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DISTRIBUTION OF 35 ELEMENTS IN PEAT CORES FROM OMBROTROPHIC BOGS STUDIED BY EPITHERMAL NEUTRON ACTIVATION ANALYSIS

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Фронтасьева М. В., Стайнес Е. E14-2004-64
Изучение распределения 35 элементов
в торфяных колонках омбротрофных болот
с помощью эпитеплового нейтронного активационного анализа

В поверхностный слой торфа омбротрофных болот химические вещества поступают только из атмосферы. Следовательно, торфяные колонки могут использоваться для изучения временных трендов в атмосферных выпадениях поллютантов. Впервые в данной работе эпитепловой нейтронный активационный анализ (ЭНАА) применялся для изучения распределения 35 элементов в торфяных профилях омбротрофных болот. Торфяные колонки отбирались в графстве Финнмарк в северной Норвегии: одна — вдали от каких-либо источников загрязнения, а другая — в районе, подверженном сильному длительному воздействию российских заводов по производству меди и никеля, расположенных вблизи границы с Норвегией. Элементы классифицированы с точки зрения их поведения в верхнем 40-сантиметровом слое торфа. Также обсуждается сходство и различие двух профилей. Продемонстрировано преимущество использования ЭНАА для определения полных концентраций элементов по сравнению с другими обычно используемыми аналитическими методами, основанными на растворении образцов в кислотах.

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Frontasyeva M. V., Steinnes E. E14-2004-64
Distribution of 35 Elements in Peat Cores from Ombrotrophic Bogs
Studied by Epithermal Neutron Activation Analysis

In ombrotrophic bogs the surface peat layer is supplied with chemical substances only from the atmosphere. Peat cores from these bogs therefore can be used to study temporal trends in atmospheric deposition of pollutants. In this work epithermal neutron activation analysis was applied for the first time to study the distribution of 35 elements in peat profiles from ombrotrophic bogs. The selected examples were from Finnmark county in northern Norway: one pristine site far from any local pollution source, and another strongly affected by long-term operation of Russian copper-nickel smelters located close to the border. The elements are classified with respect to their behavior in the uppermost 40 cm of the peat, and similarities and differences between the two profiles are discussed. As compared with other more commonly used analytical techniques based on acid decomposition of the sample ENAA has the advantage of providing the total concentrations of the elements.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR and at the Department of Chemistry of Norwegian University of Science and Technology (Trondheim).

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INTRODUCTION

Among the natural archives available for retrospective studies of atmospheric deposition of elements ombrotrophic bogs are perhaps the most useful. An ombrotrophic bog is a peatland where the uppermost peat layer receives supply of chemical elements only from the atmosphere. The surface of these bogs grows by accumulating new organic matter and preserves a temporal deposition record of any substance that binds strongly to the peat. In some bogs the ombrotrophic layer may extend down to a depth of more than 200 cm, corresponding to a time span of several thousand years [1]. The most obvious alternatives are ice cores from glaciers [2] and lake sediments [3]. Ice cores, however, can be safely used only where the temperature stays below freezing point all the year, restricting the geographical regions mainly to the high Arctic. Moreover the concentrations encountered are in most cases extremely low, placing very strict requirements to contamination-free sampling [2] and highly sensitivity analytical techniques. Lake sediments receive their supply of trace elements not only from the atmosphere but also from inflowing rivers, which may sometimes make the interpretation difficult.

Ombrotrophic peat cores thus remain a very useful medium for the study of time trends in atmospheric deposition of any substances that are not appreciably leached vertically in the peat over time, and have been found useful in a large number of recent studies related to air pollution history [1, 4–10]. In general, these studies have employed analytical techniques such as atomic absorption spectrometry (AAS) and inductively-coupled plasma mass spectrometry (ICP–MS) which require the sample to be brought into solution. Usually this has been achieved by using mixtures of strong acids, which do not completely dissolve the sample. This is not necessarily a problem when dealing with the most typical pollutants from industrial processes. If a comparison with contribution from crustal material is to be done, however, a reference element such as Al or Sc is normally used [10]. Since these elements are to a great extent present in mineral particles not dissolved in the most commonly used mineral acids, an analytical technique allowing the determination of the total content, such as instrumental neutron activation analysis (INAA), must be employed.

