



# Determination of rare earth elements in rock samples by inductively coupled plasma mass-spectrometry after sorption preconcentration using Pol-DETATA sorbent

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## ABSTRACT

Sorption preconcentration of rare earth elements prior to introduction in inductively coupled plasma mass spectrometry is developed. For the first time Pol-DETATA sorbent was used for REEs preconcentration after digestion of wide classes of rock samples. The developed technique is based on lithium metaborate fusion, preconcentration on Pol-DETATA sorbent, elution with nitric acid and flow-injection sample introduction to the ICP-MS spectrometer. The efficiency of REEs extraction from the resulting solutions in the presence of high amounts of iron is examined. 5-sulfosalicylic acid was used as a masking reagent. Flow-injection introduction of 50  $\mu\text{L}$  of eluate obtained after desorption was used to avoid corrosion of the parts of the ICP-MS instrument due to high acidity of the eluate. The accuracy of the developed technique is checked by the analysis of the certified reference materials of rock samples. The REEs recoveries within 85–100% interval were attained for most REEs in tested reference materials.

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## 1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used technique for determination of rare earth elements (REEs) in different types of rock samples [1]. Laser Ablation ICP-MS (LA-ICP-MS) is the perfect technique for direct analysis of the solid samples, which does not need any sample digestion and pretreatment [2]. But this technique has its own drawbacks, in particular, small diameter of the laser focal spot and small volume of the ablated material. In many routine analyses of the mineral samples the representative amount of the minerals (0.5–50 g) has to be analyzed for meeting the final conclusion on the economic perspectives of the geological area. For certain types of analyses larger volumes of minerals have to be analyzed, dictated by the sample pretreatment.

Prior to the ICP-MS analysis a rock sample has to be digested. Microwave digestion and fusion with lithium metaborate (LMB) are the most widely applied techniques for digestion of rock samples, but the resulting solutions contain very high amounts of acids and other mineral components. As a consequence, these solutions have to be diluted prior to their introduction to the ICP-MS spectrometer. As a result the limits of detection (LOD) are increased. Besides, the analytical signals of the polyatomic ions of

matrix components (such as  $\text{BaO}^+$ ,  $\text{BaOH}^+$ ) can interfere with the signals of REEs, biasing the accuracy of determination. In some cases these interferences can be mathematically accounted for, but these corrections are not effective if the concentrations of the interferents are higher than concentrations of the analytes. Besides that, application of such corrections inevitably increases LODs.

The preconcentration of REEs is an alternative technique to minimize or remove the interferences without the increase of LODs. Removal of the matrix elements during the analysis of geological samples is usually performed with ion-exchange separation [3,4], although this technique is time consuming and a multi-step procedure, which requires large volumes of acids. To avoid the above-mentioned problems, sorption preconcentration of REEs using chelating sorbents is being intensively developed [5–8].

To our mind sorption preconcentration using chelating sorbents is the most promising technique of preconcentration because the same sorbent can be used for numerous subsequent sorption and desorption cycles, higher preconcentration factors of the analytes can be achieved as compared to ion-exchange and on-line coupling of preconcentration and analysis can be developed. So far the chelating sorbents were used only for preconcentration of REEs from natural waters and digested carbonate rocks [5–8]. To our knowledge there is no published data on the use of chelating sorbents for extraction of REEs from digested rock samples containing large amounts of Fe, Ni, Cu, and Ba. Probably, it can be explained by low selectivity of such sorbents. To our

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mind, a sorbent based on polystyrene grafted with diethylenetriaminetetraacetic groups (Pol-DETATA) seems to be the most suitable for extraction of REEs from digested rock samples because of high efficiency of preconcentration and high mechanical stability of the sorbent [9]. The use of Pol-DETATA for the preconcentration of REEs is reported in [8]: metal ions were extracted from solutions containing high concentrations of Ca and Fe in the presence of masking agents and from digested limestone solutions. It was shown that up to 100 cycles of sorption and desorption can be carried out with the same column packed with Pol-DETATA sorbent [8]. The use of Pol-DETATA sorbent for the determination of REEs in more complex solid samples (such as magmatic rocks or black shales) has not been reported previously.

