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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF ESTONIAN ALUM SHALE AND SOME OTHER OIL SHALES

The aim of the present study is to apply an instrumental neutron activation analysis to the determination of major, minor and trace elemental abundances in the organic matter and mineral residue of the enriched alum shale.

The alum shale sample deposit was subjected to enrichment according to the following scheme.

Scheme of enrichment of Estonian alum shale

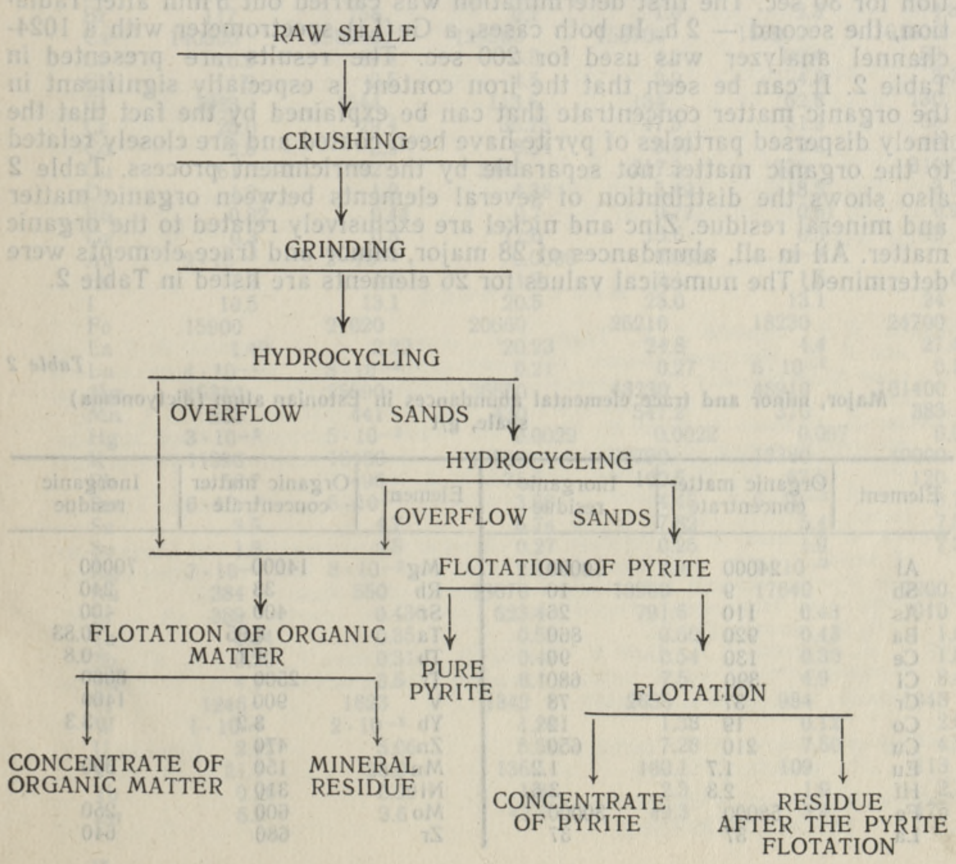

Table 1

Enriched products in Estonian alum shale

Abundance of the organic matter in raw shale 17.3%

	Concentrate of organic matter, %	Mineral residue, %
Yield	27.9	44.6
Abundance	46.7	4.1
Recovery	75.3	10.7
	Concentrate of pyrite, %	**Quartz, %**
Yield	16.1	11.4
Abundance	32.0	0.6
Recovery	83.6	1.1

The determination of major, minor and trace elemental abundances in alum shale by the instrumental neutron activation method has been reported in [1, 2]. The organic matter concentrate and mineral residue obtained by enriching alum shale was examined by the above-mentioned method at the Institute of Physics, the Latvian SSR Academy of Sciences. The experiments were carried out in a nuclear reactor at a flux density of $(1-3)\cdot 10^{13}$ n/cm^2 and under the analysis conditions described in [2].

