

SOIL CHEMISTRY

Improvement of the X-ray Radiometric Method of Lanthanides' Diagnostics in Soils

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Abstract—There are scarce data on the content of lanthanides in the soils of Russia, which is explained by the difficulties in their identification. The improvement of X-ray radiometric analysis permitted us to analyze a significant group of lanthanides in soils, i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy. Methods of diagnostics are developed for different groups of lanthanides. The new procedure permitted achieving high accuracy in the measurement; the limit of the lanthanide identification in soils is equal to 2–5 mg/kg. The new procedure allows revealing the particularities of heavy lanthanides' distribution depending on the lithogenic and anthropogenic factors. The procedure is applicable for revealing the technogenic anomalies of heavy lanthanides and determining their content in soils within positive and weakly negative anomalies.

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INTRODUCTION

Lanthanides (Ln) include 14 elements from lanthanum La ($Z = 57$) to lutetium Lu ($Z = 71$), which are classified as a special group in the periodic system. Yttrium Y ($Z = 39$) is also related to this group. Lanthanides are subdivided into two groups: (1) the cerium group includes lighter elements, i.e., lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), and europium (Eu), whereas (2) the yttrium group comprises heavier elements, i.e., gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and yttrium (Y).

For a long time, the lanthanides were considered to be biologically inert elements, although their high reactive capacity was well known [4]. Later, it was found out that lanthanides interact intensely with proteins binding calcium [19]. Lanthanides intensify the biological cycle of nitrogen with the redox conditions of the medium being of decisive importance for this process: nitrification is intensified under oxidative conditions, while ammonification is intensified under reductive conditions [27].

Some microorganisms (iron-reducing chemolithotrophic bacteria, in particular) favor the accumulation and biogenic fractionation of lanthanides [23]. The *Gallionella ferruginea* bacterium is wide spread among them; it is capable of accumulating lanthanides in amounts thousands of times exceeding their content in rocks and millions of times their concentrations in the soil–ground water [18]. Iron-oxidizing chemolithotrophic bacteria induce the accumulation of a high amount of lanthanides in Fe–Mn concretions.

Recently, lanthanides were found to impact plants intensely [10]. Agrochemists revealed the positive effect of a low dosage of lanthanides on the development of a number of plants [20, 24–26]. At the same time, this effect was not universal, which was explained by the insufficient knowledge of soils. Identifying territories with negative anomalies of lanthanides, where the application of Ln fertilizers must be the most efficient, appears to be the most important task. Without knowledge of the lanthanide content in natural soils, the extension of Ln fertilizers applicability beyond China's boundaries (where they are widely applied) will be difficult. There are absolutely insufficient data on the content of lanthanides in Russian soils, which is explained by their identification difficulty.

Physical methods appear to be the most reliable for the identification of lanthanides, because they permit analyzing solid samples and do not require the preliminary decomposition of soils. Spectrometric methods such as atomic absorption (AAS) and mass spectrometry with inductively bound plasma (IBP–MS) need sample preparation (conversion of a powder sample to a true solution). The routine procedures of soil decomposition for determining the total content of lanthanides either do not provide for the high productivity of the analytic work with acceptable labor expenditures or lead to significant analytic errors caused by the loss of elements during the sample preparation for the analysis [6]. Neutron activation analysis (NAA), γ -spectrometry (γ -S), and X-ray fluorescence are the most efficient physical methods for analyzing the total content of lanthanides in soils.

NAA with heat neutrons is divided into two types, i.e., instrumental and radiochemical analyses. The former implies γ -spectrometric measurement of samples activated in reactors after certain cycles of exposure [8]. In the latter case, the considered radionuclides are extracted by radiochemical methods, and then their induced activity is measured. The instrumental method, being purely physical, shows a higher sensitivity (the detection threshold is equal to the first mg/kg for the bulk of lanthanides, and the analytic error is about 20%). However, for a number of reasons, it does not permit analyzing some lanthanides, e.g., Gd (because of the low sensitivity to this element) and Dy (due to the short life time of nuclides obtained by activation) [9]. The radiochemical method is still more sensitive, and the list of identified elements is still wider, though it is much more laborious [5] and it cannot be considered to be purely physical.

γ -spectrometry also uses direct sample analysis; after the content of natural nuclides is determined, the total content is calculated from the isotope ratios. The applicability of this method for the analysis of lanthanides is limited to a short list of natural radionuclides. The detection threshold reaches units of mg/kg [7].