In our previous paper [10] the efficiency of rock samples digestion by microwave technique was examined for a wide range of rocks. The typical continuous sample introduction mode was used. The dilution of the complex final solutions was used to obtain acceptable acidity of the analyzing solutions. The results of the preliminary experiments on the REEs preconcentration using Pol-DETATA sorbent were reported. The present paper is emphasized on the detailed description of the preconcentration procedure, and the optimization of flow-injection sample introduction to ICP-MS as an alternative technique to dilution, used in [10].

## 2. Experimental

### 2.1. Instruments

The details of the instrumentation used in our investigations are described in our previous publication [10]. Here we present only brief summary of the instrumentation, reagents and procedures. Only details regarding preconcentration technique and flow-injection sample introduction will be discussed in detail.

Analyses were performed on a quadrupole ICP mass spectrometer Agilent 7500c (Agilent Technologies, Waldbronn, Germany). The RF power was 1450 W, plasma gas flow rate was 15 L min<sup>-1</sup>, auxiliary gas flow rate was 1.1 L min<sup>-1</sup>. The Babington nebulizer with a Scott spray chamber (Agilent Technologies) cooled by a Peltier element (2 °C) was used. Data were acquired and processed with ICP-MS ChemStation (version G1834B) software package (Agilent Technologies). Two modes of measurements—"Spectrum" and "Time Resolved," were used for continuous sample introduction and introduction of small volumes, respectively. When the mode of continuous sample introduction was used, the detection conditions were as follows: dwell time 0.05–0.1 s, 3 points on a mass peak, and 3 replicates. In the "Time Resolved" mode the detection conditions were as follows: dwell time 100 ms, full time of the measurement cycle 80 s, and 1 replicate.

The following isotopes were used: <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>143</sup>Nd, <sup>147</sup>Sm, <sup>151</sup>Eu, <sup>153</sup>Eu, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>167</sup>Er, <sup>169</sup>Tm, <sup>173</sup>Yb, and <sup>175</sup>Lu. For most elements only one isotope was used because for flow-injection mode the total number of isotopes is limited by the volume of the loop (see below). Two isotopes for Eu were used to control interferences from Ba containing complexes.

The sorbent was packed into a homemade acrylic microcolumn (2.5 cm length, 0.5 cm i.d.); a peristaltic pump Elpan 372.C (Laboratory Instruments Elpan, Poland) was used for pumping.

Solid samples were weighed using the balance Sartorius 1702MP8 (Sartorius, Germany), with ± 0.1 mg accuracy.

Flow-injection sample introduction to the ICP-MS spectrometer was performed using a HPLC pump "STAIER system" (Akvilon, Russia) and six-port two-position sample injector with external sample loop and needle port Rheodyne 9740 (USA). Sample loops were made of polyether ether ketone; 20, 50, 100 and 200 µL loops were used.

The fusion was performed in platinum vessels in a closed muffle furnace SNOL 10/11B (Technoterm, Russia).

### 2.2. Reagents and reference materials

The Pol-DETATA sorbent used for REEs preconcentration was based on cross-linked polystyrene (Ekoanalytica, Russia). The content of DETATA (diethylenetriaminetetraacetate) groups was 1–1.1 mmol g<sup>-1</sup>, the cross-linking degree was 2%, and the average particle size was 40–80 µm. The procedure of sorbent synthesis is described in [9]. 5-sulfosalicylic acid (SSA p.a. grade, Fluka, China) was used as a masking agent [8].

The standard solutions were prepared from stock solutions using manual samplers 100–1000 µL (LabMate, Poland); 1–5 mL and 2–10 mL (Thermo Scientific, Finland); disposable tips (VWR, USA), 15 mL and 50 mL low-density polypropylene test tubes (Greiner Bio-One GmbH, Germany) and 50 mL (± 0.08 mL accuracy) and 25 mL (± 0.04 mL accuracy) polypropylene volumetric flasks (Vitalab, Germany).

To adjust the pH of a solution 1 M ammonium acetate buffer with pH 5 was added.

Model sample solutions were prepared from single element stock solutions with a concentration of 1 g L<sup>-1</sup> of Fe (SRS 7766-2008, Russia), Ba and Cu (High Purity Standards, USA).

The validation of the developed preconcentration scheme was performed using the following reference materials (RM): SBC-1 (black shale), AND (andesite), AGV-1 (andesite, USGS), and SG-1A (albitized granite, Russia). Among these four only AGV-1 is certified according to ISO Guide rules [11]. The AND and SBC-1 are the RMs certified within GeoPT27, 28 round robin tests [12]. SG-1A is produced by the A.P. Vinogradov Institute for Geochemistry, Irkutsk, the Siberian Branch of the RAS [13]. For many decades many analytical laboratories of the Geologic Service in Russia have successfully used the RMs produced by this institute.