INAA is a multi-element technique allowing the simultaneous determination of a considerable number of elements, and was first applied as such to the study of trace elements in peat by Njåstad et al. [11], but later applications have been few [12]. Combined with radiochemical separations NAA facilitated the determination of key pollutant elements in peat such as As, Sb, and Se before data for these elements were available from other techniques [7, 13–15]. At present however the use of NAA for investigations of peat appears to be mainly justified in studies where it is desirable to obtain the total concentrations of elements in the peat profile. The purpose of the present paper is to demonstrate the feasibility of this technique on peat cores, using a specific variant named epithermal NAA [16] which allows determination of a number of trace elements at lower concentrations by suppressing the induced radioactivity caused by some major components in the sample. For this study two peat cores were selected: one representing conditions with very little deposition of air pollutants, and the other from the vicinity of a strong industrial pollution source.

1. MATERIALS AND METHODS

The peat bogs sampled for the present work are situated in Finnmark county, northern Norway. Bog A (Kistrand: 70.50°N, 24.92°E) is situated in a sparsely populated area practically unaffected by local pollution sources and also very little affected by long-range atmospheric transport. The area is sparsely vegetated and somewhat exposed to wind erosion of surface material. Bog B (Svanvik: 69.47°N, 30.06°E) is located close to the Norwegian–Russian border, only 8 km west of Nikel, one of the major copper-nickel smelters in Russia, which has been in operation since the 1930s. This bog is surrounded by pine forests on three sides and a lake on the fourth. Sampling of peat cores was carried out with a steel corer of 10 cm internal diameter, down to a depth of 40 cm in the peat. The recovered peat core was divided into 2.5-cm sections in the field and subsequently transported to the laboratory, where the peat samples were air dried at 35 °C and homogenized.

The bogs were selected on the basis of the surface vegetation with dominance of *Sphagnum fuscum* and oligotrophic vascular plants. The results indicate that Bog B was ombrotrophic at least down to 40 cm, whereas indications of ground water influence were evident in the Bog A core, starting at 37.5 cm depth in the form of increased levels of some typical lithogenic elements (Al, K, REE).

Epithermal neutron activation analysis was carried out in the IBR-2 pulsed fast reactor at Dubna with a very high ratio of epithermal to thermal neutrons. The samples of about 0.5 g were packed in aluminium foil for long-term irradiation and heat-sealed in polyethylene foil bags for short-term irradiation. The characteristics of irradiation channels connected with the pneumatic system of the IBR-2 reactor are listed in [17].

To determine long-lived isotopes, irradiation channel Ch1 was used. The samples were irradiated for five days, repacked and measured two times, after being kept for 4 and 20 days. The measurement time varied from 1.5 to 10 hours. To determine short-lived Mg, Al, Cl, Ca, V, Mn and I isotopes, irradiation channel Ch2 was used. Samples were irradiated for three minutes and measured two times, after being kept for 3–5 and 20 minutes. The measurement time was 5–8 and 20 min, respectively. The gamma spectra of induced activity were recorded with a large-volume high-purity germanium detector with a resolution of 1.96 keV for the ^{60}Co 1332.4-keV gamma line and the recording efficiency of 30% with respect to the $3 \times 3''$ NaI detector efficiency for the same line.

The radionuclides used for the quantification of each element are listed in Table 2. The data were processed and the element concentrations were determined with certified reference items normally used at the laboratory [18].

2. RESULTS AND DISCUSSION

The main trends exhibited by the 36 elements in the two bogs are illustrated in the Table. In order to simplify the presentation, individual values are combined for the intervals 5–10 cm, 10–20 cm, and 20–40 cm. In some cases, where a finer distribution is evident, the details are shown in graphs. A rough classification of the elements with respect to their behaviour in the two profiles may be done as follows:

A. Elements associated with the Cu–Ni smelter, enriched in the surface of Bog B: Mn, Co, Ni, Cu, As, Se (and to a lesser extent Fe, Sb). Examples of this type distribution are shown in Fig. 1 for Ni (logarithmic scale) and Co.

B. Elements carried with windblown soil dust; higher surface enrichment in Bog A: Na, Mg, Al, Ca, Sc, Rb, Cs, REE (La, Ce, Sm, Eu, Tb, Yb), Hf, Ta, Th. An example is shown in Fig. 1 in the case of Hf.

C. Elements with similar surface enrichment in both bogs: K, V, Cr, Zn, Ag. K and Zn are essential plant nutrients and probably enriched due to circulation between living plant biomass and the surface peat. The same is certainly the case for Mn and probably also to some extent for Rb and Cs in Bog A. In the case of V and Cr the reason seems more likely to be a coincidence between windblown dust in Bog A and smelter emissions in Bog B. The distributions of K and Mn in the two peat cores are shown in Fig. 1.