X-ray fluorescent analysis (RFA) appears to be the simplest and the cheapest method of analyzing heavy metals in soils [13]. However, not all rare metals can be studied by this method. It is used for detecting the content of zirconium and niobium and yttrium among lanthanides. Naturally, the classic RFA is not applicable for the study of the lanthanide content. On excitation of the X-ray fluorescent spectrum of soil samples using an X-ray tube with an Mo, Rh, or Ag anode (voltage of 30–35 kV), only *L*-lines of lanthanides (much less bright than *K*-lines) will be excited; these weak *L*-lines will be superimposed on bright *K*-lines of macroelements, the content of which is several orders higher than the content of lanthanides. For exciting *K*-lines of lanthanides, it appears convenient to use the RFA variety, i.e., the X-ray radiometric (RRA) method; it implies excitation of the analyzed sample with the isotope source radiation. We used the ^{241}Am isotope source with the emission line energy of 59.48 keV and radiation intensity of $1 \text{ Ci} = 3.7 \times 10^{10}/\text{sec}$. Note that the *K*-lines of the lanthanides are not superposed by any lines of microelements.

The aims of the present study are as follows: (1) to improve the X-ray radiometric method of lanthanide diagnostics in soils; (2) to verify the method's efficiency for soils with increased or decreased (with respect to the clarke) contents of lanthanides.

PROCEDURE OF THE X-RAY RADIOMETRIC ANALYSIS

Formally, the ^{241}Am isotope source is classified as a γ -source, because its emission line is generated upon nuclear transitions. However, soil samples emit X-ray lines upon excitement by this source due to the elec-

tron transition from the upper to lower shells. The electron transitions to the closest to the nucleus *K*-shell appear to be the most interesting as it is these transitions that produce the characteristic *K*-lines of elements [11].

Although Ba is not related to the group of lanthanides, it is appropriate to consider its identification simultaneously with lanthanides, since it is an interfering element upon measuring the intensities of their lines. Earlier, we proved the applicability of the RRA method for the identification of the Ba, La, and Ce content in soils [21]. The further improvement of the RRA approach permitted the identification of Pr, Nd, and Sm [12]. These two groups of elements differ both in the energy interval of the analytic lines (31–35 and 35–41 keV, for the former and the latter group, respectively) and the laboriousness of the analysis.

The first group of elements (Ba, La, and Ce) posed practically no difficulties in the measurement of the true intensities of the analytical lines with a sufficient number of standard soil and rock samples being available for building the calibration plots. These elements may be distinguished at their clarke content and lower.

For the second group (Pr, Nd, and Sm), the measurement of the true intensities of the spectral lines is complicated by the fact that their analytical α -lines are superposed by β -components of lines produced by the first-group elements. Therefore, to analyze the second-group elements, we have to subtract the interfering β -components of the lines produced by the first-group elements. The insufficient number of the standard soil and rock samples certified for these elements poses another difficulty for the diagnostics of the second-group elements. This problem was solved by building a generalized calibration curve, which assumed a constant ratio between the spectral line intensity and the content of the analyzed elements from La to Sm. The forwarded hypothesis is proved by a few standard samples. The identification of elements of the second group is possible at the clarke level and higher.

In this paper, by the RRA method's improvement we mean its extension for the identification of a group of still heavier lanthanides, i.e., Eu, Gd, Tb, and Dy (the third group of elements).

Equipment. The analytical measurement of all the groups of elements was performed using the X-ray fluorescent energy dispersion analyzer ReSPEKT [16]. The RRA method implies the sample excitement by the irradiation from a radioisotope source rather than by the emission from an X-ray tube. The choice of the isotope source proceeded from the following condition: the energy of the exciting radiation line should exceed the energy of the *K*-edge of the adsorption band of the heaviest analyzed element. In our case, the energy of the *K*-edge of the adsorption band constitutes 53.79 keV for Dy. The isotope source has the following advantages over an x-ray tube for the analysis of elements with high energy of the characteristic *K*-lines:

the high energy of the emission line (which is hardly available for tubes); high stability (its half life time is about 465 years); high monochromatism, i.e., a high ratio between the radiation line's intensity and the continuum's intensity; and small a geometric size.

The sample preparation is very simple for RRA. The powder ground to 70–150 μm (without any special requirements concerning the grinding process due to the high energy of the analyzed line quanta) was poured into a polyethylene dish 32 mm in diameter with a 5- μm thick polystyrene bottom. The mass of the analyzed powder was about 8 g (there are no strict requirements concerning the specimen weight). The sample was not used up upon the analysis. To achieve the required detection threshold (about 2 mg/kg), the exposition period was equal to 1.5–2.5 hours.