### 2.3. Procedures

#### 2.3.1. Lithium metaborate fusion

0.1 g of a sample and 0.5 g of LMB were placed in a platinum crucible. The crucible was heated at 950 °C for 15 min in a muffle furnace. The residue was leached from the cooled crucible by addition of 2 mL of 65% HNO<sub>3</sub> and 2 mL of deionized water. The solution obtained was transferred to a volumetric flask and diluted by Milli-Q water to 50 mL.

#### 2.3.2. REEs preconcentration

An aliquot of digested sample solution was placed in a 15 mL polypropylene test tube, then 0.1 mL of 5 M sulfosalicylic acid was added and the pH of the solution was adjusted to 5 by addition of ammonium acetate buffer. The pH was controlled by a test paper strip. The volume of the aliquot was selected depending on the actual concentration of REEs in an analyzed sample and, consequently, on the required preconcentration factor. Before the experiments the column was cleaned by 2 M HNO<sub>3</sub>. This solution was pumped through a column packed with Pol-DETATA sorbent; flow rate was 2 mL min<sup>-1</sup>. Then the column was washed with 0.5 mL of Milli-Q water and then with 0.5 mL of the buffer solution. The analytes were desorbed by 2 mL of 2 M HNO<sub>3</sub>. After desorption the column was regenerated by 5 mL of ammonium acetate buffer. Flow rates and the regeneration procedure were selected according to [8]. The volume and the concentration of the eluent were optimized as in Section 3.1.

Flow-injection sample introduction to ICP-MS spectrometer was used for the analysis of the eluate after desorption. A manifold consisting of an HPLC pump and a 6-port sample injector was

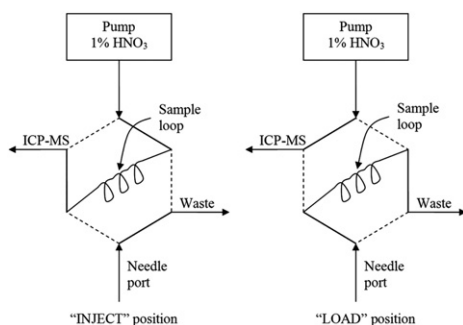


Fig. 1. Schematic diagram for flow-injection introduction of small sample volumes into ICP-MS.

connected to the spray chamber of the ICP-MS spectrometer, see Fig. 1. Diluted  $\text{HNO}_3$  (1% solution in Milli-Q water) was constantly pumped through the nebulizer.  $50 \mu\text{L}$  of eluate obtained after desorption step was introduced to the sample loop by a syringe while the injector was in “Load” position. Then the injector was manually switched to the “Inject” position and the measurements (the recording of the transient concentration profile) were started. After the end of the measurements the injector was switched back to “Load” position and the loop was washed by 1%  $\text{HNO}_3$ . After washing the system was ready for the next cycle. The data were proceeded using the “Time Resolution” mode of “ChemStation” software package supplied with the ICP-MS spectrometer.

### 3. Results and discussion

#### 3.1. Optimization of the REEs preconcentration step

Pol-DETATA is not a selective sorbent for extraction of REE; it efficiently sorbs several other metal ions, such as Fe, Co, Cd, Cu, Ni, Pb and Zn [14,15]. The iron content in any rock samples is much higher than the concentrations of REEs; besides that iron forms stable complexes with chelating groups of Pol-DETATA sorbent. It was experimentally found that Fe depresses the REEs sorption if no masking agent is used.

The authors of [8] have succeeded to minimize Fe extraction during the analysis of sedimentary rocks by introducing SSA as the masking reagent. The affinity of SSA to iron ions is much greater than to REE ions [16]. It was found that 0.1 M of SSA is sufficient for quantitative recovery of REEs; higher SSA concentrations resulted in decline of recovery due to formation of REE–SSA complexes.

In order to increase the overall sensitivity of the analysis technique, minimum volume of the eluent used for desorption should be selected. 2 M  $\text{HNO}_3$  was used for desorption. The efficiency of desorption was checked for different acid volumes (0.5–5 mL). It was found that the minimum required volume of 2 M  $\text{HNO}_3$  was 1 mL.

