

Control of cerium content in Li, Ca, or Sr fluoro-aluminates

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Cerium, aluminum, calcium and strontium complexing reactions with chlorophosphonazo III have been studied using spectrophotometry. The conditions have been selected for Ce determination in microgramm amounts in the presence of Al, Ca, and Sr in macroscale amounts. A procedure has been developed to determine cerium in cerium-doped lithium-calcium and lithium-strontium fluoro-aluminates at the standard deviation not exceeding 0.12.

Изучены реакции комплексообразования церия, алюминия, кальция и стронция с хлорфосфоназо III спектрофотометрическим методом. Выбраны условия определения микрограммовых количеств Ce в присутствии макроколичеств Al, Ca и Sr. Разработана методика определения церия во фторалюминатах лития-кальция и лития-стронция, активированных церием. Относительное стандартное отклонение не превышает 0,12.

LiCaAlF₆ and LiSrAlF₆ single crystals exhibit numerous advantages evidencing a good promise for application thereof in various scientific and engineering fields. The multi-component composition of those materials makes it possible to vary purposefully the properties thereof by introducing various activating additives. The rare-earth ions, in particular, cerium, are used most successfully as luminescent dopants in fluorides. The cerium-doped fluoro-aluminates take the laser properties [1]. It has been established that a similar emission in LiCaAlF₆:Ce and LiSrAlF₆:Ce may be caused not by photons but also by ionizing radiation [2]. The material has been found to be of promise as a fast scintillator for low-energy radiation. Moreover, those crystals possess the dosimetric properties and can be used in thermoluminescence dosimeters [3].

Chlorophosphonazo III (CP), 2,7-bis(4-chloro-2-phosphonobenzolazo)1,8-dihydroxynaphtalene-3,6-disulfonic acid, is known to be a reagent used to determine a number of elements, including rare-earth (RE) [4–7] and alkali-earth elements (AE) [8, 9]. In a

weakly acidic medium, chlorophosphonazo III forms 1:1 composition green-colored complexes ($K = 1.6 \cdot 10^{16}$ [10]), with cerium subgroup RE, blue-colored ones with Al and blue-green ones with AE.

We have selected chlorophosphonazo III as a reagent because its reaction with Ce(III) is characterized by a high sensitivity and contrast. The presence of $-\text{PO}_3\text{H}_2$ group in the CP molecule provides its ability to interact with cations in solutions having a higher acidity as compared to reagents containing other analytical groups, such as $-\text{AsO}_3\text{H}_2$ in arsenazo (III) [11]. Moreover, the contrast of the RE ion reactions with CP is higher than in those with the widely used arsenazo (III), that is due to Cl introduction into the *p*-position with respect to azo group in the reagent molecule [6]. The reagent selectivity is relatively low, therefore, when determining the microgramm amounts of RE in the presence of macroscale amounts of other ions, the component to be analyzed is usually separated, most often using extraction procedures. The separation methods

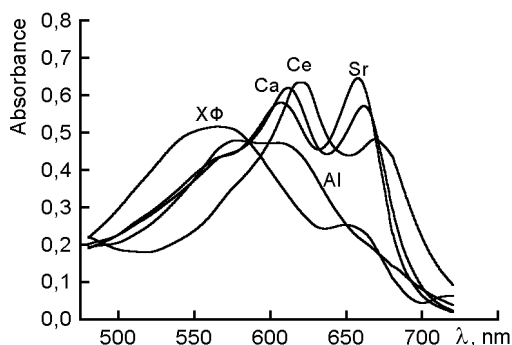


Fig. 1. Absorption spectra of chlorophosphonazo III and its complexes with Ce(III), Al, Ca, and Sr at pH 3.5. $c(\text{CP}) = 2 \cdot 10^{-5}$ mol/L, $c(\text{Ce}) = c(\text{Al}) = c(\text{Ca}) = c(\text{Sr}) = 8 \cdot 10^{-5}$ mol/L.

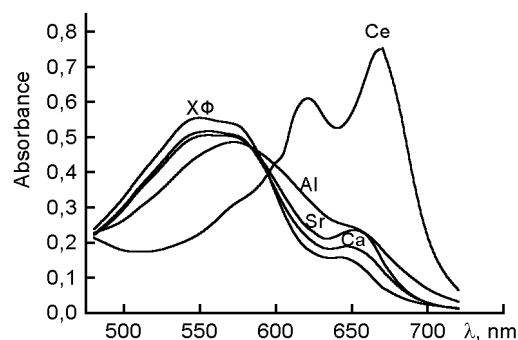


Fig. 2. Absorption spectra of chlorophosphonazo III and its complexes with Ce(III), Al, Ca, and Sr at pH 1.7. $c(\text{CP}) = 2 \cdot 10^{-5}$ mol/L, $c(\text{Ce}) = c(\text{Al}) = c(\text{Ca}) = c(\text{Sr}) = 8 \cdot 10^{-5}$ mol/L.

are laborious and time-consuming enough [5, 12].

