

RADIOCHEMICAL DETERMINATION OF TRACES OF CERIUM BY ISOTOPIC EXCHANGE IN ORGANIC PHASE

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Received March 30th, 1971

A new radiochemical method for selective determination of traces of cerium has been developed. The method is based on isotopic exchange between cerium(III) and cerium(IV) chelates with di(2-ethylhexyl)phosphoric acid in toluene.

Two-phase isotopic exchange between silver ions in aqueous phase and silver 110m dithizonate in tetrachloromethane was applied for the determination of traces of silver by Pierce¹. Handley² used similar principle for the determination of traces of mercury. However, applicability of the two-phase isotopic exchange for analytical purposes is limited by slow kinetics and relatively low selectivity. All metals which can substitute the studied metal in chelate compound interfere. In our recent communications³⁻⁶ the homogeneous isotopic exchange between various complexes of the studied metal was investigated in organic phase. It was found that in these systems the isotopic exchange is very fast. Equilibrium was reached in a few seconds or minutes even for the concentrations of complexes in the order of magnitude of 10⁻⁶M. Homogeneous isotopic exchange was utilized in the determination of traces of bismuth³, arsenic⁴, antimony⁵ and thallium⁶.

In the present paper the isotopic exchange between chelates of cerium(III) and (IV) with di(2-ethylhexyl)phosphoric acid was studied in toluene in order to develop a selective method for determination of cerium.

THEORETICAL

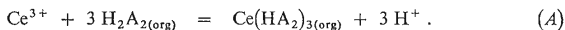
The principle of this method consists in the extraction of an unknown amount (x) of metal M into organic phase in the form of a complex MA_N with a known yield of extraction E (in %). A standard solution of complex MX_N in organic solvent, which contains a known amount (y) of metal M, is added to the separated extract. If only one of the complexes is originally labelled by radioisotope of M then, after reaching isotopic equilibrium, the specific activities of both complexes are equal:

$$100A_1/xE = A_2/y, \quad (1)$$

where A_1 and A_2 are relative activities of metal M in complexes MA_N and MX_N , resp. After the separation of both complexes the activities A_1 and A_2 can be determined and the unknown amount (x) of the metal M in the analysed sample can be calculated. The precondition for utilizing the isotopic exchange in the organic phase for analytical purposes is the possibility of separating both complexes quantitatively. The quantitative separation occurs only in the case of significant

difference of the extraction constants MA_N and MX_N . This is fulfilled *e.g.* in the case of metal chelates with organic reagents and halo complexes of the same metal³⁻⁵. Homogeneous isotopic exchange between chelates of the same metal in different valent states can be used for developing a very selective method for determination of the metal. In this case neither the excess of the organic reagent nor the presence of chelates of other metals interfere.

To determine an unknown amount (x) of cerium(III) a known amount (m) of radioactive cerium with the activity A is added to the analysed sample. The resulting mixture is extracted with the excess of di(2-ethylhexyl)phosphoric acid (present as a dimer H_2A_2 in organic phase)⁷ according to reaction



The yield of extraction $E = 100A'/A$ can be determined by measuring the activity of the separated organic phase (A'). After the addition of a known amount of inactive cerium (y) in the form of a chelate $Ce(HA_2)_4$, the isotopic exchange occurs in the organic phase and according to relation (1):

$$A_1 A / A' (x + m) = A_2 / y , \quad (2)$$

where A_1 and A_2 denote cerium activities in the complexes $Ce(HA_2)_3$ and $Ce(HA_2)_4$, resp. For measuring both activities A_1 and A_2 it is necessary to separate both chelates. The best way how to do it is to reextract cerium(III) into aqueous phase in such conditions under which cerium(IV) remains in the organic phase, for the extraction constant of cerium(IV) chelates is significantly higher than that of cerium(III) chelates⁷. The amount of cerium in the analysed sample can be calculated according to relation

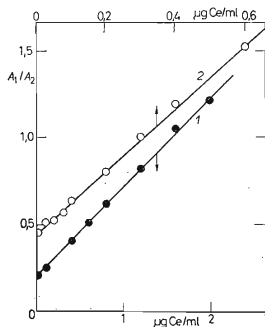


FIG. 1
Calibration Curve for Determination of Cerium(III)
Amount of cerium(IV) added y 8 μ g (1)
and y 4 μ g (2).

$$x = yA_1A/A_2(A_1 + A_2) - m, \quad (3)$$

considering $A' = A_1 + A_2$. In the case of quantitative extraction of cerium(III) from the sample $A/(A_1 + A_2) = 1$ and equation (3) simplifies. From the practical point of view it is more convenient to determine cerium content by means of calibration curve $x = f[A_1A/A_2(A_1 + A_2)]$ or $x = f(A_1/A_2)$. In these cases the exactly same amounts y and m have to be added to all samples.