Preparation of standard samples. For the studied elements of the third group (Eu, Gd, Tb, and Dy), there are no certified standard samples of soils and rocks in the range of concentrations above 6 mg/kg. For constructing the calibration curves, we made up artificial standard samples for the analyzed elements. The standard sample MU-2 (dunite) was selected from the set of standard samples of magmatic rocks collected in the IGEM RAS as a basis (matrix) of the standard samples (or a reference sample) [17]. The minimal content of Pr, Nd, Sm, Eu, Gd, Tb, and Dy (less than 2 mg/kg) was the reason for selecting this sample as a matrix. The compounds of five elements (Nd, Sm, Eu, Gd, and Dy) were added to this matrix. A similar method was used to produce a set of standard soil samples contaminated with heavy metals, i.e., a soddy-podzolic sandy-loamy soil, a krasnozem, a calcareous sierozem, and a typical chernozem [15]. The following compounds were used for manufacturing the artificial standard samples: neodymium oxide, samarium carbonate, gadolinium sulfate, and dysprosium sulfate. The double dilution method was applied for error mitigation upon the samples' preparation. At the first stage, five preliminary standard samples (one for each element) were prepared; 60 mg of each of the enumerated standard elements were mixed into 10 g of the powdered matrix to achieve a concentration equal to 6000 mg/kg of each element in the preliminary standard samples. At the second stage, the final poly-element standard samples were produced from the preliminary standard samples in a similar way; the element concentrations ranged from 5 to 150 mg/kg by varying the dilution coefficient for each element.

Measurement of the true intensities of the spectral lines. Figure 1a shows the spectrum of an artificial standard sample with the content of Gd and Dy equal to 25 and 66 mg/kg, respectively. Similar to the other spectra, the background radiation in this spectrum was approximated according to the *background template* correction [21] with the MU-2 dunite matrix spectrum having been taken as a template. This spectrum shows the true ratio between the intensities of the $K_{\alpha 1}$ - and $K_{\alpha 2}$ -lines of the Gd and Dy elements, which is

