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ARTICLES

Analysis of Niobium—Rare-Earth Ores by Inductively Coupled Plasma Mass Spectrometry

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Abstract—To determine the composition of niobium—rare-earth ores by atomic emission spectrometry and inductively coupled plasma mass spectrometry, two procedures are developed for sample preparation based on autoclave decomposition and flux fusion. Autoclave decomposition is carried out in a mixture of HF and HNO_3 at a temperature of up to 220°C and a pressure of up to 160 atm using a developed system with resistive heating. Subsequent evaporation to dry salts ensures the removal of F^- ions and silicon as SiF_4. The residue is dissolved in a mixture of HCl and H_2O_2 at 160°C under elevated pressure. The resulting solutions (10% with respect to HCl with the addition of H_2O_2) are diluted before measurements. The dissolution process is monitored for each sample using stable highly enriched isotopes of ^{91}Zr, ^{100}Mo, ^{149}Sm, and ^{178}Hf. The second procedure is based on fusing samples with a mixture of Na_2CO_3 and $Na_2B_4O_7$ at 1050°C in a muffle furnace and dissolving the resulting melt in a mixture of HCl and H_2O_2. The procedures were tested using the national (NFS-23) and foreign standard samples of composition (OREAS-462, 463, 464, 465, Australia) and real samples of niobium—rare-earth ores.

Keywords: niobium—rare-earth ores, inductively coupled plasma mass spectrometry and atomic emission spectrometry

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Discovered in 1959, the Tomtor deposit of rare earth metals is one of the largest in the world and includes a unique set of elements. These ores, along with rare earth elements (REEs), the concentration of which in some fields reach tens of percent, include large amounts of such elements as Nb, Ta, Zr, Y, Sr, Ba, V, U, Th, P, and Fe [1, 2]. When conducting exploration work at the open Tomtor field, the whole complex of analytical methods available to analysts of that time was used. Along with the conventional single-element methods (titrimetry, photometry, atomic absorption), some of multielement methods like neutron activation analysis, X-ray spectral analysis, and luminescence and atomic emission spectrometry were used. In the latter case, both arc and inductively coupled plasma that just appeared at that time were used as sources of excitation of the emission of atoms [3].

The consumption of rare-earth elements, which has increased over the last decade, makes the problem of the development of the Tomtor deposit actual for the domestic industry. This complex problem involves the need in the elemental analysis of a large number of different samples using modern powerful methods, among which inductively coupled plasma atomic emission spectrometry with (ICP AES) and inductively coupled plasma mass spectrometry (ICP MS) occupy leading positions. The application of these two methods, as a rule, involves the preliminary dissolution of test samples; however, there are no description of the decomposition procedures used earlier in the analysis of the Tomtor deposit in the available publications. The existing ICP MS and ICP AES procedures for analyzing rocks are mainly intended for samples with REE concentrations no more than $n \times 10^{-1}$% [4]. Ores from Tomtor contain up to tens of percent of REEs and yttrium and comparable amounts of niobium and zirconium, the chemical properties of which differ significantly from the properties of REEs. This further complicates the task of the development of procedures for analyzing such samples by ICP MS and ICP AES.

The present study is devoted to the development of procedures for the high-performance sample preparation of ores from the Tomtor deposit for the subsequent elemental analysis by ICP MS and ACP AES to determine both the main (REEs and niobium) and impurity elements. This article describes the developed procedures for the decomposition of samples of Tomtor ores and the use of the ICP MS method for the analysis of the solutions obtained. The next publication will focus on the application of ICP AES.

EXPERIMENTAL

Reagents and materials. The following concentrated acids were used in the autoclave decomposition of samples: nitric acid HNO_3 (65%, max 0.0000005% Hg, GR, ISO) and hydrofluoric acid HF (40%; GR, ISO) (Merck, Germany). In the fusion of samples, followed by their dissolution, we used sodium carbonate (cp grade), sodium tetraborate pentahydrate (cp grade), hydrogen peroxide (high-purity grade) from Reakhim (Russia), and concentrated hydrochloric acid HCl (cp grade, Sigma Tek, Russia).

Deionized water with a resistivity of 18.2 MΩ cm was used. Solutions of single-element and multielement standard samples (High-Purity Standards, United States), a standard sample of rare-earth ore OSO 250-91 NFS-23, a standard sample of niobium–rare-earth ore SOP 46-15 VIMS048RzO, and international standard samples of rare-earth ores OREAS 463, 462, 464, and 465 (ORE Research & Exploration, Australia) were applied.

The following chemical elements enriched with isotopes were used: ^{100}Mo (enrichment level 96.1%) as a metal powder (Elektrokhimicheskii zavod, Zelenogorsk, Russia); ^{91}Zr (95.0%), ^{149}Sm (95.1%), and ^{178}Hf (95.2%) as powdered oxides (Elektrokhimpribor, Lesnoy, Russia). To prepare stock solutions of these isotopes, their accurately weighed portions were dissolved in a mixture of HCl and HNO_3 (3 : 1) in glass flasks, and the volume of the solution was adjusted to the mark with 2% HNO_3. To prepare a working solution-additive containing all four isotopes, appropriate aliquot portions of their stock solutions were placed into a volumetric flask, and the volume of the solution was adjusted to the mark with 2% HNO_3.

To store the solutions, glass volumetric flasks were used with ground-glass stoppers according to *GOST* (State Standard) *1770-74*, disposable 20-mL polyethylene bottles (Narofominsky zavod plasticheskikh mass, Russia), and disposable 15- and 50-mL polyethylene test tubes from Labcon (United States) and Deltalab (Spain). The glassware was presoaked for 4–5 days in 5% HNO_3 and washed with deionized water prior to use.

