

Determination of cerium valence state in alkali and alkali-earth borates

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Procedures have been elaborated for rapid, selective, and high-precise determination of Ce(IV) and total cerium content in the raw blends and single crystals of scintillators on the basis of cerium-doped alkali and rare-earth borates. Ce(IV) was determined by photometry after dissolution of the samples in sulfuric acid containing *o*-tolidine at room temperature.

Разработаны методики, позволяющие быстро, селективно и с высокой точностью определить содержание Ce(IV) и общего церия в шихте и монокристаллах сцинтилляторов на основе боратов щелочных и редкоземельных элементов, активированных церием. Ce(IV) определяли фотометрическим методом после растворения анализируемого образца в сернокислом растворе *o*-толидина при комнатной температуре.

Borate single crystals are materials of a wide application potential. Along with the well-known efficiency in the non-linear optics and acousto-electronics fields, those exhibit a radiation sensitivity. The scintillation characteristics of borate single crystals allow to consider those crystals as a material of good prospects in thermal neutron detection.

Cerium is among the most widely used activators improving the performance of numerous scintillators. The determination of cerium valence state in borate single crystals allows to elucidate the nature of radiation centers and thus to influence purposefully the scintillation efficiency of the matrix.

The high oxidizing ability of Ce(IV) ions ($E_0 = 1.44$ V in sulfuric acid medium) makes it possible, on the one hand, to determine it in the presence of other rare-earth elements; but, on the other hand, it makes it necessary to pay a special attention to the conservation of its valence state during the dissolution of a sample containing the component in micro-scale amounts.

The photometric methods of cerium determination in microgram amounts are

based most often on redox reactions. It is just the method based on *o*-tolidine oxidation that is the most suitable to determine Ce(IV) in the presence of Ce(III) in a much larger amount [1–3]. This method is sufficiently sensitive and selective to determine up to 3 $\mu\text{g/ml}$ Ce(IV). The methods making use of oxidation of some organic dyes, such as methyl orange or methyl red [4] and Rhodamine 6G [5] are very sensitive but exhibit worsened metrologic characteristics.

The correctness of Ce(IV) determination is influenced significantly by the sample preparation process. To dissolve the sample, sulfuric acid is used most often, because cerium sulfate solutions are the most stable. According to [1–3], after cerium precipitation and calcination, the precipitate is dissolved in hot concentrated sulfuric acid. It has been found, however, that the heating of Ce(IV) solution in sulfuric acid causes always a loss of the component to be analyzed due to its interaction with the organic reducing agents or sulfur dioxide present in sulfuric acid, while at room temperature, the cerium concentration is changed only slightly.

Table 1

Introduced Ce(IV), μg	Found Ce(IV), μg , after dissolution in H_2SO_4					
	s.p.		c.p.		a.p.	
	18 mole/l	4 mole/l	18 mole/l	4 mole/l	18 mole/l	4 mole/l
10	1.2	9.1	0	8.9	0	5.8
20	9.8	18.4	9.2	18.6	2.2	15.3

Our studies have shown that if the sample is dissolved in concentrated sulfuric acid of "special purity" (s.p.) or "chemically pure" (c.p.) grade even at room temperature, the cerium loss due to reduction amounts up to 10 μg (see Table 1). To reduce the loss of the component to be analyzed, the samples should be dissolved in diluted H_2SO_4 without heating. The "analytically pure" (a.p.) grade sulfuric acid is not advisable to be used at all. Moreover, as it is seen from Table 2, the sample should be dissolved in the presence of *o*-tolidine to exclude any loss of the ion to be determined. The correct and well-reproducible analytical results can be obtained only in the latter case.

To eliminate the hindering effect of Fe(III) ions that may be present in the solution, ortho-phosphoric acid was added that stabilizes also the solution color.

It is just H_2SO_4 concentration of 2 to 4 M that is an optimum for the dissolution of borates to be analyzed. At lower acid concentrations, the sample is dissolved slowly, while at high concentrations, the trivalent rare-earth sulfates are precipitated. The *o*-tolidine concentration variation within the 10^{-4} to 10^{-5} mole/l range does not affect the Ce(IV) determination result. The calibration plot is linear in the Ce(IV) concentration range of 0.08 to 1.0 $\mu\text{g}/\text{ml}$.

When determining Ce(IV) in borate single crystals, a weighed sample was dissolved in a mixture containing 0.2 M H_3PO_4 $2 \cdot 10^{-4}$ M *o*-tolidine and 2 M H_2SO_4 at room temperature. The solution volume was adjusted to 25 ml and centrifuged if being turbid. The light absorption at 440 nm was measured against a cerium-free control solution.