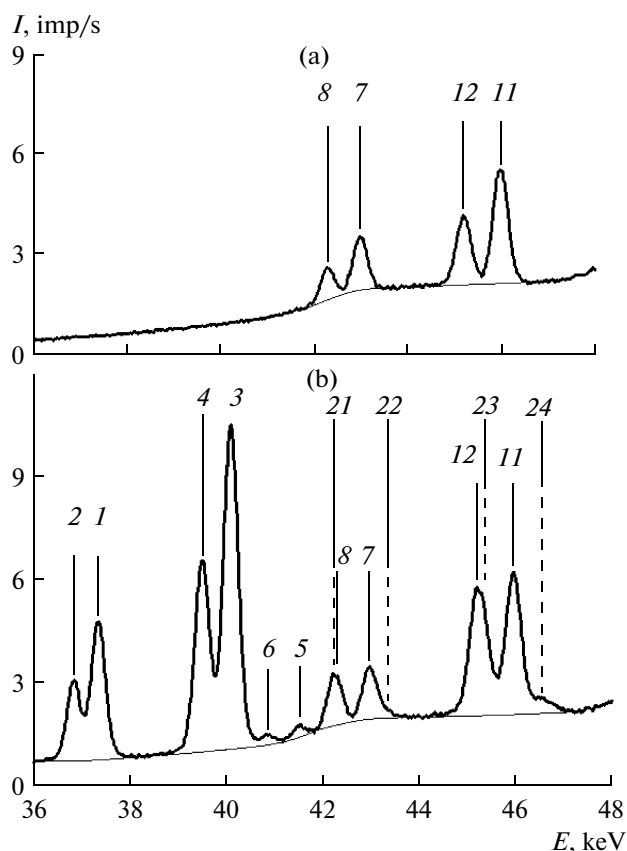


Fig. 1. X-ray radiometric spectra of the artificial standard samples with the background irradiation approximation. Content of elements, mg/kg: (a) Gd, 25; and Dy, 66; (b) Nd, 60; Sm, 145; Eu, 6; Gd, 25; and Dy, 66. Here and in Fig. 2, the position of the spectral lines is as follows. The α -components used for the identification of the elements are as follows: (1) Nd $K_{\alpha 1}$; (2) Nd $K_{\alpha 2}$; (3) Sm $K_{\alpha 1}$; (4) Sm $K_{\alpha 2}$; (5) Eu $K_{\alpha 1}$; (6) Eu $K_{\alpha 2}$; (7) Gd $K_{\alpha 1}$; (8) Gd $K_{\alpha 2}$; (9) Tb $K_{\alpha 1}$; (10) Tb $K_{\alpha 2}$; (11) Dy $K_{\alpha 1}$; (12) Dy $K_{\alpha 2}$. The β -components interfering with the actual intensities of the lines are as follows: (13) Ba $K_{\beta 1}$; (14) Ba $K_{\beta 2}$; (15) La $K_{\beta 1}$; (16) La $K_{\beta 2}$; (17) Ce $K_{\beta 1}$; (18) Ce $K_{\beta 2}$; (19) Pr $K_{\beta 1}$; (20) Pr $K_{\beta 2}$; (21) Nd $K_{\beta 1}$; (22) Nd $K_{\beta 2}$; (23) Sm $K_{\beta 1}$; (24) Sm $K_{\beta 2}$.

close to 3 : 2. However, this is an ideal case with no superimposed lines of other elements.

The further approximation to the actual spectrum is necessary for revealing the effect of the superimposed lines of other elements. For this purpose, we analyzed the spectrum of the artificial standard sample with the following content of elements (mg/kg): Nd, 60; Sm, 145; Eu, 6; Gd, 25; and Dy, 66 (Fig. 1b). The proportion between the lines in this spectrum differs from the actual one for Gd and Dy because of the superposition of the β -components of the Nd and Sm elements. However, the $K_{\alpha 1}$ -components of the Gd and Dy lines remain almost undistorted by the superposition.

Figure 2a manifests the spectrum of an actual soil sample from the mineral horizon sampled in the place

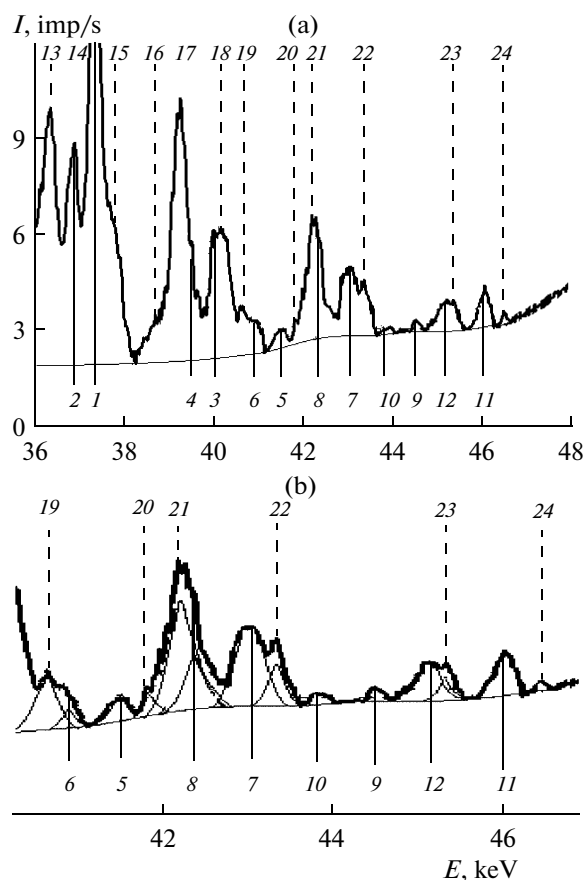


Fig. 2. X-ray radiometric spectrum of the natural soil sample from the mineral horizon of the strong geochemical anomaly in the Lovozero province: (a) a general outline of the spectrum in the interval of the analytic lines from Nd to Dy with the background irradiation approximation; (b) a detailed view of the spectrum in the interval of the analytic lines from Eu to Dy with the background irradiation approximation and the deconvolution of the lines (the deconvolution is shown in those spectral areas where the effect caused by the superposition of the lines is substantial).

of a strong geochemical anomaly of the Lovozero province. The K_{α} - and K_{β} -lines of all the elements in the energy range of 36–48 keV (Pr, Nd, Sm, Eu, Gd, Tb, and Dy) are marked in this spectrum. The pattern of the lines' superposition is rather complicated. As is seen from this spectrum, the β -components of the second-group elements (Pr, Nd, and Sm) are superimposed on the $K_{\alpha 2}$ -lines of Eu, Gd, and Dy; at the same time, the $K_{\alpha 1}$ -lines are subject to very weak superposition, which may be overcome by a routine procedure of the spectrum deconvolution. The spectrum deconvolution is the procedure of finding the true intensities of the spectral lines under the conditions of their mutual superposition; it is common for the X-ray fluorescent analysis of macro- and microelements in soils [14]. Deconvolution refers to inverse tasks. However, all the approaches to solving this inverse task assume a fixed ratio between the intensities of the spectral line