Equipment. The autoclave decomposition of samples was carried out in the autoclave sample digestion system developed at the Institute of Microelectronics Technology Problems and High-Purity Materials, Russian Academy of Sciences, which is a continuation of the well-proven MKP-05 system (Ankon-At-2, Russia). The system enables heating of 30-mL Teflon reaction chambers to a maximum temperature of 240°C and a pressure of 20 MPa (200 bar). The thermostat unit for 6 autoclaves is equipped with two independent thermocouples and an automatic control unit based on a TRM-251 programmable PID temperature controller (OVEN-K, Russia). The control unit implements a five-stage program for heating the thermostat; the temperature, the duration of heating and maintaining the selected temperature are set at each stage.

RP-1 electric plates with variable output (Tom'analit, Russia) were used for the heating and evaporation of solutions. The samples were fused in a SNOL 10/10 laboratory muffle furnace (Tekhnoterm, Russia). A CE224-C analytical balance (Sartogosm, Russia) was used for weighing.

For the mass spectrometric determination of elements, an X-7 quadrupole mass spectrometer (ThermoScientific, United States) was used with the following operation parameters: generator output power 1300 W; set of standard nickel cones; concentric atomizer PolyCon; quartz conical spray chamber cooled to 3°C; the flow rate of the plasma-forming argon flow 13 L/min; the flow rate of the auxiliary argon flow 0.9 L/min; the flow rate of argon in the atomizer 0.95 L/min; and the sample flow rate 0.8 mL/min. The list of elements under determination, the isotopes used, and the main spectral interference are given in Table 1.

Decomposition of samples. *The autoclave decomposition* of samples was carried out in batches of 4–5 samples, the weight of which was 15 mg. In each lot, one control sample was decomposed together with the test samples, and in each third lot, a standard sample was decomposed. Samples were placed into fluoroplastic reaction vessels of autoclaves, and 0.05 mL of a solution containing elements enriched with ^{91}Zr, ^{100}Mo, ^{149}Sm, and ^{178}Hf isotopes (200, 10, 200, and 10 mg/L, respectively) were added. At the same time, 0.05 mL of a solution of a mixture of the same isotopes was added to a clean test tube; 0.5 mL of conc. HNO_3 was added, and the volume of the resulting solution was adjusted to 10 mL with deionized water. Portions of HF (1.7 mL) and HNO_3 (0.5 mL) were added to reaction chambers, and the chambers were closed with lids and sealed in titanium enclosures of autoclaves. The autoclaves were placed in an electric heater and heated at 160°C (1 h), 180°C (1 h), 200°C (1 h), and 220°C (1 h). After cooling, the autoclaves were opened, the reaction chambers were placed on an electric plate, and the solution was evaporated to dryness at 170–180°C. Then, 1 mL of HCl and 0.5 mL of H_2O_2 were added to each reaction chamber, and the autoclaves were heated again at 160°C (1 h) in the

Table 1. List of elements determined in the Tomtor ores by ICP MS, isotopes used and their abundances, and main interfering polyatomic ions

