ground waters near ash disposal landfill sites. Coal ashes are much more readily leached than original coals; therefore their disposal presents potential future environmental stresses.

### References

1. C. BLOCK, R. DAMS, *Anal. Chim. Acta.*, 68 (1974) 11.
2. D. E. BRYAN, H. R. LUKENS, V. P. GUINN, *Nuclear Techniques in Environmental Pollution* (1970) IAEA, p. 347.
3. C. BERGERIOUX, L. ZIKOVSKY, *J. Radioanal. Chem.*, 46 (1978) 285.
4. O. I. MILNER, *Analysis of Petroleum for Trace Elements*, Pergamon Press, 1963.
5. R. H. FILBY, K. R. SHAH, *Role of Trace Metals in Petroleum*, T. F. YEN (Ed.), Ann Arbor Sci. Publ. Inc., Michigan, 1975.
6. J. S. BALL, W. J. WENGER, H. J. HYDEN, C. A. HERR, M. T. MEYERS, *J. Chem. Eng. Data*, 5 (1960) 553.
7. Alberta Research Council, Edmonton, Canada, 1979.
8. R. H. FILBY, B. HITCHON, K. R. SHAH, *Reference 5: chapter 6*, 1975.
9. H. J. GLUSKOTER, R. R. RUCH, W. G. MILLER, R. A. CAHILL, G. B. DREHER, J. K. KUHN, circular 499 (1977) Illinois State Geol. Survey, U. S.