D. Elements mainly supplied from the marine environment which show relatively constant levels from 5 cm and down the profile: Na, Cl, Br, I, and partly Mg. Na, Br, and I are significantly higher in Bog A situated nearer the coast.

Table. Vertical distribution of 36 elements in surface peat cores from two ombrotrophic bogs in northern Norway (μg/g)

Element	Radionuclide	Bog A (Kistrand)				Bog B (Svanvik)			
		0–2.5 cm	5–10 cm	10–20 cm	20–40 cm	0–2.5 cm	5–10 cm	10–20 cm	20–40 cm
Na	Na-24	698	300	345	298	306	167	152	153
Mg	Mg-27	2210	1770	1890	1350	1500	960	1080	1000
Al	Al-28	3920	560	602	617*	1210	356	176	123
Cl	Cl-38	862	773	677	838	366	1096	971	719
K	K-42	1465	639	413	283*	1345	636	390	262
Ca	Ca-49	3830	2290	2600	2620	2780	2540	2350	2020
Sc	Sc-46	0.52	0.11	0.17	0.19	0.32	0.090	0.045	0.030
V	V-52	3.75	0.72	0.61	0.91	4.41	1.31	0.42	0.29
Cr	Cr-51	12.5	3.07	1.60	0.87	8.8	0.94	0.37	0.39
Mn	Mn-56	75.4	6.8	3.6	3.6	243	78	8.7	10.5
Fe	Fe-59	2050	807	1130	489	2920	976	956	813
Co	Co-60	0.93	0.79	0.59	0.50	8.47	2.32	1.06	0.49
Ni	Co-58	4.30	2.22	1.07	1.50*	251	123	31.9	4.20
Cu	Cu-64	<5	<5	<5	<5	161	22	15	<5
Zn	Zn-65	48	34	11	5	30	22	20	10
As	As-76	0.50	0.40	0.23	0.14	4.24	2.03	1.05	0.32
Se	Se-75	0.37	0.31	0.36	0.42	1.17	0.32	0.24	0.18
Br	Br-82	44	66	120	97	12.7	21.2	33.8	22.4
Rb	Rb-86	6.01	1.91	0.84	0.25	1.85	1.05	0.58	0.20
Mo	Tc-99m	0.85	0.84	1.59	1.00	1.56	1.40	0.97	1.07
Ag	Ag-110m	0.064	0.022	0.041	0.037	0.076	0.046	0.035	0.041
Sb	Sb-122	0.194	0.137	0.051	0.017	0.420	0.189	0.106	0.031
I	I-128	8.0	7.7	13.3	10.4	3.0	6.2	5.3	5.4
Cs	Cs-134	0.141	0.043	0.026	0.012	0.076	0.029	0.013	0.006
La*	La-140	1.14	0.39	0.70	0.62	0.36	0.23	0.18	0.11
Ce*	Ce-141	8.7	3.2	2.0	2.5	1.42	0.41	0.35	0.21
Sm*	Sm-153	0.245	0.078	0.101	0.097	0.072	0.033	0.016	0.011
Eu*	Eu-152	0.025	0.040	0.031	0.020	0.015	0.014	0.009	0.008
Tb*	Tb-160	0.044	0.012	0.017	0.011	0.012	0.004	0.004	0.004
Yb*	Yb-175	0.182	0.042	0.045	0.033	0.042	0.011	0.011	0.005
Hf	Hf-181	0.861	0.069	0.036	0.046	0.148	0.026	0.007	0.016
Ta	Ta-182	.0502	.0057	.0056	.0063	.0193	.0065	.0020	.0026
Au	Au-198	.001	.006	.003	.002	.009	.011	.001	.002
Th	Pa-233	0.330	0.107	0.164	0.174	0.076	0.048	0.024	0.015
U	Np-239	0.067	0.085	0.235	0.156	0.044	0.015	0.032	0.014