No.	Element	Isotope	Abundance, %	Main interfering ions (in parentheses abundance for isobar is given, %)
1	Li	${}^{6}\mathrm{Li}$	7.5	–
		${}^{7}\mathrm{Li}$	92.5	–
2	Be	${}^{9}\mathrm{Be}$	100	–
3	Sc	${}^{45}\mathrm{Sc}$	100	${}^{29}\mathrm{Si}^{16}\mathrm{O}^+$, ${}^{28}\mathrm{Si}^{16}\mathrm{OH}^+$, $\mathrm{CO_2H}^+$, ${}^{90}\mathrm{Zr}^{++}$, ${}^{31}\mathrm{P}^{14}\mathrm{N}^+$
4	V	${}^{51}\mathrm{V}$	99.8	${}^{35}\mathrm{C1}^{16}\mathrm{O}^+$, ${}^{34}\mathrm{S}^{16}\mathrm{OH}^+$, ${}^{32}\mathrm{S}^{18}\mathrm{OH}^+$
5	Cr	${}^{52}\mathrm{Cr}$	83.79	${}^{35}\mathrm{Cl}^{16}\mathrm{OH}^+$, ${}^{37}\mathrm{C1}^{15}\mathrm{N}^+$, ${}^{34}\mathrm{S}^{18}\mathrm{O}^+$, ${}^{38}\mathrm{Ar}^{14}\mathrm{N}^+$, ${}^{35}\mathrm{C1}^{17}\mathrm{O}^+$
		${}^{53}\mathrm{Cr}$	9.5	${}^{37}\mathrm{Cl}^{16}\mathrm{O}^+$, ${}^{37}\mathrm{C1}^{15}\mathrm{NH}^+$, ${}^{40}\mathrm{Ar}^{12}\mathrm{CH}^+$
6	Mn	${}^{55}\mathrm{Mn}$	100	${}^{39}\mathrm{K}^{16}\mathrm{O}^+$, ${}^{37}\mathrm{C1}^{18}\mathrm{O}^+$, ${}^{37}\mathrm{Cl}^{17}\mathrm{OH}^+$, ${}^{23}\mathrm{Na}^{32}\mathrm{S}^+$
7	Co	${}^{59}\mathrm{Co}$	100	${}^{43}\mathrm{Ca}^{16}\mathrm{O}^+$, ${}^{42}\mathrm{Ca}^{16}\mathrm{OH}^+$, ${}^{24}\mathrm{Mg}^{35}\mathrm{Cl}^+$, ${}^{36}\mathrm{Ar}^{23}\mathrm{Na}^+$
8	Ni	${}^{60}\mathrm{Ni}$	26.1	${}^{44}\mathrm{Ca}^{16}\mathrm{O}^+$, ${}^{23}\mathrm{Na}^{37}\mathrm{Cl}^+$, ${}^{43}\mathrm{Ca}^{16}\mathrm{OH}^+$
9	Cu	${}^{63}\mathrm{Cu}$	69.17	${}^{40}\mathrm{Ar}^{23}\mathrm{Na}^+$, ${}^{47}\mathrm{Ti}^{16}\mathrm{O}^+$, ${}^{46}\mathrm{Ca}^{16}\mathrm{OH}^+$
		${}^{65}\mathrm{Cu}$	30.83	${}^{40}\mathrm{Ar}^{25}\mathrm{Mg}^+$, ${}^{49}\mathrm{Ti}^{16}\mathrm{O}^+$, ${}^{32}\mathrm{S}^{33}\mathrm{S}^+$, ${}^{33}\mathrm{S}^{16}\mathrm{O}_2^+$
10	Zn	${}^{66}\mathrm{Zn}$	27.9	${}^{40}\mathrm{Ar}^{26}\mathrm{Mg}^+$, ${}^{50}\mathrm{Ti}^{16}\mathrm{O}^+$, ${}^{34}\mathrm{S}^{16}\mathrm{O}_2^+$, ${}^{32}\mathrm{S}^{16}\mathrm{O}^{18}\mathrm{O}^+$, ${}^{32}\mathrm{S}^{34}\mathrm{S}^+$, ${}^{33}\mathrm{S}_2^+$
		${}^{68}\mathrm{Zn}$	18.8	${}^{136}\mathrm{Ba}^{2+}$, ${}^{36}\mathrm{S}^{16}\mathrm{O}_2^+$, ${}^{34}\mathrm{S}^{16}\mathrm{O}^{18}\mathrm{O}^+$, ${}^{34}\mathrm{S}_2^+$, ${}^{35}\mathrm{Cl}^{16}\mathrm{O}^{17}\mathrm{O}^+$
11	Ga	${}^{71}\mathrm{Ga}$	39.9	${}^{142}\mathrm{Ce}^{2+}$, ${}^{142}\mathrm{Nd}^{2+}$, ${}^{55}\mathrm{Mn}^{16}\mathrm{O}^+$, ${}^{40}\mathrm{Ar}^{31}\mathrm{P}^+$, ${}^{35}\mathrm{Cl}^{18}\mathrm{O}_2^+$, ${}^{37}\mathrm{Cl}^{17}\mathrm{O}_2^+$, ${}^{36}\mathrm{Ar}^{35}\mathrm{Cl}^+$,
12	Rb	${}^{85}\mathrm{Rb}$	72.2	${}^{170}\mathrm{Er}^{2+}$, ${}^{170}\mathrm{Yb}^{2+}$
13	Sr	${}^{86}\mathrm{Sr}$	9.86	${}^{86}\mathrm{Kr}^+(17.3)$, ${}^{46}\mathrm{Ti}^{40}\mathrm{Ar}^+$, ${}^{172}\mathrm{Yb}^{2+}$
		${}^{88}\mathrm{Sr}$	82.6	${}^{48}\mathrm{Ti}^{40}\mathrm{Ar}^+$, ${}^{48}\mathrm{Ca}^{40}\mathrm{Ar}^+$
14	Y	${}^{89}\mathrm{Y}$	100	${}^{88}\mathrm{SrH}^+$, ${}^{49}\mathrm{Ti}^{40}\mathrm{Ar}$, ${}^{178}\mathrm{Hf}^{2+}$
15	Zr	${}^{90}\mathrm{Zr}$	51.5	${}^{50}\mathrm{Ti}^{40}\mathrm{Ar}^+$, ${}^{50}\mathrm{Cr}^{40}\mathrm{Ar}^+$, ${}^{180}\mathrm{Hf}^{2+}$
		${}^{91}\mathrm{Zr}$	11.2	${}^{51}\mathrm{V}^{40}\mathrm{Ar}^+$, ${}^{182}\mathrm{W}^{2+}$
16	Nb	${}^{93}\mathrm{Nb}$	100	${}^{53}\mathrm{Cr}^{40}\mathrm{Ar}^+$, ${}^{186}\mathrm{W}^{2+}$
17	Mo	${}^{95}\mathrm{Mo}$	15.9	${}^{55}\mathrm{Mn}^{40}\mathrm{Ar}^+$, ${}^{94}\mathrm{ZrH}^+$
		${}^{100}\mathrm{Mo}$	9.63	${}^{100}\mathrm{Ru}^+(12.6)$, ${}^{60}\mathrm{Ni}^{40}\mathrm{Ar}^+$, ${}^{84}\mathrm{Sr}^{16}\mathrm{O}^+$
18	Rh	${}^{103}\mathrm{Rh}$	100	${}^{87}\mathrm{Sr}^{16}\mathrm{O}^+$, ${}^{86}\mathrm{Sr}^{16}\mathrm{OH}^+$, ${}^{40}\mathrm{Ar}^{63}\mathrm{Cu}^+$, ${}^{206}\mathrm{Pb}^{++}$
19	Pd	${}^{105}\mathrm{Pd}$	22.3	${}^{88}\mathrm{Sr}^{16}\mathrm{OH}^+$, ${}^{89}\mathrm{Y}^{16}\mathrm{O}^+$, ${}^{40}\mathrm{Ar}^{65}\mathrm{Cu}^+$
		${}^{108}\mathrm{Pd}$	26.5	${}^{108}\mathrm{Cd}^{++}(17.3)$, ${}^{92}\mathrm{Zr}^{16}\mathrm{O}^+$, ${}^{92}\mathrm{Mo}^{16}\mathrm{O}^+$
20	Ag	${}^{107}\mathrm{Ag}$	51.8	${}^{91}\mathrm{Zr}^{16}\mathrm{O}^+$, ${}^{90}\mathrm{Zr}^{16}\mathrm{OH}^+$
21	Cd	${}^{111}\mathrm{Cd}$	12.8	${}^{94}\mathrm{Zr}^{16}\mathrm{OH}^+$, ${}^{95}\mathrm{Mo}^{16}\mathrm{O}^+$
		${}^{114}\mathrm{Cd}$	28.7	${}^{114}\mathrm{Sn}^+(0.65)$, ${}^{98}\mathrm{Mo}^{16}\mathrm{O}^+$
22	In	${}^{115}\mathrm{In}$	95.7	${}^{115}\mathrm{Sn}^+(0.36)$, ${}^{98}\mathrm{Mo}^{16}\mathrm{OH}^+$
23	Sn	${}^{118}\mathrm{Sn}$	24.2	–
		${}^{120}\mathrm{Sn}$	32.6	${}^{120}\mathrm{Te}^+(0.10)$
24	Sb	${}^{121}\mathrm{Sb}$	57.3	–
		${}^{123}\mathrm{Sb}$	42.7	${}^{91}\mathrm{Zr}^{16}\mathrm{O}_2^+$

