

Determination of cerium valent state in solution of CeO_{2-x} nanoparticles

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Received October 25, 2017

Determination of different valence forms cerium in solution of CeO_{2-x} nanoparticles was performed using spectrophotometric method. Ce(IV) was determined from the reaction of *o*-tolidine oxidation in sulfuric-acid medium. The total cerium concentration was determined after reducing Ce(IV) by sodium oxalate. In the capacity of reagent, there was used chlorophosphonazo III which formed the complex of the composition of 1:1 with cerium(III). The influence of sodium citrate, the stabilizer of the nanoparticles, in cerium determination, was studied. There were developed reliable and sensitive techniques for determination of Ce(IV) and the total cerium mass concentrations in the solution of CeO_{2-x} nanoparticles. Relative standard deviations at of the cerium determination were found not to exceed 0.05.

Keywords: cerium(III), cerium(IV), *o*-tolidine, chlorophosphonazo III, nanoparticles CeO_{2-x} , spectrophotometry.

Проведены исследования по определению церия различного валентного состояния в растворе наночастиц CeO_{2-x} спектрофотометрическим методом. Ce(IV) определяли по реакции окисления *o*-толидина в сернокислой среде. Общую концентрацию церия определяли в виде трехвалентного церия после восстановления Ce(IV) оксалатом натрия. В качестве реагента использовали хлорфосфоназо III, образующий с церием(III) комплекс состава 1:1. Изучено влияние на определение церия стабилизатора наночастиц — цитрата натрия. Разработаны надежные чувствительные методики для определения массовой концентрации Ce(IV) и общей концентрации церия в растворе наночастиц CeO_{2-x} . Относительные стандартные отклонения при определении церия не превышают 0.05.

Визначення валентного стану церію у розчині наночастинок CeO_{2-x} . O.V.Гайдук.

Проведено дослідження з визначення церію різного валентного стану у розчині наночастинок CeO_{2-x} спектрофотометричним методом. Ce(IV) визначали за реакцією окиснення *o*-толідіну в сірчаноокислому середовищі. Сумарну концентрацію церію визначали у вигляді тривалентного церію після відновлення Ce(IV) оксалатом натрію. В якості реагенту використовували хлорфосфоназо III, який утворює з церієм(III) комплекс складу 1:1. Вивчено вплив на визначення церію стабілізатора наночастинок — цитрату натрію. Розроблено надійні чутливі методики для визначення масових концентрацій Ce(IV) та загального церію у розчині наночастинок CeO_{2-x} . Відносні стандартні відхилення при визначенні церію не перевищують 0.05.

1. Introduction

Recent years are characterized by considerable rise in investigations and production of nanoparticles to be widely used in various fields of materials science and biomedicine. Change in physical

and chemical properties of substances during their transition into the nanocrystalline state is a subject of close attention of researchers. Unusual properties of the nanoparticles were found to depend on their individual features, size and shape [1–3].

Nanocrystalline cerium dioxide is one of the most promising materials for biomedicine. Unique redox activity of this compound is defined by the presence of two stable degrees of oxidation (Ce^{3+} and Ce^{4+}) and low energy of their formation. Diminution of the size of CeO_{2-x} nanoparticles raises the oxygen non-stoichiometry of cerium and, consequently, the concentration of $\text{Ce}(\text{III})$ ions. The change in the oxygen non-stoichiometry and partial reduction of cerium in the surface layer influence the electronic and electrophysical properties of the nanodisperse cerium dioxide which define its high biological activity and antioxidative properties [4, 5]. Prospects of the use of CeO_{2-x} nanoparticles in biological systems depend on two major factors: high oxygen non-stoichiometry and low toxicity. As recently established, sols of the nanocrystalline cerium dioxide are able to protect living organisms from free radicals. Thereat, biological activity of the sols is defined by the ratio of the cerium valent forms [6–8].

Qualitative determination of different valence forms of elements is most often realized by spectrophotometric methods due to their simplicity, reliability and selectivity. As a rule, microgram quantities of cerium (IV) are determined by means of redox reactions, in particular, by the methods based on oxidation of triphenylmethane dyes with cerium(IV) followed by formation of the colourless reaction products [9]. Though such methods are selective, their sensitivity is not sufficient.

Stoianov et al. [10] determined $\text{Ce}(\text{IV})$ in nanodisperse CeO_2 powders from absorption of the phosphate complex at 320 nm. This method has a low sensitivity and is suitable for the analysis of those materials which contain cerium(IV) in quantities of a few percent. For photometric determination of cerium(III) the authors used cerium(III) oxidation with permanganate ion. The content of $\text{Ce}(\text{III})$ was determined as weakening of the KMnO_4 color. This method is not applicable to $\text{Ce}(\text{III})$ determination in the nanodisperse sols, since the latter contain organic acids as stabilizers which are capable of reacting with KMnO_4 .