*Suspected groundwater contribution (minerotrophic layer) below 37.5 cm in Bog A

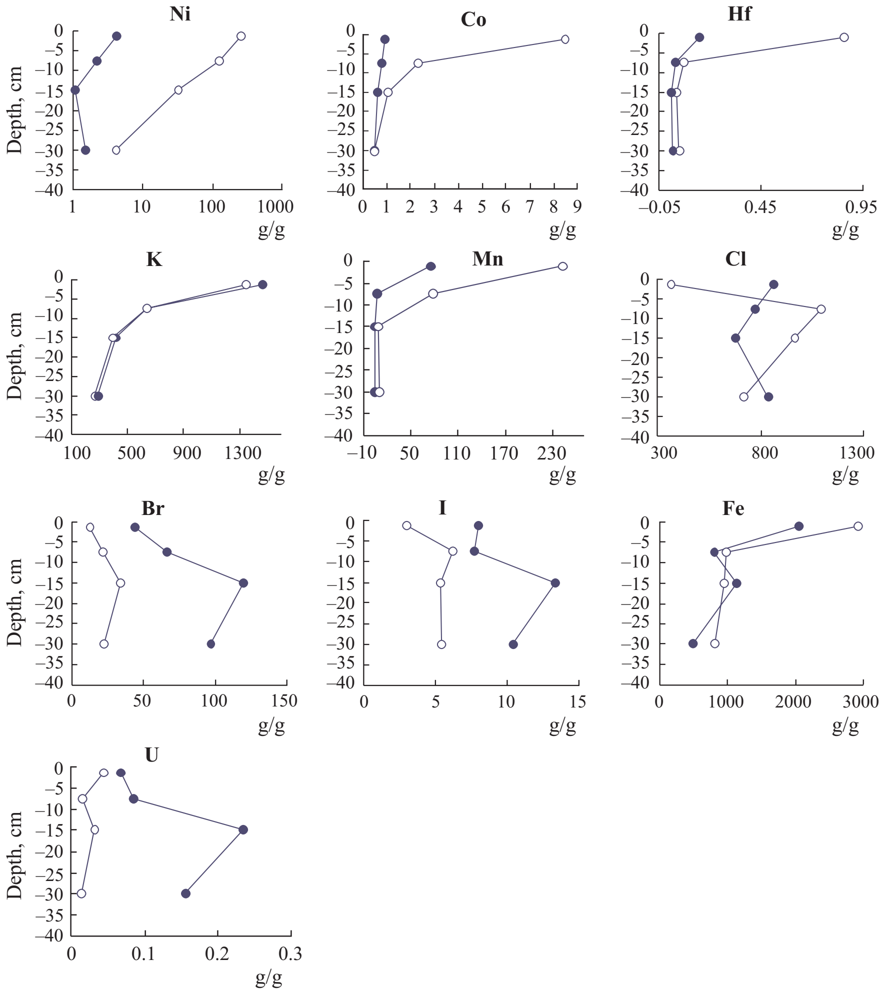

Fig. 1. Concentrations of selected elements in peat cores from ombrotrophic bogs: ● — Bog A (Kirstrand); ○ — Bog B (Svanvik)

Why the same is not the case for Cl is not clear; presumably there are sources of atmospheric Cl in the industrial town of Nikel. The halogens Cl, Br, and I (Fig. 1) are depleted in the surface of Bog B, presumably because of replacement with sulfate from oxidation of SO_2 emitted from the smelter.

E. The elements Fe and U (Fig. 1) show an «erratic» behaviour in Bog A exhibiting higher concentration around 15 cm depth than elsewhere along the core. This behaviour of Fe is well known and has to do with the fact that Fe^{2+}

which is stable under reducing condition is readily soluble in the peat water, and may be transported upward with the water table until conditions favour oxidation to the immobile Fe^{3+}. Uranium is also a redox-unstable metal and may behave similarly in the peat.

F. The REE are present at low concentrations and some of the values are very close to the respective detection limits. Nevertheless the data has a story to tell when considering elemental ratios. The La/Yb ratio increases regularly down the profile from 6.3 to 19 in Bog A and from 8.6 to 22 in Bog B. The corresponding La/Sm ratios vary between 4.6 and 6.4 in Bog A and between 5.0 and 10.0 in Bog B. This means that the RE distributions are different in the surface layer and at depth in both bogs, which may indicate that the excess REE concentrations in the surface may at least in part be from other atmospheric sources than local soil dust.

The selective irradiation with epithermal neutrons, using 0.7 mm Cd to exclude the thermal neutron component, facilitates enhancement of those radionuclides formed from a stable nuclide with a high ratio of resonance neutron activation integral/thermal neutron cross section ($R = I_0/\sigma_0$) relative to those who more closely follow the $1/v$ law. In the latter case the ratio is 0.4, whereas for some nuclides such as ^{238}U the ratio may be as high as 103.4 [19]. Several trace elements studied in this work have high R-values relative to the nuclides responsible for the major γ-activity in the samples. For nuclides formed by fast-neutron induced reactions such as $^{58}\mathrm{Ni}(n,p)^{58}\mathrm{Co}$ the advantage of epithermal activation is particularly high since these reactions are not affected at all by the Cd filter. The 35 elements studied in this work may be classified as follows with respect to their epithermal activation using the R-values (elements in bold are main contributors to γ-activity in the present samples):