components, e.g., the α - and β -components. As was noted earlier [12], these ratios are actually subject to a matrix effect; i.e., they depend on the sample composition. It is this circumstance that prevented us from using deconvolution for finding the true line intensities for the second-group elements (Pr, Nd, and Sm) and forced us to match the ratio coefficient individually for each sample. If we take the intensity of the $K_{\alpha 1}$ -components as a measure of the spectral line intensity for the third group of elements (Eu, Gd, Tb, and Dy), the deconvolution procedure may produce satisfactory results and permit avoiding the superposition effect.

Figure 2b shows in detail the spectrum of the same sample in the area of the identified elements from Eu to Dy with deconvolution of the spectral lines, i.e., with the displayed true intensities of the spectral lines. The true line intensities are represented in the spectral areas with the significantly superposed lines. The $K_{\alpha 1}$ -components of the identified element lines are vividly shown to be virtually unaffected by the superimposed β -components of the second-group elements (these $K_{\alpha 1}$ -components are numbered 5, 7, 9, and 11 in the figures) unlike the $K_{\alpha 2}$ -components (numbers 6, 8, 10, and 12). Both analytical lines of terbium are free from superposition due to the absence of promethium in the soils (all the isotopes of which are radioactive and short-living). As the β -components of the lines influence weakly the $K_{\alpha 1}$ -lines of Eu, Gd, Tb, and Dy lanthanides, the intensities of their $K_{\alpha 1}$ -lines may be taken as a measure of the true intensities of their spectral lines.

Building calibration plots. The calibration plots were compiled for Eu, Gd, and Dy. Ten artificial standard samples were prepared with varying contents of Eu, Gd, and Dy from 5 to 100 mg/kg. We changed the content of Gd and Dy in inverse proportion, we randomly varied the content of Nd and Sm, and we took deliberately too high concentrations as compared to the true soil samples. A wide range of Nd and Sm variation was taken for revealing the efficiency of the deconvolution procedure, which should overcome the interfering influence of their β -components on the useful analytic lines of Gd and Dy.

The ratio between the true intensity of the spectral line and the intensity of the incoherent scattered exciting radiation I_i/I_{nc} was selected as an analytic parameter of the i -th element; i.e., the standard background method was applied, which took into consideration the sample composition's influence on the analytic parameter value [21]. The K -factor, i.e., the ratio between the absolute error in the concentration measurement and the square root of the measured concentration $K = \Delta C/\sqrt{C}$, was taken as an error measure. The independence of this value from the concentration (unlike the absolute ΔC or relative $\Delta C/C$ deviation) appears to be the main advantage of this error measure, which was comprehensively scrutinized by us earlier [21]. The value of the K factor of about a unit

Table 1. Metrological data on the X-ray radiometric determination of barium and lanthanides in soils

Group of elements	Element	Natural standard samples		Artificial standard samples		Analytic lines; method of measuring actual intensities	Detection limit, mg/kg
		Relative sensitivity	K -factor	Relative sensitivity	K -factor		
1	Ba	1	1.28	Not det.	Not det.	$K_{\alpha 1,2}$; Direct	2
	La	0.997	1.02	0.998	1.04	"	2
	Ce	0.995	1.07	0.993	1.08	"	2
2	Pr	Not det.		0.991	1.96	$K_{\alpha 1,2}$; subtraction of interfering β -components	2
	Nd	"		0.988	1.85	"	2
	Pm*						
	Sm	"		0.980	1.91	"	2
3	Eu	"		0.975	1.16	$K_{\alpha 1}$; deconvolution	5
	Gd	"		0.967	1.12	"	5
	Tb	"				"	
	Dy	"		0.955	1.17	"	5

* All the isotopes of Pm are radioactive and short-living.

(upon concentrations of the analyzed elements of about 10 mg/kg) corresponds to the third accuracy category as agreed by the Scientific Council on Analytic Methods [1].

Metrological data. The following values of the K -factors were obtained from the dependences between the analytic parameter and the concentrations of the analyzed elements: 1.16 for Eu, 1.12 for Gd, and 1.17 for Dy. The K -factor was equal to about 2 for the elements of the second group. As is seen, the error was less for Eu, Gd, and Dy, because, having chosen the $K_{\alpha 1}$ -lines as an intensity measure, we avoided the subtraction of the interfering β -components increasing the error.