While analyzing the nanodisperse cerium sols the authors of [10] determined $\text{Ce}(\text{IV})$ from the reaction of Methanyl Yellow oxidation by cerium(IV) ion which occurs with a weakening of the indicator solution colour. The cerium total content was determined by complexometric titration with Arsenazo

III as an indicator. Before the titration $\text{Ce}(\text{IV})$ was reduced by hydrogen peroxide, and the solution was concentrated to wet salts. For this method the quantity of the analyzed sample is to be a large.

Earlier for determination of $\text{Ce}(\text{IV})$ in various functional materials we proposed the method based on oxidation of *o*-tolidine [11, 12]. This simple, sensitive and selective method makes it possible to determine $\text{Ce}(\text{IV})$ in quantities up to 0.05 $\mu\text{g}/\text{ml}$.

The present work is devoted to development of reliable methods for determination of cerium valent forms in the nanodisperse CeO_{2-x} sols.

2. Experimental

All utilized reagents were analytically pure. All solutions were prepared on the base of deionized water. We used the solutions of *o*-tolidine chloride and chlorophosphonazo III with concentrations of $1 \cdot 10^{-3}$ mol/l. Calibration graphs were constructed using $\text{Ce}(\text{SO}_4)_2$ and CeCl_3 . Absorbance measurements were made with a spectrophotometer SF-2000. The value of pH was measured by ionometer I-160.

Colloidal solution of CeO_{2-x} nanoparticles was prepared as a model system to study the unique antioxidant properties of nanocerium [13]. The nanoparticles of a diameter of 1.9 ± 0.3 nm were stabilized by sodium citrate with the molar ratio of $\text{CeO}_2/\text{NaCitr} = 1:1$. The obtained hydrosol which was then stored in sealed ampoules remained stable for more than 6 months. The ultra-microheterogeneous dispersion in water was found to correspond to a typical hydrophobic colloidal system with negatively charged surface of the particles.

3. Results and discussion

3.1 Determination of cerium(IV) concentration

The high oxidative ability of $\text{Ce}(\text{IV})$ ions ($E_0 = 1.44$ B in sulfuric-acid medium) [14] causes the need to pay particular attention to conservation of the cerium valence state in the solution. For this purpose we used sulfuric acid, since sulphuric-acid solutions of cerium(IV) are the most stable [14]. An ampoule containing the colloidal solution was unsealed directly before the procedure of $\text{Ce}(\text{IV})$ determination. The solution was diluted by water with addition of sulfuric acid to obtain the 1 mol/l concentration which was necessary for retaining the valent state of cerium(IV). For determination

Table 1. Effect of sodium citrate concentration on Ce(IV) determination with *o*-tolidine

$c(\text{Citr})$, mol/l	Introduced Ce(IV), μg	Found Ce(IV), μg
$3 \cdot 10^{-5}$	4.0	3.97
$6 \cdot 10^{-5}$	4.0	4.13
$1 \cdot 10^{-4}$	4.0	4.32
	7.0	7.03
	10.0	10.16
$2 \cdot 10^{-4}$	4.0	3.82

of cerium(IV) in the nanodisperse CeO_{2-x} sols we used the reaction of *o*-tolidine oxidation with formation of a yellow product which had an absorption maximum at 440 nm. The procedure of the reagents addition is of great importance: the analyzed solution should be added to sulphuric-acid *o*-tolidine solution. The concentration of sulfuric acid in the solution equal to 0.35 mol/l was found to be optimal. As is known, in acidic medium the cerium(IV) can interact with citric acid that reduces it valence to Ce(III) [15]. We have found that sodium citrate does not interfere in cerium determination with *o*-tolidine, if its concentration in the solution is not higher than $4 \cdot 10^{-5}$ mol/l (Table 1).

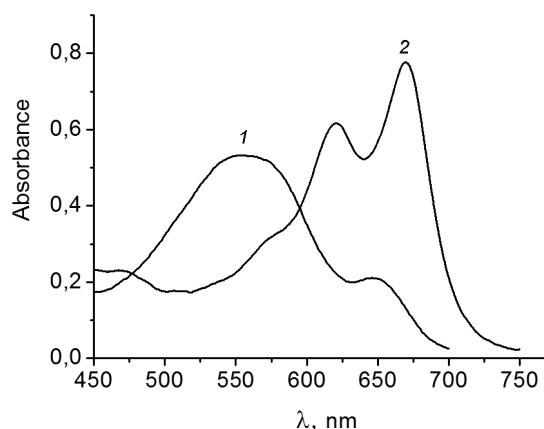
The processes of dissolution of CeO_{2-x} colloidal particles and formation of the true solution are somewhat slow, therefore the optical density of the solution should be measured 30–35 min following preparation of the solution, when the said value is stabilized. Changes in the concentration of *o*-tolidine in $1 \cdot 10^{-5}$ – $1 \cdot 10^{-4}$ mol/l interval do not influence the results of Ce(IV) determination. The absorption of the solution is proportional to the concentration of Ce(IV) in 0.06–0.5 $\mu\text{g}/\text{ml}$ interval. The testing results of the proposed technique are presented in Table 2.