The radiation time in vertical channels was 70 h. After a 3-day cooling the samples and standards were repacked into polyethylene bags and analyzed for the first time, using a semiconductor γ-ray spectrometer with a 4000-channel analyzer for 5 min. The second determination of samples was performed after a 20-day cooling using the same spectrometer for 5 min. Short-lived nuclides were analyzed on a horizontal reactor channel equipped with a pneumatic conveyer. The samples were exposed to radiation for 30 sec. The first determination was carried out 5 min after radiation, the second — 2 h. In both cases, a Ge(Li)-spectrometer with a 1024-channel analyzer was used for 200 sec. The results are presented in Table 2. It can be seen that the iron content is especially significant in the organic matter concentrate that can be explained by the fact that the finely dispersed particles of pyrite have been coated and are closely related to the organic matter not separable by the enrichment process. Table 2 also shows the distribution of several elements between organic matter and mineral residue. Zinc and nickel are exclusively related to the organic matter. All in all, abundances of 28 major, minor and trace elements were determined. The numerical values for 26 elements are listed in Table 2.

Table 2

Major, minor and trace elemental abundances in Estonian alum (dictyonema) shale, g/t

Element	Organic matter concentrate	Inorganic residue	Element	Organic matter concentrate	Inorganic residue
Al	24000	10000	Mg	14000	70000
Sb	9	10	Rb	33	240
As	110	26	Sr	400	400
Ba	920	860	Ta	0.65	0.83
Ce	130	90	Tb	1.1	0.8
Cl	390	680	Ti	2500	8000
Cr	37	78	V	900	1400
Co	19	12	Yb	3.2	3.3
Cu	210	650	Zn	470	
Eu	1.7	1.2	Mn	150	300
Hf	2.3	3.6	Ni	310	
Fe	58000	30000	Mo	600	250
La	37	37	Zr	680	640

The abundances of K and Na in alum shale have been reported earlier [2] and are therefore not given in Table 2. Very often fossil fuels, such as coal, oil shales and peat, are rich in useful major, minor and trace elements, part of which, however, being toxic (Cd, Hg, Pb, As, Cr, Ni, V) [3] as well as in radioactive heavy metal isotopes. While the content of several elements in the raw material (fuel) is relatively low, then in power units on burning their concentration may increase tens of times and they pass to atmosphere in flue gases as fly ash. Fly ash contains substantial amounts of toxic elements that may be detrimental to the environment besides SO_2.

Therefore it would be of interest to estimate major, minor and trace elemental abundances in the Estonian and Green River formation oil shales and their ashes. Data pertaining have been given in a report which was presented at the 2nd USA/USSR workshop on health effects of oil shale development, Tallinn, Estonia, USSR, June 22—25, 1981, published in Los Alamos National Laboratory, New Mexico, 1983 (Table 3) [4].

Table 3

Major, minor and trace elemental abundances of Estonian and Green River raw and spent shale solids, g/t [4]

Element	Estonian raw	Estonian spent	Green River raw	Paraho spent	Tosco spent	Occidental spent
Al	1694	2069	39430	45410	9090	47300
Sb	0.31	0.37	2.44	2.06	2.7	2.4
As	4.2	11.0	42.65	41.4	66.9	31.9
Ba	156	188	0.042	7949	155	658
Br	117	158	0.7	1.0	2.3	4.8
Ca	140500	296200	129500	156700	157000	161800
Ce	16.9	29.4	3.5	4.9	39.4	59
Cs	1.9	2.5	4.5	2.9	4.8	3.7
Cl	1023	1644	113.6	134	62.8	130
Cr	25.0	29.4	35.75	47.5	31.9	55
Co	2.5	2.9	8.54	8.45	10.2	10.0
Cu	61	72	2486	217.3	276	310.0
Dy	1.2	1.2	4.38	5.49	18.5	3.51
Eu	0.32	0.44	0.7	0.77	0.61	0.92
Ga	0.3	0.3	12.6	13.6	0.3	49
Au	$2\cdot10^{-5}$	$2\cdot10^{-5}$	0.0006	0.0007	$1.4\cdot10^{-5}$	
Hf	1.3	1.5	1.7	2.1	1.5	1.6
I	10.5	13.1	20.5	25.0	13.1	24
Fe	15900	27020	20660	26210	18230	24700
La	1.49	2.22	20.23	24.8	4.4	27.4
Lu	$4\cdot10^{-2}$	$8\cdot10^{-2}$	0.21	0.27	$6\cdot10^{-2}$	0.13
Mg	15310	25590	36650	43230	48910	101400
Mn	203	441	430	541.2	370	383
Hg	$3\cdot10^{-2}$	$5\cdot10^{-2}$	0.0029	0.0022	0.097	0.03
K	11390	16400	19560	23790	13380	40000
Rb	58.7	496	75.5	100.5	67.6	120
Sm	$6\cdot10^{-3}$	$6\cdot10^{-3}$	3.68	4.45	$6\cdot10^{-3}$	3.7
Sc	3.5	4.7	5.74	7.82	5.4	7.5
Se	1.8	0.8	0.27	0.25	1.9	7.3
Ag	$7\cdot10^{-3}$	$8\cdot10^{-3}$	2.3	2.9	$7\cdot10^{-3}$	
Na	384	550	18670	18960	17640	7200
Sr	389	0.436	623.4	791.6	0.43	1010
Ta	0.24	0.35	0.52	0.60	0.43	1.6
Tb	0.20	0.31	0.49	0.54	0.30	1.8
Th	4.1	3.5	6.1	7.5	4.9	8.4
Ti	1246	1623	1842	2630	984	1948
W	$1\cdot10^{-3}$	$2\cdot10^{-3}$	1.26	1.38	0.12	2.6
U	2.12	3.06	5.59	7.28	7.50	4.77
V	21.1	28.0	136.1	160.1	109	113
Yb	0.26	0.99	1.9	2.3	1.9	2.7
Zn	6.9	3.6	47.1	49.3	3.4	175