Table 1. (Contd.)

No.	Element	Isotope	Abundance, %	Main interfering ions (in parentheses abundance for isobar is given, %)
25	Te	^{125}Te	7.14	–
		^{126}Te	19.0	$^{126}Xe^+(0.09)$
26	Cs	^{133}Cs	100	$^{93}Nb^{40}Ar^+$
27	Ba	^{135}Ba	6.6	$^{95}Mo^{40}Ar^+$
		^{137}Ba	11.2	$^{121}Sb^{16}O^+$
28	La	^{139}La	99.9	$^{138}BaH^+$
29	Ce	^{140}Ce	88.5	$^{139}LaH^+$
30	Pr	^{141}Pr	100	$^{140}CeH^+$, $^{125}Te^{16}O^+$
31	Nd	^{143}Nd	12.2	$^{142}CeH^+$
		^{145}Nd	8.3	$^{144}SmH^+$
		^{146}Nd	17.2	$^{130}Ba^{16}O^+$
32	Sm	^{147}Sm	15.0	$^{130}Ba^{16}OH^+$, $^{146}NdH^+$
		^{149}Sm	13.8	$^{132}Ba^{16}OH^+$, $^{148}NdH^+$
33	Eu	^{151}Eu	47.8	$^{134}Ba^{16}OH^+$, $^{135}Ba^{16}O^+$
		^{153}Eu	52.2	$^{136}Ba^{16}OH^+$, $^{137}Ba^{16}O^+$
34	Gd	^{160}Gd	21.9	$^{160}Dy^+(2.34)$, $^{144}Nd^{16}O^+$, $^{144}Sm^{16}O^+$
35	Tb	^{159}Tb	100	$^{143}Nd^{16}O^+$
36	Dy	^{163}Dy	24.9	$^{146}Nd^{16}OH^+$, $^{147}Sm^{16}O^+$
		^{164}Dy	28.2	$^{164}Er^+(1.61)$, $^{148}Sm^{16}O^+$
37	Ho	^{165}Ho	100	$^{149}Sm^{16}O^+$
38	Er	^{167}Er	23.0	$^{151}Eu^{16}O^+$
		^{168}Er	26.8	$^{168}Yb^+(0.13)$, $^{152}Sm^{16}O^+$, $^{152}Gd^{16}O^+$
39	Tm	^{169}Tm	100	$^{153}Eu^{16}O^+$
40	Yb	^{171}Yb	14.3	$^{155}Gd^{16}O^+$
		^{172}Yb	21.9	$^{156}Gd^{16}O^+$, $^{156}Dy^{16}O^+$
41	Lu	^{175}Lu	100	$^{159}Tb^{16}O^+$
42	Hf	^{178}Hf	27.3	$^{162}Dy^{16}O^+$, $^{162}Er^{16}O^+$
		^{180}Hf	35.1	$^{180}Ta^+(0.01)$, $^{180}W^+(0.13)$, $^{164}Dy^{16}O^+$, $^{164}Er^{16}O^+$
43	Ta	^{181}Ta	99.9	$^{165}Ho^{16}O^+$
44	W	^{184}W	30.7	$^{184}Os^+$, $^{168}Er^{16}O^+$, $^{168}Yb^{16}O^+$
		^{186}W	28.6	$^{186}Os^+$, $^{170}Er^{16}O^+$, $^{170}Yb^{16}O^+$
45	Re	^{185}Re	37.4	$^{169}Tm^{16}O^+$
		^{187}Re	62.6	$^{187}Os^+$, $^{171}Yb^{16}O^+$
46	Ir	^{191}Ir	37.3	$^{175}Lu^{16}O^+$
		^{193}Ir	62.7	$^{177}Hf^{16}O^+$
47	Pt	^{195}Pt	33.8	$^{179}Hf^{16}O^+$, $^{178}Hf^{16}OH^+$
		^{196}Pt	25.3	$^{180}Hf^{16}O^+$, $^{179}Hf^{16}OH^+$

Table 1. (Contd.)