$R < 1$: **Na**(0.59), Mg(0.64), **Al**(0.71), Cl(0.69), K(0.97), **Sc**(0.55), V(0.55), Cr(0.53), **Fe**(0.97), La(0.88), Ce(0.83), Eu(0.87);

$1 < R < 2$: Ca(1.30), **Mn**(1.05), **Co**(1.99), Cu(1.14), Zn(1.91);

$2 < R < 10$: Yb(7.2), Hf(2.58);

$10 < R < 20$: As(13.6), Se(10.0), **Br**(19.3), Rb(14.8), Ag(17.5), Cs(12.7), Au(15.7), Sm(14.4), Tb(17.9), Th(11.5).

$R > 20$: Mo(53.1), Sb(28.8), I(24.8), Ta(32.3), U(103.4).

Except in the case of ^{82}Br the major activities induced in the peat samples are substantially reduced relative to many trace element radioisotopes by the epithermal activation. The problem with ^{82}Br however is not serious because other nuclides in the same half-life and γ-energy range (e.g. ^{76}As and ^{122}Sb) are also favoured by the epithermal activation. It is thus clear that ENAA of peat samples is to be preferred to conventional INAA for trace elements such as As, Se, Rb, Ag, Mo, Sb, I, Cs, Tb, Hf, Ta, Au, Th, and U, whereas conditions are less favourable for Sc, Cr, Zn, Ce, and Eu. In the case of V, Mn, Co, and Yb there is little difference.

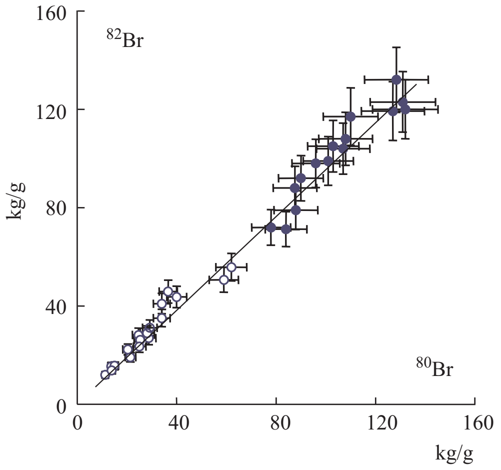

Fig. 2. Comparison of values for bromine in peat obtained by measurement of respectively 17.6 min ^{80}Br and 35.4 h ^{82}Br: ○ — ^{80}Br; ● — ^{82}Br

Another detail of interest is associated with bromine. Normally in INAA 35.4 h ^{82}Br is used for the determination of Br. In the present work, Br was also determined via 17.6 min ^{80}Br, which is also an excellent opportunity in ENAA ($R = 11.0$). Figure 2 demonstrates a very good agreement obtained between Br values using ^{80}Br and ^{82}Br respectively.

As mentioned above [10], Sc in peat determined by INAA has been used in order to monitor the crustal component in peat cores. Recently the even more refractory element Zr has been suggested as a possible replacement [20]. Since the sensitivity for Sc determination is poorer by ENAA than by conventional INAA and Zr has poor sensitivity in both cases this might be an argument against the use of ENAA for peat analysis. However, hafnium, which is very closely associated with Zr and well determined by ENAA, might be an interesting alternative candidate to Zr in this respect.

In the recent paper [21] where ICP–MS, AAS and INAA were compared for the determination of Sb and As in peat, the two former techniques were preferred because «less sample is needed» and «As and Sb can be determined simultaneously». Both these statements are misleading. In the present work samples of ~ 0.5 g were used, and there was no problem with the simultaneous determination of As and Sb in the backgound peat A with low levels of both elements. Another conclusion in that work was that INAA gave systematic low values compared to the other techniques. The INAA values were from a commercial laboratory with no accompanying quality assurance data. When properly executed INAA is capable of giving very accurate data for the total contents of elements in the sample. Since INAA determines the total content of elements in the sample, any differences between INAA and techniques based on acid dissolution of the sample would be expected to show lower results for the latter if all analyses were correctly carried out.

As demonstrated in this paper, INAA in general and the epithermal variety in particular is a versatile analytical technique for the study of a large number of elements in peat. A strong aspect is the determination of the total concentrations of elements regardless their physical and chemical form, and the fact that any problems due to reagent contamination are avoided since there is no chemical treatment.

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