# DETERMINING CERIUM IN A MIXTURE OF RARE-EARTH ELEMENTS BY FILM POLAROGRAPHIC ANALYSIS

(UDC 543)

Kh. Z. Brainina and T. A. Rygailo

Donets Branch, All-Union Scientific Research Institute of Chemical Reagents and Extra-Pure Chemicals
Translated from Zavodskaya Laboratoriya, Vol. 31, No. 1, pp. 28-30, January, 1965

The method consists of concentrating the element to be determined in the form of cerium hydroxide (IV) on a graphite electrode in an acetate buffer solution with subsequent electrodissolution of the deposit. The maximum value of the cathode current is proportional to the Ce(III) ion concentration in the solution. The sensitivity of determination is $4 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$%.

The methods of polarographic determination of cerium in a mixture of rare-earth elements in [1] are based on cerium oxidation to tetravalent cerium and recording of the cathode wave, which is observed at the very beginning of the polarogram. Since Ce(IV) is easily hydrolyzed, it is recommended that oxidation be carried out in an acid medium—which is not always convenient. The wave of reduction of tetravalent cerium in a sulfuric acid medium can be used to determine comparatively large amounts of cerium within a narrow range of concentrations [2]. In addition, reading of the limiting current according to a wave that does not have an initial area is very inaccurate. The difference between the chemical properties of Ce(III) and Ce(IV) can be used for its polarographic determination by concentrating the element on an electrode [3].

In the present work, to determine admixtures of cerium in a mixture of rare-earth elements, it is suggested that the ability of Ce(IV) ions to undergo hydrolysis in an acetate buffer solution in which the salts of the other rare-earth elements and Ce(III) are fairly easily dissolved be used.

With anode polarization of the electrode, in such a solution trivalent cerium is oxidized, and, as a result of hydrolysis, a deposit can then be subjected to electrodissolution with a linearly varying electrode potential. In this case, the characteristic polarization curve with a maximum whose value is proportional to the Ce(III) ion concentration in the solution under definite conditions must be observed [4].

A model 7—77-4/B (Hungary) recording polarograph was used in the work. The indicator electrode was a graphite electrode (class V-3 graphite) whose lateral surface was insulated with ED-6 epoxy resin with polyethylenepolyamine. A saturated calomel electrode was used as the auxiliary electrode. The designs of the electrolyzer and the graphite electrode were described earlier in [5]. Oxygen was removed from the solution with a nitrogen stream.

The polarographic base was an acetate buffer solution (0.1 N $NaCH_3COO$ + 0.1 N $CH_3COOH$) and a sodium acetate solution containing 50 g/liter La, 50 g/liter (Nd + Pr) and 10 g/liter Y (pH = 4 to 5). The latter solution was purified beforehand of the cerium admixture contained in the rare-earth element salts. For this, a few drops of hydrogen peroxide were added to the solution. The solution was boiled until the excess oxidizer was decomposed, and the precipitated cerium hydroxide was filtered out. 25% $(NH_4)_2S_2O_8$ is sometimes used as an oxidizer.

The limiting current of cerium (III) ions is reached at a potential of 0.9 V. Therefore, the element can be concentrated in the form of its hydroxide at any more positive electrode potential. The effect of the electrode potential during the concentration cycle on the form of the polarization curves is illustrated by the data in Fig. 1.

The optimum electrode potential is + 1.0 V (curve 2), since accumulation of a determinable amount of the substance does not occur at a lower potential (curve 1). Concentration at a more positive potential is accompanied by distortion of the cathode polarization curve (curves 3 and 4), which is probably due to the accumulation of oxygen in the electrode.

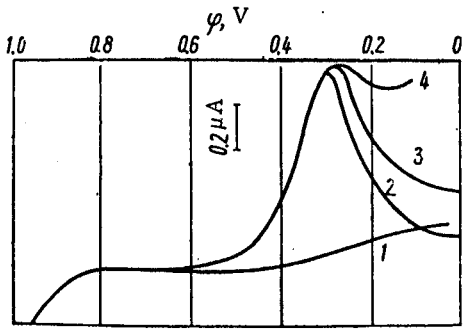


Fig. 1. Polarization curves of reduction of cerium hydroxide (IV) electrodeposited from a solution containing $2 \cdot 10^{-4}$ M Ce(IV) during 1 min at electrode potentials of 0.8, 1.0, 1.3, and 1.6 V (curves 1 through 4, respectively).