No.	Element	Isotope	Abundance, %	Main interfering ions (in parentheses abundance for isobar is given, %)
48	Au	^{197}Au	100	^{181}Ta^{16}O$^+$, ^{180}Hf^{16}OH$^+$
49	Tl	^{203}Tl	29.5	^{187}Re^{16}O$^+$, ^{186}W^{16}OH$^+$
		^{205}Tl	70.5	–
50	Pb	^{206}Pb	24.1	–
		^{207}Pb	22.1	–
		^{208}Pb	52.4	–
51	Bi	^{209}Bi	100	–
52	Th	^{232}Th	100	–
53	U	^{238}U	99.3	–

thermostat. After cooling, the autoclaves were opened, the resulting solution was transferred to polyethylene test tubes, and the volume of the solution was adjusted to 10 mL with deionized water. The solutions obtained from the reaction chambers, underwent the above procedures and containing no sample, were used as blank samples. Before the beginning of measurements, all the solutions, including the solution of elements enriched with isotopes, were diluted 20-fold, and an internal standard of 10 μg/L of indium was added to them. The decomposition time of one batch of samples was no more than 7 h.

The fusion of samples was carried out in platinum crucibles. Weighed portions of samples (50 ± 1 mg) were mixed in platinum crucibles with 500 ± 1 mg of a fusion mixture, consisting of Na_2CO_3 and $Na_2B_4O_7$ in the ratio 2 : 1. Sodium tetraborate was predried at 350°C for 3 h and then triturated in an agate mortar. The crucibles were placed in a chamber of a muffle furnace heated to 1050°C and held for 20 min. After that, the crucibles were removed and cooled; 4 mL of deionized water was added to each of them and allowed to stand for 3–4 h. Then, 4 mL of conc. HCl was added to the crucibles, and, after neutralization and partial dissolution, 1 mL of H_2O_2 was added; the resulting solutions with their suspensions were transferred to glass cups. The cups were held for 10–15 min at 60°C on the electrical plate until the melt dissolved completely. Eight milliliters of HCl was added to empty crucibles; the crucibles were heated to 90°C, and the heated acid was combined with the solution in the cup. Then, 1 mL of H_2O_2 was added, the resulting solution was transferred to a 200-mL volumetric flask, an internal standard (10 mg/L of indium) was introduced, and the mixture was diluted to the mark. Simultaneously, all of the above-described procedures were performed for a blank solution without a sample. Decomposition was carried out in batches of 30 samples. To control the decomposition procedure, a standard sample was decomposed with each batch. The total time of the decomposition of one batch did not exceed 8 h. In the case of ICP AES, the solution was analyzed without dilution, and in the case of ICP MS, a 20-fold dilution was performed.

RESULTS AND DISCUSSION

When developing procedures for the decomposition of Tomtor's ores necessary for subsequent analysis by ICP MS and ICP AES, the following requirements conventional for decomposition procedures were taken into account.

(1) It is necessary to achieve the complete dissolution of all constituent components of the test sample.

(2) Low level of uncontrolled contamination from laboratory dishes, air, reagents, etc. should be ensured.

(3) It is necessary to eliminate or minimize the uncontrolled losses of analytes through sputtering, volatility, adsorption, incomplete transfer of solutions, etc.

(4) The solutions obtained after dissolving test samples must be stable for at least several days necessary for measurements.

In addition to the decomposition procedure itself, the subsequent method for determining impurity elements in the solutions obtained has a great effect both on the list of elements to be determined and on the limits of their determination. In the case of ICP AES, because of the large number of intense emission lines of rare-earth elements, niobium, and a number of other matrix elements, the selection of wavelengths free of spectral interferences is limited for many the elements to be determined. For Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Yb, the elimination of spectral interference is possible only by using a mathematical correction; the description of this procedure will be given in our next publication. In the case of ICP MS, spectral overlaps, although have a negative effect on the determination of a number of elements, can be taken into account. At the same time, the low tolerance of this method to the concentration of matrix elements in the solution under analysis leads to the need for its additional dilution, which may lead to a decrease in its stability and, accordingly, to losses of the elements to be determined.

General approaches to the dissolution of various samples of rocks and ores were developed in the last century, suitable to the determination of their elemental composition by photometry, atomic absorption spectrometry, atomic emission spectrometry, etc., and summarized in a number of monographs [5–10]. As was noted above, there were no descriptions of methods for the decomposition of niobium–rare-earth ores in publications; nevertheless, we used the experience accumulated earlier to develop them.

Real ore samples from the Tomtor deposit and the only standard sample of the composition of the rare-earth ore NFS-23 available in 2014 (at the beginning of the study) were used to develop procedures for the decomposition of niobium–rare-earth ore samples. Preliminary experiments with real ore samples and the standard NFS-23 sample showed that they were not completely dissolved in an open system upon the action of different combinations of conventional acids (HF, HNO_3, and HCl, as well as $HClO_4$ and H_2SO_4, that is, acids with higher boiling points). As a rule, a large amount of undissolved black precipitate was remained.

