DETERMINATION OF MICROQUANTITIES OF Fe, Mg, Ca, Cu, AND Pb IN LANTHANOID MINERALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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The decomposition of two lanthanoid minerals, *viz.* fluorocarbonate bastnasite and phosphate monazite, is described. Iron present in the solution obtained is removed on anion exchanger. Atomic absorption spectrophotometry was applied to the determination of the minor elements present in the mineral, *viz.* copper, lead, calcium and magnesium. The measurement conditions for the determination of these elements in microquantities were established by using model solutions, and the accuracy and precision of determination were evaluated.

The objective of this study was decomposition of two concentrates of two lanthanoid minerals, *viz.* bastnasite and monazite. Two methods have been suggested[1] for the decomposition of lanthanoid minerals – acidic and alkaline. Experience concerning decomposition of the bastnasite concentrate is, however, lacking. The aim of this work was to establish methodics for decomposition of bastnasite containing 75% lanthanoids based on experience gained with the decomposition of monazite, whose alkaline treatment has been studied at our Department[2,3], and to work out method for rapid analytical control of the lanthanoids obtained (determination of the iron, copper, calcium, lead, and magnesium impurities, which in the presence of high excess of lanthanoids has not been so far reported[4]).

EXPERIMENTAL

Chemicals and Apparatus

The concentrates used were from monazite (China) and bastnasite (locality Karunge, Burundi); their elemental composition was[5] as follows: Bastnasite: 75·03% Ln_2O_3, 18·76% CO_2, 6·21% F; monazite: 63·75% Ln_2O_3, 9·30% ThO_2, 26·95% P_2O_5 (Ln denotes lanthanoids). The reference solutions were prepared for Fe, Mg, and Cu from metals, for Ca from $CaCO_3$, and for Pb from $Pb(NO_3)_2$ (all chemicals were *p.a.* purity).

The stock solutions contained 1 mg of the element and 20 ml of concentrated hydrochloric acid in one litre. The solutions for use were prepared by dilution in 100 ml volumetric flask with addition of 5 ml of concentrated HCl. The acids used were *p.a.* purity. Lanthanum salt solution, concentration 5 mg La(III)/ml, was prepared from $La(NO_3)_3$ *p.a.* purity.

The atomic absorption measurements were carried out on a spectrophotometer AAS 1 (Zeiss, Jena) (acetylene–air) employing hollow cathode sources Narva and a 5 cm three-slot burner in the position of the longest absorption pathway for the most sensitive resonance lines.

Decomposition of the Bastnasite and Monazite Concentrates

The concentrates were ground to grain size below 0·10 mm; 1 g samples were applied. The bastnasite concentrate was decomposed with sulfuric acid at 100°C. The lanthanoid sulfates were further converted to low soluble hydroxides, which were dissolved in hot hydrochloric acid; thus lanthanoid chlorides were obtained in solution contaminated by iron present in the mineral.

In order to separate iron chlorides from lanthanoids in the form of $[MCl_6]^{3-}$, strongly basic anion exchanger Dowex 2X8 was used in 3M-HCl (ref.[2]) prior freed from iron on the same column. The flow rate was 0·5 ml/min. 5 ml fractions were collected on a fraction collector SF 62 and tested for the presence of iron and lanthanoids.

TABLE I

Conditions for Atomic Absorption Spectrophotometric Determination of Iron, Magnesium, Calcium, Lead and Copper

Element	λ, nm	Lamp current mA
Fe	248·4	7·5
Mg	285·2	2·5
Ca	422·7	7·5
Pb	217·0	5·0
Cu	324·75	5·0

TABLE II

Characteristic Parameters of the Resonance Lines of the Elements Examined

Element	λ, nm	Characteristic concentration μg/ml 1%	Concentration region recommended μg/ml
Fe	248·4	0·2	2—30
Mg	285·2	0·1	1—20
Ca	422·7	0·25	2·5—30
Pb	217·0	0·5	5—60
Cu	324·75	0·2	2—30

