

The Analysis of Rare Earth Elements by Mass Spectrometry Method

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Abstract. To perform a comprehensive analysis of the whole periodic system with low limits of proof, the spark source mass spectrometer has been used.

After examination of lanthanoid containing geological samples based on qualitative analysis we can conclude, that rare earth determination makes more difficult by the presence of clusters with weight number equivalent to some of lanthanoid group elements. Such interference effects can be caused by barium oxide and carbide ions, which are often contained in geological materials.

On the other hand, the presence of double ionized atoms of lanthanoids is favourable, since it is a unique proof of the rare earth content.

Key words: rare earth elements, lanthanoid, mass spectrometry

In recent two decades, the interest in the rare earths has increased in both practical life as well as in scientific research. Their research is challenging and requires the use of appropriate analytical methods. From practical point of view the preferred methods are those based on the atom nucleus properties, as the mass spectroscopy and the neutron activation analysis (NAA). For general lanthanoid analyses the mass spectroscopy with spark ion source is applicable. In our research we solve two main problems: superposition of cluster ions and concentration dependence of analyse results.

According to the atomic mass number, various isotopes of lanthanoids are partially overlapping, but each of the elements has one or two isotopes which can not be confused with any other element or isotope with the identical mass number.

Some difficulties are caused merely by superposition of ion clusters, particularly oxides and carbides of barium (Cornides, 1982; Cornides, Gál, 1978). The occurrence of superposition is especially counteracting the analysis, if it overlaps the bands of mono and polyisotopic elements, which are being analyzed (Tab.1).

Tab.1 Ions caused superposition.

Mass number	Overlaped ion	Overlapping ion
146	Nd ⁺	¹³⁴ Ba ¹² C ⁺
147	Sm ⁺	¹³⁵ Ba ¹² C ⁺
151	Eu ⁺	¹³⁵ Ba ¹⁶ O ⁺
159	Tb ⁺	¹³⁵ Ba ¹² C ₂ ⁺
161	Dy ⁺	¹³⁷ Ba ¹² C ₂ ⁺
166	Er ⁺	¹³⁴ Ba ¹⁶ O ₂ ⁺
167	Er ⁺	¹³⁵ Ba ¹⁶ O ₂ ⁺
169	Tm ⁺	¹³⁷ Ba ¹⁶ O ₂ ⁺

The possible method for elimination of quantitative errors is the separation of bands (Dietre, Becker, 1982; Oláh, Cornides, 1986). To prevent superposition problems we utilized equipment with high differentiating ability (10000).

The second approach is uses the doubly ionized atoms. In the case of lanthanoids our measurements (based on the mass spectra of six different samples) showed that their occurrence is approximately the same as the occurrence of single ionized atoms (Tab. 2).

Tab. 2 The ratio of exposition for single- and double ionifed atoms.

Element	La	Ce	Pn	Nd	Sm	Eu	Gd
A ⁺ /A ²⁺	1.3	1.2	1.8	1.5	1.2	1.9	1.3
	0.3	0.6	0.5	0.7	0.6	0.9	0.4
	1.1	-	1.3	1.4	1.9	2.2	0.9
	0.8	-	1.1	1	1.1	0.9	0.5
	1.4	-	1.8	1.5	1.4	1.2	0.8
	1.1	-	1.1	1.1	1.3	1.2	0.9
average	1	0.9	1.25	1.2	1.25	1.4	0.8
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu
A ⁺ /A ²⁺	1.3	1.4	1.4	1.5	0.5	0.6	1.2
	0.4	0.8	0.9	0.8	1	0.9	0.6
	1.2	2.4	1.1	1.2	1.6	1.6	0.8
	0.8	0.8	0.8	1.3	0.8	1.1	0.8
	0.7	1.3	1.1	1.5	0.5	1.2	1.1
	1.4	1	0.9	1.2	0.8	1.4	1.2
average	0.95	1.3	1.05	1.25	1.1	1.15	0.95

The differences result from the fact that double ionization depends to the high extent on the spark plasma conditions.

For one sample 20 – 30% differences for each element have been found and the average of averages is 1.1. In the case of double ionized atoms the result is more convenient then in the case of single ionized atoms, where 3 30A⁺/A²⁺ values have been found. Since the ratio from the ion cluster was min 100, the superposition in the spectra of doubly ionized rare earths can be eliminated by using the isotopes with the odd atomic mass number. The effect of concentration on the results of analyze is still not resolved. To some extent our observations may be considered as model experiments.

The mass spectroscopy analysis was repeatedly measured for samples of rare earth concentrations 500, 50, 5 and 0.5 ppm. Indium was used as the internal standard. According to our results, the relative sensitivity changes with different concentrations, but differences in concentration area 5–500 ppm have not exceed 25%. The variations of sensibility with respect to concentration were not proportional.

The dispersion of the results is acceptable since it is known that the size of particles of rare earth in geologi-

cal formations is $\approx 10 \mu\text{m}$, and the homogeneity can not be increased according to ones needs.

Reference

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