To create more severe conditions for acid decomposition, an autoclave decomposition system with resistive heating was used, ensuring temperature up to 220°C and pressure up to 20 MPa (200 bar), which is sufficient for the transfer of most of the known minerals into a solution. It was found that a 15-g sample of NFS-23 can be completely decomposed in a mixture of HF and HNO_3 (1.7 and 0.5 mL, respectively) after only 2-h heating at 160 and 180°C (1 h at each temperature). The developed procedure was supposed to be used for analyzing a wide range of niobium–rare-earth ores, possibly containing more stable minerals than in NFS-23; therefore, we further used 4-h heating at 160, 180, 200, and 220°C (1 h at each temperature). In this case, as shown earlier [11], even such a sparingly soluble mineral as zircon completely passes into solution.

The options for the removal of fluorides after the dissolution and subsequent stabilization of the resulting solution were studied. It was found that, to remove an excess of F^- ions from the primary solution (obtained by autoclave heating to 220°C and situated in the reaction Teflon chamber), it was sufficient to evaporate the solution once to dry salts by heating the reaction chambers on the electric plate at 170–180°C. Note that evaporation is an important step in the decomposition procedure, and it is necessary to evaporate precisely to dry salts. If evaporated to moist salts, then REE and yttrium precipitate as insoluble fluorides in further operations with solutions. The more complete removal of F^- ions by the addition of $HClO_4$ or H_2SO_4 at the evaporation stage also results in the precipitation of the elements to be determined, primarily of Nb, Zr, and Ta. To dissolve the resulting dry residue, several mixtures of acids were tested, as well as the addition of various complexing agents (oxalic, ethylenediaminetetraacetic, and hydroxyethylidenediphosphonic acids) and hydrogen peroxide. The best results can be achieved after the treatment of the dry residue with a mixture of HCl and H_2O_2 (2 and 0.5 mL, respectively) in an autoclave at 160°C for 1 h. In this case, a clear yellowish solution was present in the reaction chambers after cooling and opening the autoclave. In order to fix better niobium, 0.2 mL of hydrogen peroxide was additionally added after cooling.

Finally, the effect of the weight of test sample on the completeness of decomposition was studied. Experiments with NFS-23 were carried out with the sample weight varying from 10 to 40 mg. It was found that, at a sample weight greater than 15 mg, the final solution was unstable. Experiments have shown that even if the final solution did not contain a sediment at such a weight of the sample, thorium and part of light REEs were completely lost. At a sample weight of 20 mg, a visible white precipitate often formed when the sample was transferred from the reaction chamber to the test tube and diluted. With an increase in the weight of the sample to 30 mg, the precipitate always appeared. The composition of this precipitate included both REEs, Y, and Th and Nb, Zr, and Ta. If the weight of the sample did not exceed 15 mg, then the autoclave dissolution enabled the quantitative transfer most elements usually determined by ICP MS from Li to U into the solution.

As an alternative to autoclave dissolution, the possibility of using a fusion to decompose samples of niobium–rare-earth ores was studied. Various flux agents (lithium metaborate, lithium tetraborate, and sodium carbonate) were tested in different ratios with the sample; fusion temperature was varied from 950 to 1050°C. In addition, the composition of the solution was varied to transfer the resulting glass into a solution, which, on the one hand, would reliably fix all elements to be determined in the solution and, on the other hand, would be convenient for the subsequent analysis. For this purpose, solutions of hydrochloric acid with various additives (oxalic and tartaric acids, hydrogen peroxide) were tested.

It was found that, for samples of Tomtor ores, fusion with a mixture of sodium tetraborate and sodium carbonate (2 : 1) in platinum crucibles at temperatures above 1000°C was optimal. The optimum weight ratio of the flux agent and the sample was not less than 10 : 1. At a lower ratio, fusion did not always occur, and an increase in the excess of the flux agent resulted in an undesirable increase in the salt background. When analyzing samples containing more than 15–20% of niobium and REEs, incomplete fusion sometimes occurred even at a weight ratio of the sample and the flux agent of 1 : 10. In this case, sample weight should be reduced by a factor of 2 to obtain an easily soluble borosilicate glass. From the point of view of the stability of the solution, leaching in 6 M HCl was optimal for dissolving this glass. Hydrogen peroxide was the best additive for stabilizing high concentrations of niobium. Experiments with standard samples showed that, in this case, all REEs, Sc, Y, Th, U, Nb, Ta, P, Ca, Ti, Mn, Fe, Sr, and Ba remained quantitatively in the solution. As for zirconium, it can be partially lost at the leaching stage, apparently, because of hydrolysis. The hydrolysis of zirconium can be prevented by the addition of 0.05–0.1 mL of HF at the stage of dissolving the glass in 6 M HCl upon heating to 60°C. Some of F^- ions bind to a stable complex with zirconium, and the remaining fluoride ions form a strong HBF_4 compound. As experiments with the standard NFS-23 sample showed, the addition of HF at this stage did not lead to the loss of REEs, Y, U, or even Th. Note that the latter method (the addition of HF) should be used with caution and only if it is necessary for the accurate determination of zirconium and a possibility of the control of the dissolution stage of each test sample using stable highly enriched isotopes.