EXPERIMENTAL

Reagents and Apparatus. 5% solution of di(2-ethylhexyl)phosphoric acid (H_2A_2) (Lachema, Brno) in toluene was shaken with 0.5M- HNO_3 and filtered. As an isotope the solution of ^{144}Ce ($T_{1/2} = 284$ days) + ^{144}Pr ($T_{1/2} = 17.3$ min) (Institute for Research Development and Production of Radioisotopes, Prague) with high specific activity was used in 0.001M- H_2SO_4 . The chelate of cerium(IV) with di-(2-ethylhexyl)phosphoric acid, $Ce(HA_2)_4$, was prepared by 1 min extraction of 1 ml 0.001–0.002M-Ce (IV) sulphate in 0.25M- H_2SO_4 with 20 ml of the reagent solution. The extract was shaken before use with the same volume of 0.5- HNO_3 and filtered.

Cerium extraction. It was found that cerium(III) can be quantitatively extracted at pH higher than 2.5. However only 5% and less than 0.1% of cerium(III) is extracted from 0.1M and 0.5M- HNO_3 , resp., for the equilibrium constant of reaction (A) is given by $\log K - 0.7$. In these conditions chelate $Ce(HA_2)_4$ remains nearly quantitatively in the organic phase. Further kinetics of isotopic exchange was studied in the cases when chelate of cerium(III) or (IV) was alternately labelled. It was found that in the concentration range studied, the isotopic equilibrium was reached in a few minutes. On the basis of these experiments the following working procedure was developed.

Procedure. 0.5 ml of solution of radioactive ^{144}Ce (activity A) was added to 5 ml of analysed solution in test tube with ground stopper. Acidity was adjusted to pH 2.5 and solution was extracted with 1.50 ml of the reagent in toluene for 2 min. After both phases were separated, 1.0 ml of extract was transferred into another test tube with ground stopper, 0.5 ml of solution of $Ce(HA_2)_4$ chelate in toluene was added and the mixture was thoroughly mixed. After 5–10 min 1.5 ml of 0.5M- HNO_3 was added into test tube and the mixture was shaken for 30 s. From both aqueous and organic phases 0.3 ml of solutions were pipetted into small aluminum plates. The solutions were evaporated by drying lamp. After 3 h *i.e.* after the radioactive equilibrium had been reached between ^{144}Ce and ^{144}Pr , the activities A_1 and A_2 were determined by Geiger-Müller counting tube.

RESULTS

Samples with a known content (x) of cerium(III) (0.5–10 μg) were analysed according to the above mentioned procedure. Amount of cerium(IV) (y) which was added to all samples in the form of $Ce(HA_2)_4$ chelate equaled to 8 μg . From the measured values of activities of both organic and aqueous phases, A_1 and A_2 , resp., the calibration curve $A_1/A_2 = f(x)$ (Fig. 1, curve 1) was constructed. The samples with lower content of cerium(III) (0.1–3 μg) were treated in a similar way. In this case the amount of added cerium(IV) was reduced to 4 μg (Fig. 1, curve 2). Applicability

of the method was verified for determination of cerium(III) (3.0 µg) in synthetic samples containing a great number of other metals. The presence of 30–100 µg of Be, Mg, Ca, Sr, Ba, Sc, La, Eu, Zr, Th, Cr(III), Mo(VI), W(VI), U(VI), Mn(II), Mn(VII), Fe(III), Co, Ni, Pd, Au(III), Cu, Ag, Zn, Cd, Hg, Al, Ga, Tl(III), Ge, Sn(II), Pb, Bi, As(III), Sb, Se(IV) does not interfere. The mean deviation of the individual determination was better than 3% rel.

The developed method of determination of traces of cerium is simple, fast and highly selective. It enables determination of microgram amounts of cerium even in the presence of other lanthanides. The method does not require oxidation of cerium(III) into cerium(IV), which is rather difficult for trace concentrations. The addition of ^{144}Ce to the sample before the extraction of $\text{Ce}(\text{HA}_2)_3$ chelate enables an easy determination of the yield of the extraction. Hence the isolation of cerium need not be quantitative.

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Translated by V. Hančil,