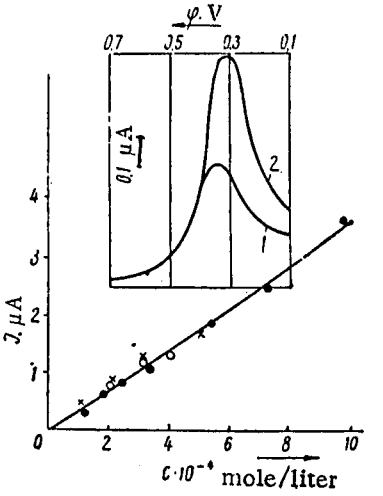


Fig. 2. Maximum current of electrodissolution of cerium hydroxide (IV) versus Ce(III) ion concentration in solution of 0.1 N $CH_3COOH$ + 0.1 N $CH_3COONa$: 1) $1 \cdot 10^{-5}$ M Ce(III) (crosses); 2) $1 \cdot 10^{-4}$ M Ce(III) (points).

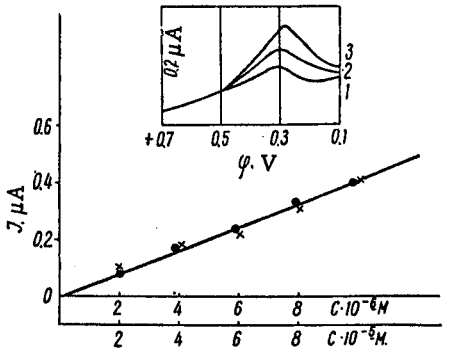


Fig. 3. Polarization curves of electrodissolution of cerium hydroxide and the relationship between the maximum electrodissolution current and the cerium ion concentration: 1) 0.1 N $CH_3COOH$ + 0.1 N $CH_2COONa$ + Ce(III) (points); 2) 50 g/liter La (III) + 50 g/liter (Nd (III) + Pr (III)) + Ce(III) (crosses); 3) solution of rare-earth elements + Ce(IV).

Results of Cerium Determination in Solution of Salts of Rare-Earth Elements, μg/20 ml

| Introduced | Found | Introduced | Found |
|---|---|---|---|
| 5 | 4; 5; 5 | 110 | 115; 110; 105 |
| 10 | 9; 11; 10 | 220 | 225; 215; |
| 15 | 14; 16; 15; 17 | | 220; 240 |
| 20 | 19; 20; 20 | 280 | 285; 280; 265 |
| 56 | 55; 55; 60 | 560 | 580; 520 |
| | | 840 | 825; 845; |
| | | | 865; 835 |

The data in Fig. 2 illustrate the dependence of the form of the polarization curves and of the maximum electrodissolution current for cerium hydroxide (IV) upon the Ce(III) ion concentration in the solution. This dependence is directly proportional over a wide range of concentrations. An analogous relationship between the Ce(III) ion concentration and the maximum electrodissolution current of cerium hydroxide (IV) is observed even in the presence of a large amount of other rare-earth elements (Fig. 3).

A weighed portion of the substance* to be analyzed was dissolved in nitric or hydrochloric acid, a few drops of hydrogen peroxide were added, and the solution was boiled until the reducer was completely decomposed. The cooled solution was placed in an electrolyzer, the dissolved oxygen was removed by a stream of nitrogen, the pH of the solution was brought up to 4.5 by adding sodium acetate, and then it was electrolyzed at a potential of + 1.0 V for 1 to 10 min. The polarization curve of the electrodissolution of the cerium hydroxide (IV) formed with a linearly varying potential was recorded. The cerium ion concentration was determined according to the value of the maximum cathode current.

*In analysis of the salts, they were dissolved in water and the solution was acidified to pH = 0–1.

The results of the cerium determination are given in the table. The maximum deviation of the found value from the average value is 13%.

The sensitivity of determination is $3 \cdot 10^{-4}$% Ce for a 2-g weighed portion of the metal dissolved in 20 ml.

## LITERATURE CITED


1. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, Polarographic Analysis, Goskhimizdat (1959).
2. P. G. Desideri, J. Electroanal. Chem., 2, 1, 39 (1961).
3. Kh. Z. Brainina, Zhurnal analiticheskoi khimii, 18, 10, 1168 (1963).
4. Kh. Z. Brainina, Doklady Akad. Nauk SSSR, 154, 3, 655 (1964).
5. Collection: "Methods of Analysis of Chemical Reagents and Preparations," IREA, Nos. 5-6, (1963), pp. 110 and 129.


---



---