Stable highly enriched isotopes are used to control the dissolution stage of the sample by means of the standard addition method, similar to the recommendations [11]. A 0.05-mL portion of an additive solution containing a mixture of highly enriched isotopes (^{91}Zr, ^{100}Mo, ^{149}Sm, and ^{178}Hf) was added to all samples and to an empty tube prior to the dissolution. At the measurement stage, Zr, Mo, Sm, and Hf were determined by several isotopes indicated in Table 1. As the natural abundances of isotopes are incorporated in the software of the mass spectrometer, the concentrations of these elements found by enriched isotopes (c_{enr}) are higher than those of the same elements found by isotopes with natural distribution (c_{nat}). The difference of $c_{\text{enr}} - c_{\text{nat}}$ is proportional to the amount of enriched isotope in the sample, and its comparison with the concentration in the solution of the isotope mixture in a separate tube enables the estimation of the possible loss and, accordingly, the quality of the dissolution stage. If the values of the difference of $c_{\text{enr}} - c_{\text{nat}}$ for the test sample and the solution with four isotopes coincided within 5–10% for all four enriched isotopes, then we could assume that its decomposition was performed properly.

To obtain correct results in the ICP MS analysis of solutions obtained by the decomposition of samples of Tomtor ores, it was necessary to take into account the effect of polyatomic ions indicated in Table 1. The oxide and hydroxide ions of Ba, Nd, Sm, Gd, and Tb have the most significant effect on the determination of Eu and the following REEs. In this work, we used a calculation method to account for these interferences. For this purpose, auxiliary single-element solutions of Se, Nd, Sm, Eu, Gd, and Tb with a concentration of 500–2000 μg/L were analyzed along with the samples, and the yield of interfering polyatomic ions with $m/z = j$ was determined experimentally at the given settings of the mass spectrometer (that is, the value of K_j). The concentration of an analyte (c_i) was determined by the simplest equation

$$c_i = c - c_k K_j,$$

where c was the total concentration of element i, measured by the isotope with $m/z = j$; c_k was the concentration of element k forming the interfering polyatom with $m/z = j$.

On the basis of these studies, two procedures were developed for analyzing samples of Tomtor ores, based on the autoclave decomposition and fusion of niobium–rare-earth ore samples and subsequent ICP MS analysis of the solutions obtained. The results of analyses of the standard NFS-23 sample are presented in Table 2; it can be seen that the possibilities of these two procedures differ both in terms of limits of detection (LOD, calculated by the 3σ test) and in terms of the range of elements being determined. The autoclave decomposition of samples proceeds in a closed system using pure reagents, which minimizes the possible contamination of solutions obtained after the dissolution. At the same time, the fusion of a sample with 500 mg of a flux agent in a muffle furnace at a high temperature (1050°C) and using HCl of cp grade certainly increase both the risk of uncontrolled contaminations and the total background. Namely because of the high concentrations of Li, Be, Cr, Cu, Zn, and Sb in the control samples after the fusion, these elements were excluded from the list of elements to be determined. The addition of a flux agent increased the salt background and caused a need in using more dilute solutions in IPC MS measurements (the dilution factors are 80000 and 13333 for fusion and autoclave decomposition, respectively). For this reason, the determination limits for Co, Ni, Rh, Pd, Ag, and some others are rather high using fusion, and their determination at such levels is of no practical interest. It is also necessary to note such an important advantage of the fusion procedure as its higher productivity in comparison with the autoclave decomposition procedure. In addition, the weight of the test sample in the case of autoclave decomposition is only 15 mg, which is significantly inferior to the fusion procedure (50 mg). This is a significant difference from the point of view of the representativeness of the test sample, especially in analyzing poorly homogenized samples. In our opinion, the developed procedures of the ICP MS analysis based on autoclave decomposition and fusion of niobium–rare-earth ores perfectly complement each other.

Table 2. Results (μg/g) of the ICP MS analysis of a standard sample of rare-earth ore NFS-23 using autoclave decomposition and fusion ($n = 5$, $P = 0.95$)

Element	Autoclave decomposition		Fusion		Certified concentration, μg/g
	LOD, μg/g	found	LOD, μg/g	found	
Li	0.08	13.5 ± 0.3	N.d.*		
Be	0.06	240 ± 15	N.d.		
Sc	0.4	515 ± 19	N.d.		640 ± 100
V	5	5690 ± 40	N.d.		5500 ± 170
Cr	4	216 ± 7	N.d.		
Mn	2	1490 ± 20	25	1520 ± 20	
Co	0.6	14 ± 1	N.d.		
Ni	2	29 ± 2	N.d.		
Cu	1	63 ± 5	N.d.		
Zn	3	1900 ± 100	N.d.		
Rb	0.1	7.8 ± 0.3	14	<LOD	
Sr	1	18900 ± 400	8	19400 ± 200	18400 ± 1000
Y	0.04	7400 ± 300	3	7340 ± 70	7500 ± 300
Zr	0.2	1700 ± 80	7	1700 ± 200	
Nb	0.2	43000 ± 3000	6	45300 ± 700	46000 ± 1200
Mo	0.1	23 ± 1	5	27 ± 2	
Rh	0.5	<LOD	N.d.		
Pd	1	<LOD	N.d.		
Ag	3	<LOD	N.d.		
Cd	0.6	23 ± 2	N.d.		
Sn	0.5	40 ± 1	12	47 ± 3	
Sb	0.2	25 ± 1	N.d.		
Cs	0.01	1.1 ± 0.1	1	Internal standard	
Ba	0.8	17700 ± 300	8	17600 ± 200	17600 ± 900
La	0.2	52000 ± 2000	1	51400 ± 500	54700 ± 900
Ce	0.3	103000 ± 3000	2	102000 ± 2000	108100 ± 2400
Pr	0.2	11100 ± 300	0.5	10900 ± 200	11500 ± 300
Nd	0.1	37000 ± 1000	1	36200 ± 400	36700 ± 1300
Sm	0.07	4350 ± 80	0.5	4360 ± 80	4400 ± 200
Eu	0.2	1180 ± 30	0.7	1170 ± 10	1230 ± 60
Gd	0.08	2680 ± 60	0.5	2660 ± 30	2600 ± 100
Tb	0.03	324 ± 5	0.3	343 ± 4	390 ± 50
Dy	0.05	1640 ± 30	0.5	1630 ± 20	1700 ± 100
Ho	0.06	281 ± 5	0.4	280 ± 5	300 ± 10
Er	0.08	707 ± 13	0.3	681 ± 9	660 ± 60
Tm	0.02	90 ± 1	0.5	85 ± 4	–
Yb	0.03	530 ± 9	0.4	532 ± 5	450 ± 50
Lu	0.02	76 ± 1	0.4	77 ± 1	80 ± 16
Hf	0.1	47 ± 2	2	39 ± 3	
Ta	0.06	20 ± 2	3	25 ± 2	
W	0.09	159 ± 7	4	180 ± 14	
Re	0.06	<LOD	N.d.		
Ir	0.2	<LOD	N.d.		
Pt	0.4	<LOD	N.d.		
Au	0.6	<LOD	N.d.		
Tl	0.01	1.5 ± 0.1	N.d.		
Pb	0.2	2500 ± 50	8	2800 ± 200	
Bi	0.06	17 ± 1	1	18 ± 1	
Th	0.1	1000 ± 500	1	1600 ± 70	1470 ± 70
U	0.04	79 ± 1	0.4	76 ± 1	