TABLE III

Precision of Determination in the Presence of High Excess of Lanthanum

Element	Addition of La, mg/ml			
	0		5	
	$\bar{A}^a$	s_r, %[b]	$\bar{A}$	s_r, %
	Element concentration 1 μg/ml			
Fe	0·049	1·16	0·045	1·2
Mg	0·46	1·22	0·41	2·65
Ca	0·082	3·4	0·078	3·05
Pb	0·105	2·85	0·097	2·85
Cu	0·039	1·7	0·037	2·5
	Element concentration 10 μg/ml			
Fe	0·415	2·3	0·406	2·56
Mg	1·470	2·2	1·329	3·2
Ca	0·810	1·8	0·760	2·4
Pb	1·091	1·9	1·079	2·35
Cu	0·360	2·6	0·359	2·6

[a] Average absorbance obtained from 10 measurements; [b] relative standard deviation.

TABLE IV

Accuracy of Determination in the Presence of High Excess (5 mg/ml) Lanthanum

Element	Concentration μg/ml	Average concentration found μg/ml	Relative error %
Fe	1	0·97	—3·0
	10	9·62	—3·8
Mg	0·1	0·09	—1·0
	1·0	0·96	—4·0
Ca	1	0·985	—1·5
	10	9·97	—3·0
Pb	1	0·98	—2·0
	10	9·98	—2·0
Cu	1	0·97	—3·0
	10	9·68	—3·2

Monazite was decomposed by applying the alkaline treatment with sodium hydroxide. The reaction product, containing lanthanoids, thorium, and iron hydroxides, was dissolved in hot hydrochloric acid, and thorium was separated as hydroxide by adding ammonia up to pH 4—4·5. Its absence was proved by the iodate test. The precipitate obtained was dissolved again in concentrated hydrochloric acid and the lanthanoid and iron chlorides created were separated analogously as in the case of bastnasite.

Determination of Iron and Trace Amounts of Mg, Ca, Pb, and Cu in Lanthanoid Chlorides

After the separation of iron from the lanthanoid chlorides on anion exchanger, the degree of separation was checked by subjecting the lanthanoid chlorides to atomic absorption spectrophotometric analysis[6]. The content of the trace quantities of Mg, Ca, Pb, and Cu was determined as well. The working conditions, found for model solutions, are given in Tables I—IV.

RESULTS

A modified procedure was suggested for the decomposition of bastnasite containing 75% lanthanoid oxides: it is heated to 100°C with sulfuric acid to remove fluorides, annealed at 650–750°C with the formation of lanthanoid sulfates soluble in water, which are conveniently converted to hydroxide form and further dissolved in hydrochloric acid to give chlorides, a form suitable for practical use. Iron present in the mineral was removed by separation on anion exchanger, on which both iron and lanthanoids are bonded in the form of $[MCl_6]^{3-}$ complexes ($M = Ln(III), Fe(III)$), but the lanthanoid chlorocomplexes decompose on the action of water, whereas iron remains bonded. The yields of the isolation of the lanthanoid mixture were 85·2% and 83·4% in the bastnasite and monazite concentrates, respectively, the purity of the products obtained was 99·94 and 99·93% from the two minerals, respectively.

The conditions for the atomic absorption spectrophotometric determination of Fe, Mg, Ca, Pb, and Cu in microquantities in the presence of excess lanthanoids,

TABLE V

Determination[a] of Elements in Samples of the Decomposed Concentrates

Element	Bastnasite ppm	Monazite ppm
Fe	1·1	1·9
Mg	1·5	1·1
Ca	0·7	1·1
Pb	1·7	2·1
Cu	1·1	0·9

[a] Average values from three parallel determinations.

found by using model solutions and statistically processed, are given in Table II. The precision of determination of the elements concerned was examined on model solutions in concentrations 1 and 20 μg/ml, both in the absence and in the presence of 5 mg La/ml. The relative standard deviation for ten replicates lay in an acceptable range of 2–3%. The accuracy of determination of the elements in question is affected by the presence of high excess of the main constituent, but the relative error did not exceed –4%.

The contents of the elements followed in the $LnCl_3$ solutions obtained from the samples are given in Table V.

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