Maximum concentration of acid in a sample that can be safely introduced into the ICP-MS spectrometer should be below 5% v/v (3% w/w for  $\text{HNO}_3$ ). We have investigated the minimal acid concentration, which can be used for quantitative desorption. Desorption was carried out with 1 mL of  $\text{HNO}_3$  solution; concentration of  $\text{HNO}_3$  was varied from 0.1 M to 2 M. It was found that the minimum concentration of nitric acid required for quantitative desorption of REEs was 1 M.

#### 3.2. Flow-injection sample introduction to the ICP-MS spectrometer

The chosen minimum concentration of  $\text{HNO}_3$  does not permit direct analysis of the eluate by ICP-MS. Thus we have studied the possibility of flow-injection introduction of the eluate into the

ICP-MS spectrometer. Flow-injection sample introduction is an alternative to sample dilution and is widely used when direct analysis of the sample by ICP-MS is not possible [17].

The flow-injection manifold is presented in Fig. 1. Sample volumes of 20–200  $\mu\text{L}$  were injected into the flow of the carrier (1%  $\text{HNO}_3$ ). The carrier flow rate was  $1 \text{ mL min}^{-1}$ . Samples contained  $5 \mu\text{g L}^{-1}$  of each REE in 1%  $\text{HNO}_3$ . The concentration of the analytes in the injected sample was calculated from the area of the transient concentration profile. Transient concentration profiles of europium for various injected volumes are shown in Fig. 2. Peaks tend to be more symmetric with the increase of the injected volume, which is in good agreement with theoretical predictions [18].

Limits of detection for REE determination were calculated for various injected sample volumes. It was found that LODs obtained in flow-injection mode decrease 5–10 times with the increase of the injected volume from 20  $\mu\text{L}$  to 200  $\mu\text{L}$ .

We choose to introduce 50  $\mu\text{L}$  of eluate (containing 1 M  $\text{HNO}_3$ ) into the ICP-MS spectrometer as a reasonable compromise between maximizing analysis sensitivity and minimizing the risk of corrosion of the interface.

#### 3.3. Analysis of reference materials.

The accuracy of the developed technique was checked by analysis of several RMs: SG-1A, AGV-1, SBC-1 and AND. All CRMs were digested by fusion with LMB, then the preconcentration was carried out, and 50  $\mu\text{L}$  of eluate after desorption was introduced into the ICP-MS instrument in flow-injection mode. The results of the analysis are presented in Table 1. A reasonable agreement within the experimental errors for the most REEs was observed but deviations of the results were seen for AGV-1 Dy and Ho. Our results are about 20% lower than the certified values. The reason of this discrepancy is not clear. Additional experiments should be performed. Such a deviation is probably critical for geochemistry dating, but may be acceptable for routine applications like searching fossils.

As was expected larger deviations are observed for SG-1 And point to the fact, that for Sm and Dy the reference values are given without confidential intervals, which highlights the problems of SG-1 certification. On the other hand, for most REEs the correlation between our and reference values are much better. Evidently, this RM should be better characterized.

The described procedure of REE preconcentration takes about 5–10 min and requires about 5 mL of 1 M nitric acid and buffer solution. It favorably differs from the widely used preconcentration techniques based on ion exchange and extraction chromatography [3,19]. For example, the procedure described in [3] takes

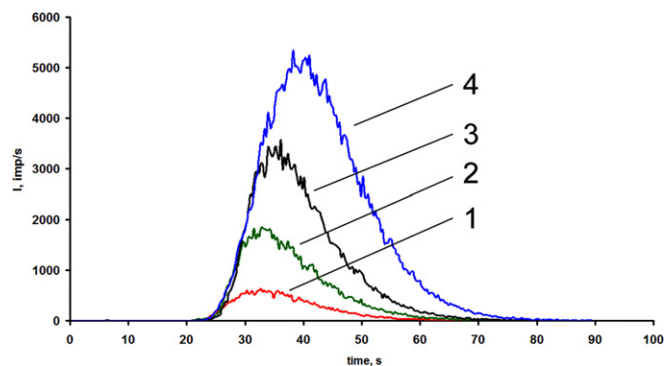


Fig. 2. Temporal profiles of Eu for different sample loop volumes: 1–20  $\mu\text{L}$ , 2–50  $\mu\text{L}$ , 3–100  $\mu\text{L}$ , and 4–200  $\mu\text{L}$  (carrier flow rate  $1 \text{ mL min}^{-1}$ ;  $c(\text{Eu})=5 \mu\text{g L}^{-1}$ ).