A comparison of Estonian and Green River Formation shales demonstrated that the abundances of major elements, such as Al, Mg, Na, K, are several times higher in the latter. The Estonian oil shale has lower concentrations of Ba and Sr, trace elements (As, Co), rare earths, and U, V, Zn.

The Estonian oil shale ash contains Ca twice as much as that of oil shale from the deposits of Paraho, Tosco and Occidentals.

The Green River formation shale is richer in clay minerals. Of major components C, O, Si and S, and of minor ones Pb cannot be identified by INAA due to their intensivity [4]. However, the authors of this report, E. J. Peterson and W. D. Spall [4], note that only two Estonian oil shale samples (raw and spent shale) with unknown histories were examined. We are of the opinion that the Estonian raw shale sample may originate from bed E or B, judging by its high Fisher Assay oil yield.

The methods of INAA and energy dispersive X-ray fluorescence analysis (XRF) are applicable to determining not only minor and trace elemental abundances, but also liquids, in our case to trace elements in oil shale. So, C. L. Wilkerson [5] has evaluated abundances of 26 trace elements in the raw and filtrated oil obtained by pyrolysis of the Green River shale (Fe, As, Mg, Ni, K, Ti, Ca, Sr, Zn, Co, Mo, Na, Cu, Cl, Se, Pb, V, Rb, Ga, Hg, Al, Br, Cr, Mn, Yb, U) their distribution between oil shale fractions and relationship with organic matter.

A thorough review of major, minor and trace elemental abundances in oil shale and oil shale ashes of the oil shale fired Baltic Power Plant has been given in [6]. It could be seen that abundances of several minor elements, such as Pb, Cl, Rb, Zn, As etc. increased severalfold in oil shale ashes and fly ash.

All in all, abundances of 11 major components and 21 minor ones were determined by using INAA and XRF [6].

The results obtained and literature data are indicative of the applicability of INAA not only to the determination of major, minor and trace elemental abundances in minerals, but also to the investigation of technological processes (e. g. minerals enrichment) and fuels. Nowadays, however, mainly quantitative methods of analysis are being used to determine major elemental abundances in minerals and fossil fuels.

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EESTI DIKTÜONEEMAKILDA JA MÕNEDE PÕLEVKIVIDE INSTRUMENTAAL-NEUTRONAKTIVATSIOONIANALÜÜS

Autorid on määranud eesti diktüoneemakilda rikastatud proovis sisalduvaid makro-, mikro- ja jälgelemente instrumentaal-neutronaktivatsioonianalüüsi meetodil. Võrdluseks on toodud kirjanduse andmeid mõnede põlevkivide makro-, mikro- ja jälgelementse koostise kohta, mille määramisel on kasutatud sama meetodit.

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ИНСТРУМЕНТАЛЬНЫЙ НЕЙТРОННО-АКТИВАЦИОННЫЙ АНАЛИЗ ЭСТОНСКОГО ДИКТИОНЕМОВОГО СЛАНЦА И НЕКОТОРЫХ ДРУГИХ ГОРЮЧИХ СЛАНЦЕВ

В пробе обогащенного диктионемового сланца и в его минеральном остатке определено содержание 28 элементов, присутствующих в макро-, микро- и следовых количествах. Полученные результаты сравнены с данными по горючим сланцам некоторых других месторождений.