The K -factor value shows that the calibration accuracy must be controlled by the sample weight precision upon the preparation of artificial standard samples. The relationship coefficients k_i between the concentration and the analytic parameter ($I_i/I_{nc} = k_i C_i$) for Eu, Gd, and Dy differs by more than 3 relative percent. This fact proves the generalized calibration curve for Eu, Gd, and Dy to be quite reliable. The same relationship coefficients may be also used for Tb.

The analytical threshold for Eu, Gd, Tb, and Dy constitutes about 5 mg/kg for the exposition time of 2 hours; therefore, their identification is possible only in soils of positive geochemical anomalies. The lower analytic threshold for the third-group elements is explained by the $K_{\alpha 1}$ -line taken as the intensity measure, because, by increasing the accuracy of the measurement of the true line intensities (and thus decreasing the K -factor), we lose the absolute intensity of the line and thus make the determination threshold worse.

Correction of the metrological data and verification of the hypotheses for lanthanides of the first and second groups. Table 1 lists in detail the metrological data.

Upon building the calibration curves for the second-group elements, we applied the approach based on the generalized calibration curve implying the permanent relationship coefficient k_i between the analytic parameter and the concentration of the analyzed elements (sensitivity). The application of artificial standard samples permits us to check this hypothesis. The artificial standard samples containing La, Ce, Pr, Nd, and Sm were prepared by the above-described method. The samples of ultrabasic rocks MU-1, MU-2, and MU-4 selected from the set of standard samples of magmatic rocks collected in the IGEM RAS were used as a matrix for their preparation.

Table 1 lists the relative sensitivity of the elements $k_{rel} = k_i/k_{Ba}$ both for the natural and artificial standard samples. First, it shows that the relationship coefficients between the analytic parameter and the concentration (sensitivity) coincide very well for La and Ce both in the natural and artificial standard samples. Second, the hypothesis of the generalized calibration curve using the artificial standard samples is confirmed for the elements of the second group. This hypothesis is also virtually true for the third-group elements with a constancy of no less than 5 relative percent. The given facts (the equal sensitivity of the natural and artificial standard samples and the wide range of the generalized calibration curve) support the validity of the developed procedure. The relative decrease in the sensitivity with the growing atomic number is explained by the decreasing efficiency of the X-ray detector efficiency with the growing quantum energy. This effect is related to the small spatial size of the crystal detecting the X-ray radiation in the Respekt analyzer.

Table 2. Content of lanthanides in the soils of the Khibiny–Lovozero province, mg/kg

Horizon	Depth, cm	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
Background											
Profile 10. Shore of Lake Umbozero. Peat-podzolic soil											
T*	0–12	19	34	55	7	16	5	—	—	—	—
E	12–18	8	16	24	4	8	—	—	—	—	—
BT	18–28	10	17	27	2	7	—	—	—	—	—
C	28–47	15	30	46	4	15	—	—	—	—	—
Profile 11. Shore of Lake Umbozero. Peat-podzolic soil											
T	0–8	23	57	97	13	30	8	—	—	—	—
E	8–10	8	20	30	3	7	—	—	—	—	—
BT	10–29	12	21	33	3	6	—	—	—	—	—
C	29–49	12	25	44	3	11	—	—	—	—	—
Profile 12. Shore of Lake Umbozero. Peat podbur											
T1*	0–6	16	41	55	11	17	7	—	—	—	—
T2	6–18	16	26	38	5	12	5	—	—	—	—
BHF	18–25	13	25	38	5	10	3	—	—	—	—
Weak geochemical anomaly											
Profile 1. Shore of Lake Lovozero. Peat soil											
T1*	9–32	53	291	553	44	141	16	—	14	—	11
T2	32–40	107	171	307	22	87	19	—	17	—	14
Profile 2. Shore of Lake Lovozero. Soddy podbur											
AT*	0–5	31	104	203	19	58	16	—	16	—	15
A1	5–12	35	61	120	14	44	11	—	11	—	9
BHF	12–40	61	108	198	13	57	10	—	10	—	9
BC	40–50	43	97	185	12	59	10	—	11	—	10
Strong geochemical anomaly											
Profile 5. Shore of Lake Seidozero. Peat-podzolic soil											
AT	0–13	130	190	390	35	144	29	—	27	—	25
E	13–24	144	145	277	21	104	18	—	17	—	14
BT	24–40	186	201	390	30	142	23	—	21	—	17
C	40–62	227	259	498	46	198	35	6	32	—	25
Profile 7. Bank of the Elmorayok River. Illuvial-humus soil											
AT	0–15	320	434	830	71	269	37	7	36	6	29
B	15–23	281	439	836	75	250	46	7	39	6	30
BC	23–40	269	423	747	58	255	40	7	36	6	29
Profile 8. Bank of the Elmorayok River. Peat podbur											
T	0–15	346	292	655	47	201	32	6	32	6	26
BÍF	15–47	231	255	500	41	158	25	—	23	—	18
Profile 9. Bank of the Elmorayok River. Podzol											
AT*	0–5	163	170	327	22	98	20	—	19	—	16
E	5–15	199	147	294	22	106	16	—	17	—	14
BT	15–30	246	218	460	36	156	26	—	25	—	20
C	30–52	281	349	785	55	224	32	—	31	—	24
Clarke											
c		31	35	66	9	40	7	2.1	6.1	1.2	4.5
s		40	26	49	7.6	19	4.5				