**Table 1**Results of CRM analysis after LMB fusion and preconcentration on Pol-DETATA sorbent ( $\mu\text{g g}^{-1}$ ; ( $n=3$ ,  $P=0.95$ ).

Element	SG-1A		AGV-1		SBC-1		AND	
	Measured	Certified	Measured	Certified	Measured	Certified	Measured	Certified
La	26 ± 2	32 ± 8	33.5 ± 0.5	38 ± 2	51 ± 1	52.5 ± 0.6	26 ± 4	25.4 ± 0.3
Ce	63 ± 3	62 ± 6	58 ± 2	66 ± 6	105 ± 1	108.2 ± 0.9	51 ± 4	53.0 ± 0.4
Pr	5.52 ± 0.07	5	6.9 ± 0.2	7.6	12.6 ± 0.3	12.6 ± 0.1	6.3 ± 0.5	6.5 ± 0.1
Nd	13.7 ± 0.1	18 ± 2	27 ± 1	33 ± 3	48 ± 1	49.2 ± 0.5	26 ± 2	26.3 ± 0.3
Sm	2.4 ± 0.2	5 ± 2	5.4 ± 0.5	5.9 ± 0.4	9.7 ± 0.2	9.6 ± 0.1	4.9 ± 0.3	5.08 ± 0.05
Eu	0.10 ± 0.03	(0.1)	1.45 ± 0.04	1.6 ± 0.1	2.00 ± 0.05	1.98 ± 0.02	1.50 ± 0.07	1.41 ± 0.01
Gd	3.40 ± 0.06	7	4.5 ± 0.4	5.0 ± 0.6	8.9 ± 0.2	8.5 ± 0.1	4.2 ± 0.3	3.96 ± 0.05
Tb	0.68 ± 0.08	(0.8)	0.59 ± 0.01	0.7 ± 0.1	1.20 ± 0.02	1.23 ± 0.02	0.51 ± 0.04	0.49 ± 0.01
Dy	5.77 ± 0.08	6	2.8 ± 0.3	3.6 ± 0.4	7.0 ± 0.2	7.10 ± 0.09	2.3 ± 0.2	2.46 ± 0.02
Ho	1.6 ± 0.1	1.5 ± 0.3	0.55 ± 0.04	–	1.34 ± 0.05	1.36 ± 0.02	0.42 ± 0.05	0.44 ± 0.01
Er	6.6 ± 0.2	6	1.6 ± 0.2	1.7	3.61 ± 0.06	3.79 ± 0.05	1.13 ± 0.08	1.16 ± 0.01
Tm	1.3 ± 0.1	1.1 ± 0.3	0.26 ± 0.01	0.34	0.55 ± 0.01	0.56 ± 0.01	0.15 ± 0.02	0.155 ± 0.002
Yb	10.7 ± 0.2	12 ± 6	1.6 ± 0.3	1.7 ± 0.2	3.64 ± 0.03	3.64 ± 0.04	1.03 ± 0.12	0.98 ± 0.01
Lu	1.62 ± 0.03	1.9 ± 0.5	0.23 ± 0.01	0.27 ± 0.03	0.47 ± 0.03	0.54 ± 0.01	0.15 ± 0.02	0.143 ± 0.002

9 h and several hundreds mL of concentrated acids. The procedure described in [19] takes about 50 min and about 100 mL of acids.

#### 4. Conclusions

The technique for determination of REEs in rock samples based on sorption preconcentration on Pol-DETATA sorbent followed by flow-injection ICP-MS determination was developed. It was shown that the proposed technique can be applied to REE determination in final solutions after rock samples fusion with LMB. 5-sulfosalicylic acid as a masking reagent was used. Optimum conditions for preconcentration were found. Flow-injection sample introduction into the ICP-MS spectrometer was studied and optimized. Flow-injection volume of 50  $\mu\text{L}$  of eluate was found as a reasonable compromise between maximizing analysis sensitivity and minimizing the risk of corrosion of the interface. The accuracy of the developed technique is checked by the analysis of the reference materials of rock samples. For most REEs and used RMs the difference between the values obtained by the developed technique and the reference concentrations is less than 15%.

In contrast to the ion exchange or extraction chromatography techniques, which are widely used for REEs pre-concentration, the developed technique is faster, needs less reagents and provides lower LODs.

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