The aim of this work is to study the complexing conditions of Ce(III), Al, Ca, and Sr with chlorophosphonazo III and to elaborate a simple and sensitive method for cerium determination in the presence of above-mentioned elements without preliminary separation.

The Ce-CP complex spectrum contains two maxima at 620 and 670 nm (see Fig. 1). The light absorption maxima of AE-CP complexes at $\text{pH} \geq 3$ are within the 610 to 660 nm range. For chlorophosphonazo III, $\lambda_{\text{max}} = 565$ nm, while in aluminum spectrum, there is a broad maximum at 580–605 nm.

It is seen in Fig. 2 that presents the absorption spectra of Ce(III), Al, Ca, and Sr complexes with chlorophosphonazo III at $\text{pH} = 1.7$, the increased acidity of the solution results in decomposition of Ca and Sr complex with chlorophosphonazo III and increased absorption intensity of the Ce(III)-CP complex at longer wavelengths. In this case, the sensitivity and selectivity of the reaction is enhanced considerably.

The study of the complex absorption dependences on the acidity has shown that at cerium determination, it is just the pH 1.2 to 1.4 interval that is optimum. Within that range, the Ce-CP absorption attains its maximum while the hindering effect of the matrix elements becomes minimized. Aluminum was masked by sulfosalicylic acid at 0.05 M concentration. However, our studies have shown that the hindering influence of the major components of Li-Ca and Li-Sr fluoro-aluminates is not eliminated completely, because the molar concen-

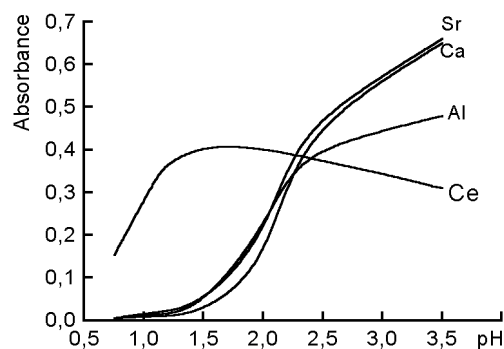


Fig. 3. Absorption of Ce, Al, Ca, and Sr complexes with chlorophosphonazo III as a function of pH. $c(\text{CP}) = 2.4 \cdot 10^{-6}$ mol/L, $c(\text{Ce}) = 1.43 \cdot 10^{-6}$ mol/L, $c(\text{Al}) = c(\text{Ca}) = c(\text{Sr}) = 6 \cdot 10^{-6}$ mol/L.

trations thereof in the solution to be analyzed exceeds that of the activating Ce by four orders of magnitude. Therefore, to provide the correct results, we have proposed to introduce the matrix elements into the reference solution when measuring the light absorption in the solution under analysis, thus eliminating the effect thereof on the cerium determination result. The reagent excess should be at a factor of 10 with respect to cerium concentration.

The light absorption in the solutions is in proportion with cerium concentration within the range of 0.08 to 0.8 $\mu\text{g/mL}$. When constructing the calibration plots, Al^{3+} , Ca^{2+} or Sr^{2+} should be introduced into the solutions at concentrations similar to the content of the elements in the samples to be studied. It has been established in experiment that the variation of the major component concentrations within 10 to

Table 1. Checking results for the Ce determination procedure ($n = 6$; $P = 0.95$)

Sample	Ce(III) introduced, μg	Ce(III) found, g	s_r
LiCaAlF ₆	5.0	4.8±0.2	0.06
	10.0	10.4±0.3	0.03
	15.0	15.3±0.3	0.03
LiSrAlF ₆	5.0	4.8±0.3	0.02
	10.0	10.4±0.2	0.02
	15.0	15.2±0.5	0.02

15 % (rel.) does not influence the cerium determination.

Basing on the studies, procedures have been elaborated for cerium determination in cerium doped Li–Ca and Li–Sr fluoro-aluminates. To solubilize the samples, perchloric acid is used. Fluoride that hinders Ce determination is removed by evaporation to dryness. The validity of procedures has been confirmed by metrological characteristics (Table 1). Table 2 presents the cerium determination results in LiCaAlF₆:Ce and LiSrAlF₆:Ce samples. The relative standard deviation does not exceed 0.12.

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Table 2. Ce determination results in cerium-doped fluoro-aluminate samples ($n = 6$; $P = 0.95$)

Sample	Ce total found, p.c. (mass)	s_r
LiCaAlF ₆ :Ca No.1	(1.33±0.12)·10 ⁻²	0.10
LiCaAlF ₆ :Ca No.2	(1.27±0.14)·10 ⁻²	0.12
LiSrAlF ₆ :Ca	(2.24±0.08)·10 ⁻²	0.08

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Контроль вмісту церію у флуоралюмінатах Li, Ca та Sr

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Вивчено реакції комплексоутворення церію, алюмінію, кальцію та стронцію з хлорфосфозано III спектрофотометричним методом. Обрано умови визначення мікрограмових кількостей Ce у присутності макрокількостей Al, Ca та Sr. Розроблено методику визначення церію у флуоралюмінатах літію-кальцію та літію-стронцію, активованих церієм. Відносне стандартне відхилення не перевищує 0,12.