* Low-ash peat horizons

Note: Hereinafter, a dash designates no data, and the doubtful clarkes are underlined.

Clarkes: c—in the earth crust; s—in soil.

Table 3. Content of lanthanides in the fine earth and the concretions of contaminated alluvial soils in the CisUrals (mg/kg), and the coefficients of the metal concentrations in the concretions (K_{concr})

Horizon, depth, cm	Substance	Y	La	Ce	Pr	Nd	Sm	Gd	Dy
Humus-gley ortstein soil in the Kama River floodplain, profile 41									
G~~, 31–55	Fine earth	—	38	57	12	26	8	7	5
	Iron nodules	—	56	191	20	53	17	15	11
	K_{conc}		1.6	3.3	1.7	2.0	2.1	2.1	2.2
Gleyic agrozem in the Mulyanka River floodplain, profile 33									
C2~~, 49–75	Fine earth	—	31	47	11	23	7	6	5
	Iron nodules	32	104	324	23	66	17	16	12
	K_{conc}		3.3	6.9	2.1	2.9	2.4	2.7	2.4
C3~~, 75–107	Fine earth	—	31	46	13	24	6	6	5
	Iron nodules	42	108	302	24	64	16	15	13
	K_{conc}		3.5	6.6	1.8	2.7	2.7	2.5	2.6
C4g,t~~, 107–137	Fine earth	—	34	45	9	21	5	5	4
	Iron nodules	37	100	243	32	64	13	13	11
	K_{conc}		2.9	5.4	3.5	3.0	2.6	2.6	2.7
C5g~~, >137	Fine earth	—	30	48	10	22	6	5	4
	Iron nodules	40	86	150	15	68	16	14	11
	K_{conc}		2.9	3.1	1.5	3.1	2.7	2.8	2.7
Average K_{conc}			3.1	5.5	2.2	2.9	2.6	2.5	2.5
Clarke									
c		31	35	66	9	40	7	6.1	4.5
s		<u>40</u>	26	49	7.6	19	4.5		

ANALYSIS OF THE CONTENT OF LANTHANIDES IN SOILS OF DIFFERENT GENESIS

We studied soils both enriched and depleted in lanthanides.

Soils of Khibini—Lovozero Province (the Kola Peninsula) were studied at two different sites. The peat—podzolic soils (profiles 10 and 11) were analyzed in the background territory on the left shore of Lake Umbzero. The region of the geochemical anomaly produced by the nearby rare-metal deposit of loparite ores is subdivided into two parts. The anomaly is weak on Lake Lovozero shore in the deposit's periphery, where the influence on the chemical composition of the soils is insignificant. A soddy podbur (profile 2) and peat soils (profile 1) are exposed on the western bank of Lake Lovozero. A strong anomaly is registered in the

centre of the ore field at the northern shore of Lake Seidozero, where it controls the soil enrichment with lanthanides. A peat—podzolic soil (Profile 5) is studied there. Three profiles are also cut at the bank of the Elmorayok River. These are the following: an illuvial—humus soil (profile 7), a peat podbur (profile 8), and a podzol (profile 9). All the soils are acidic with the water extract pH varying from 3.6 to 5.6; these are light-texture soils (ranging from sand to sandy loam) according to the particle-size distribution [3].

We studied the *Fe-Mn concretions in the alluvial soils of the Middle CisUrals (Perm)* formed in the floodplains of the Kama River and its right tributary the Mulyanka River. These concretions were described in detail by Vodyanitskii and coauthors [2].