3.2 Determination of total cerium concentration (Ce_{tot})

As a rule, the total cerium content is determined after Ce(III) oxidation to Ce(IV), most often it is realized using ammonium persulphate [14]. However, the presence of citrate impedes oxidation of Ce(III). We preferred to determine Ce_{tot} in the form of trivalent cerium. Ce(IV) was reduced by sodium oxalate, since the oxalate ion is provided its fast and effective reduction [14, 15]. Investi-

Table 2. Testing results of techniques for determination of Ce(IV) and Ce_{tot} mass concentrations in solution of CeO_{2-x} nanoparticles ($n = 3-4$; $P = 0.95$)

Determined ion	Solution aliquot, ml	Found, mg/ml	s_r
Ce(IV)	1.0	0.20 ± 0.02	0.04
	1.5	0.20 ± 0.02	0.05
Ce_{tot}	0.4	0.70 ± 0.03	0.02
	0.8	0.71 ± 0.01	0.01

Fig. 1. Absorption spectra of chlorophosphonazo III (1) and Ce(III)-CP complex (2); $c(\text{Ce}) = 4 \cdot 10^{-5}$ mol/l, $c(\text{CP}) = 2 \cdot 10^{-5}$ mol/l.

gations have shown that for complete Ce(IV) reduction in the solution of CeO_{2-x} nanoparticles the 10 % excess of oxalate is sufficient. Sodium citrate contained in the solution does not hamper the reduction, but promotes it.

As a reagent we used chlorophosphonazo III (CP) which reaction of interaction with Ce(III) is characterized by the high sensitivity and contrast range [16–19]. In slightly acidic medium the chlorophosphonazo III and Ce(III) form the complex of 1:1 composition (Fig. 1). The optical density of the solutions of this complex was measured at 670 nm, in the region of the maximal sensitivity of cerium determination.

There was studied the dependence of the absorption of Ce(III)-CP complex solutions on the solution acidity (Fig. 2). As established experimentally, the complexation reaction was the most sensitive at pH 1.3–1.6 and the optimal concentration of chlorophosphonazo III was equal to $1 \cdot 10^{-5}$ mol/l. Sodium citrate did not interfere the interaction between Ce(III) and CP. A linear dependence of the optical density of the solu-

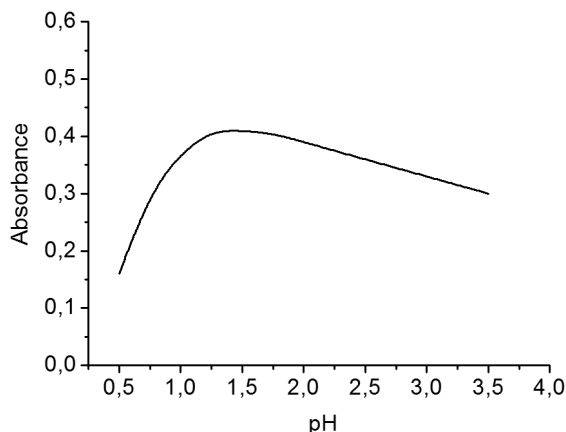


Fig. 2. Dependence of absorbance of Ce(III) — chlorophosphonazo III complex solutions on pH; $c(\text{Ce}^{3+}) = 1.43 \cdot 10^{-6}$ mol/l.

tions on Ce(III) concentration was observed in 0.08–0.6 $\mu\text{g}/\text{ml}$ interval.

The results of the performed researches were used in the development of spectrophotometric determination techniques of mass concentrations of Ce(IV) and Ce_{tot} in the solution of the CeO_{2-x} nanoparticles. The Ce(III) concentration was determined by calculations. Correctness of these techniques was confirmed by the method of variation of the solution aliquots. The results of testing the techniques and their metrological characteristics presented in Table 2 testify to the absence of significant systematic error.

4. Conclusions

The performed researches made it possible to develop the reliable and sensitive spectrophotometric techniques for determination of different valence forms of cerium in the solution of CeO_{2-x} nanoparticles. Relative standard deviations at the determination of 0.1–0.3 mg/ml of Ce(IV) and 0.5–1.0 mg/ml of Ce_{tot} in the colloidal solution did not exceed 0.05.

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