* N.d., not determined.

Table 3. Results (μg/g) of the ICP MS analysis of standard sample OREAS 463 ($n = 13$, $P = 0.95$) and OREAS 465 ($n = 14$, $P = 0.95$) using fusion for decomposition

Element	LOD, μg/g	OREAS 463		OREAS 465	
		found	certified concentration	found	certified concentration
Mn	25	1180 ± 80	1210 ± 90	2790 ± 80	2630 ± 230
Rb	14	<LOD	6.1 ± 0.3	<LOD	0.43 ± 0.05
Sr	8	913 ± 35	961 ± 26	5000 ± 100	5204 ± 182
Y	3	171 ± 9	180 ± 8	514 ± 12	524 ± 33
Zr	7	537 ± 21	576 ± 24	1700 ± 100	1880 ± 203
Nb	6	1420 ± 40	1495 ± 73	4620 ± 80	4680 ± 301
Mo	5	62 ± 4	56 ± 2.4	118 ± 4	114 ± 6
Sn	12	27.0 ± 0.8	31.4 ± 3.1	134 ± 3	136 ± 20
Ba	8	1100 ± 40	1106 ± 70	4400 ± 200	4397 ± 464
La	1	4900 ± 90	4966 ± 139	23700 ± 600	24100 ± 820
Ce	2	6800 ± 200	6590 ± 150	40300 ± 900	39500 ± 1350
Pr	0.5	989 ± 19	1004 ± 43	3770 ± 90	3772 ± 164
Nd	1	3590 ± 60	3682 ± 185	11600 ± 200	11800 ± 500
Sm	0.5	508 ± 11	538 ± 11	1300 ± 30	1361 ± 36
Eu	0.7	113 ± 3	115 ± 4	278 ± 6	286 ± 11
Gd	0.5	244 ± 8	241 ± 13	580 ± 15	584 ± 31
Tb	0.3	19 ± 2	20.3 ± 1	58 ± 2	57.0 ± 3.1
Dy	0.5	66.0 ± 6	70.0 ± 3.3	219 ± 4	217 ± 13
Ho	0.4	7.6 ± 0.7	8.7 ± 0.6	26.8 ± 0.9	27.7 ± 2.1
Er	0.3	15.7 ± 1	16.1 ± 1.1	52 ± 2	50.0 ± 3.1
Tm	0.5	1.4 ± 0.1	1.6 ± 0.1	4.4 ± 0.1	4.5 ± 0.3
Yb	0.4	6.0 ± 0.6	7.0 ± 0.4	18.0 ± 0.5	19.0 ± 0.7
Lu	0.4	0.79 ± 0.07	0.79 ± 0.04	2.3 ± 0.1	2.1 ± 0.1
Hf	2	13.1 ± 0.6	13.8 ± 0.5	40.0 ± 3	41.4 ± 7.2
Ta	3	24.7 ± 2	25.2 ± 1.3	80.0 ± 6	79.0 ± 5
W	4	<LOD	3.7 ± 0.7	7.8 ± 0.9	7.5 ± 1.2
Pb	8	120 ± 14	122 ± 6	551 ± 24	506 ± 19
Bi	1	2.8 ± 0.1	2.9 ± 0.2	17.2 ± 0.6	16.9 ± 1
Th	1	272 ± 15	292 ± 11	841 ± 25	866 ± 43
U	0.4	7.2 ± 0.5	7.9 ± 0.3	13.4 ± 0.4	13.6 ± 0.4

The accuracy of the developed procedures was confirmed by the results of analysis of international standard samples OREAS-462, 463, 464, and 465. The results obtained for OREAS-463 and 465 are given in Table 3 as an example. Both of the developed procedures have been successfully used in the certification of new standard samples VIMS039RzO, VIMS040RzO, VIMS041RzO, VIMS042RzO, and VIMS048RzO developed at the All-Russian Scientific Research Institute of Mineral Raw Materials.

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