The elaborated Ce(IV) determination procedure was checked using the "introduced/found" technique with model mixtures containing cerium-free lithium-gadolinium borate and $\text{Ce}(\text{SO}_4)_2$ solution with concentration determined by iodometry. The checking results and metrological characteristics of the procedure are presented in Table 2.

Table 2

Introduced Ce(IV), μg	Dissolution without <i>o</i> -tolidine		Dissolution in the <i>o</i> -tolidine presence	
	Found Ce(IV), μg	s_r	Found Ce(IV), μg	s_r
5	3.3 \pm 0.4	0.10	4.9 \pm 0.4	0.06
10	8.4 \pm 0.3	0.03	10.0 \pm 0.4	0.03
15	13.6 \pm 0.6	0.04	15.2 \pm 0.3	0.02
20	17.9 \pm 0.4	0.02	20.3 \pm 0.4	0.02

Table 3

Sample No.	Photometry		Atomic emission spectrometry	
	Ce _{total} , %	s_r	Ce _{total} , %	s_r
1	0.034	0.08	0.035	0.1
2	0.029	0.06	0.022	0.1
3	0.011	0.10	0.010	0.1
4	0.017	0.05	0.015	0.1

The total Ce(III) and Ce(IV) content in samples of borate single crystals was determined also using *o*-tolidine after preliminary oxidation of Ce(III) with ammonium persulfate [7]. Ag(I) or Co(II) ions are used as catalysts to eliminate the incomplete cerium oxidation. Since *o*-tolidine was used in its soluble chloride form, Co(II) ions were preferred as the catalyst, although the normal potential of the Co(II)/Co(III) system ($E_0 = 1.84$ V) is somewhat lower as compared to that of Ag(I)/Ag(II) one ($E_0 = 1.98$ V). The cobalt ion concentration in the solution should not exceed $2 \cdot 10^{-5}$ mole/l.

The studies have shown that oxidation of Ce(III) in microgram amounts with persulfate ion should be carried out in 0.5 to 1.0 M H_2SO_4 in the presence of a catalyst under slight heating. The ammonium persulfate solutions lose the oxidative ability very fast due to decomposition, therefore, we used it in the crystalline form (0.5 g). The excess oxidant was removed by boiling for 10 min, the solution being preliminarily

Table 4

Li ₆ GdB ₆ O ₉ Sample No.	Ce _{total}		Ce(IV)	
	Found, %	s _r	Found, %	s _r
5	1.33±0.04	0.01	0.098±0.002	0.01
6	3.44±0.08	0.01	0.013±0.002	0.11
7	0.034±0.005	0.08	0.027±0.001	0.04
8	0.023±0.001	0.05	0.018±0.001	0.04
9	0.019±0.001	0.05	0.015±0.0004	0.02
10	0.012±0.002	0.10	0.009±0.0004	0.04

diluted to the double volume, since the complete persulfate decomposition requires a lower acidity than the Ce(III) oxidation.

The comparison of the total cerium determination results obtained using the photometric and atomic emission methods for lithium-gadolinium borate single crystals (Table 3) has evidenced the correctness of the procedure elaborated and the absence of any systematic error.

The total Ce content in raw blends for the borate single crystal growing is much higher than that in the crystals, since, according to the chemical analysis data, the cerium entering factor to the borate crystal lattice is as low as 0.08 to 0.1. The most convenient and sensitive method to determine cerium in amounts exceeding 0.1 % in the presence of other rare-earth elements is titration with hydroquinone in sulfuric acid medium in the presence of ferroine as indicator [8]. In acidic medium, hydroquinone reduces Ce(IV) fast and quantitatively at room temperature. The hydroquinone solution in sulfuric acid (1 to 3 %) is stable when being stored. It was standardized using a Ce(SO₄)₂ solution with concentration determined by iodometry. When determining the total cerium content in the raw blend, Ce(III) was preliminarily oxidized with ammonium persulfate and the excess

thereof was removed by boiling. The procedure was checked using the model mixtures consisting of the lithium-gadolinium borate raw blend and cerium oxide standardized by complexometry. The relative standard error of the individual result (s_r) is less than 0.11 at the determination of 1 to 5 % total Ce.

The analysis results for the raw blend and Li₆GdB₆O₉ single crystal samples using the elaborated procedures (for n = 5, P = 0.95) are presented in Table 4.

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Визначення валентного стану церію у лужних та рідкісноземельних боратах

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Розроблено методики, що дозволяють швидко, селективно та з високою точністю визначити вміст Ce(IV) і загального церію у шихті та монокристалах сцинтиляторів на основі боратів лужних та рідкісноземельних елементів активованих церієм. Ce(IV) визначали фотометричним методом після розчинення зразку, що аналізується, у сірчанокислому розчині о-толідину при кімнатній температурі.