We studied the *steppe-zone soils in the southern Angara region* on the right bank of the Zalar River, the

Table 4. Content of lanthanides in the soils of the steppe zone in the southern Angara region, mg/kg

Horizon	Depth, cm	Y	La	Ce	Pr	Nd	Sm	Gd
Profile 1. Light chestnut salinized calcareous soil								
A	0–22	22	18	28	4	13	3	3
AB	22–30	20	16	30	4	12	3	3
B1ca	40–49	16	16	30	5	12	4	3
B2	49–70	18	15	27	4	12	3	3
Profile 3. Light chestnut salinized calcareous soil								
A	0–27	21	16	28	4	13	3	3
AB	27–40	15	13	23	3	10	2	3
B1ca	40–52	19	16	29	4	14	3	3
B2	52–80	20	17	27	4	13	2	3
Profile 4. Chernozem								
A	0–10	16	18	35	5	14	3	3
AB	10–30	14	16	31	4	13	2	2
B1ca	30–60	16	21	36	5	15	3	3
B2	60–100	9	8	11	2	5	—	—
Clarke								
c		31	35	66	9	40	7	6.1
s		40	26	49	7.6	19	4.5	

left tributary of the Angara River in the Nukutskii district of Irkutsk oblast (three key sites). One profile was cut at the top and one profile was made in the middle part of the hill. The soils are light chestnut salinized calcareous. One profile was cut at the foothill in the Zalar River floodplain. Chernozemic soils were formed there. The soil texture varies from medium loamy to heavy loamy in these three soils. The pH_{water} is about 8.

Soils of the Khibini–Lovozero province. The content of heavy lanthanides is below the detection limit in the reference soils of the province (profiles 10 and 11). However, within the geochemical anomaly, their content is enough to be revealed by X-ray radiometry. As is seen from Table 2, the content of gadolinium constitutes 10–16 mg/kg and that of dysprosium, 9–15 mg/kg in the area of the weak anomaly. The europium and terbium content is below the detection limit.

The content of heavy lanthanides grows in the territory of the strong anomaly. The gadolinium content

reaches 17–39 mg/kg, and that of dysprosium, 14–30 mg/kg. Europium and terbium are found not in every sample. The illuvial–humus soil on the bank of the El'morayok River turned out to be the richest one, as it contained 7 mg of Eu/kg and 6 mg of Tb/kg, which is 3–5 times higher than the clark values.

Fe–Mn concretions in the alluvial soils of the Middle CisUrals. The content of europium and terbium is below the analytical detection limit in the concretions formed in the alluvial soils of the Kama and Mulyanka Rivers floodplains. The content of gadolinium and dysprosium is detectable. The amount of gadolinium is equal to 13–16 mg/kg, and that of dysprosium, 11–13 mg/kg (Table 3). This is much higher than the clark values (6.1 and 4.5 mg/kg). Such a high degree of lanthanide content in the concretions may be related to technogenic reasons. Lanthanides are used as catalysts upon oil purification. As a result, they enter the rivers with sewage. The local oil-refining works in Perm dump poorly purified sewage into rivers

and contaminate them with lanthanides (Gd and Dy, in particular), which are fixed in concretions.

A similar situation is observed in the rivers near other oil refineries. The oil-refining enterprises situated on the river bank appear to be one of the main reasons for the sediment contamination in the Rhine River estuary [22]. For example, the Ce content exceeds 100 mg/kg in the bottom sediments.

Soils of the steppe zone in the southern Angara region. Unlike the first two objects, the steppe-zone soils in the southern Angara region represent a weak negative geochemical anomaly of rare-earth elements (Table 4), since the clark of the rare-earth element concentrations, i.e., the ratio between the element concentration to its clark concentration in the soil, equals 0.6–0.7. That is why the list of identified lanthanides is somewhat shorter than for the first two objects. As compared to the light chestnut soils in the upper part of the profile (0–62 cm), the chernozem is depleted in yttrium and enriched in cerium. These are just these steppe soils where the application of lanthanide-containing fertilizers may give a positive effect.

CONCLUSIONS

(1) The improved method of X-ray radiometric analysis permitted the determination of a significant group of lanthanides in the soils: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy. Identification procedures have been developed differing for various groups of lanthanides. Calibration plots are suggested. The new method permitted us to achieve high accuracy of the measurements; the detection limit for lanthanides in soils constitutes 2–5 mg/kg.

(2) The new procedure allows revealing the particularities of the heavy lanthanide distribution depending on the lithogenic and anthropogenic factors. The procedure is applicable for revealing the technogenic anomalies of heavy lanthanides and for the determination of their content in the soils of positive and weakly negative anomalies.

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