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FLUORIMETRIC DETERMINATION OF CERIUM WITH PARACETAMOL

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Summary—A simple, sensitive and selective method for determination of cerium(IV), based on the oxidative reaction between cerium(IV) and paracetamol, has been developed. The fluorescent species is an oxidation product of paracetamol and has excitation and emission maxima at 265 and 360 nm, respectively. The fluorescent intensity of the system is linear over the range 2.0×10^{-7}–$8.0 \times 10^{-6}M$ Ce(IV). The method has been applied in the determination of Ce(IV) in synthetic mixtures and ores with good accuracy being achieved.

Addition of small amounts of the rare-earth element, cerium, to steel significantly modified its properties. Therefore, the accurate determination of cerium at trace level is important industrially. Colorimetric methods allow the determination of cerium[1-4] also fluorimetric methods have been reported for the determination of Ce[5-9], and kinetic fluorimetric methods are available.[10-11] Inductively coupled plasma atomic-emission spectrometry has been used for the determination of Ce.[12-13]

This paper describes a fluorimetric procedure for the determination of cerium(IV), based on the reaction between Ce(IV) and paracetamol in sulphuric acid medium. The results of the extensive interference study and the application of the method to the determination of Ce(IV) in synthetic mixtures and ores are reported. The method possesses distinct advantages over the existing methods, viz. spectrofluorimetric methods,[8-9] with respect to sensitivity, selectivity, range of determination, simplicity, and speed.

EXPERIMENTAL

Apparatus and reagents

An RF-540 spectrofluorometer (Shimadzu, Kyoto, Japan) was used.

A stock solution of $Ce(So_4)_2 \cdot 4H_2O$ ($1.0 \times 10^{-2}M$) was prepared in $1M$ sulphuric acid.

Paracetamol stock solution ($0.01M$) was prepared by dissolving 0.1512 g of paracetamol in warm water, stirring for 10 min and diluting to 100 ml in a calibrated flask after cooling.

Working solutions were prepared by dilution with distilled water.

Sulphuric acid solution. $1M$ was used.

All reagents used were of analytical grade and all water used was demineralized and doubly distilled.

Procedure

A 0.5 ml solution of paracetamol ($1.0 \times 10^{-3}M$), 4.0 ml of sulphuric acid solution ($1M$) and a known volume of ceric sulphate

Table 1 Tolerance of the method towards interference ions (amount of Ce taken, 2 μg)

Ion	Ratio of ion to Ce ($\mu g/\mu g$)	Ion	Ratio of ion to Ce ($\mu g/\mu g$)
Nd(III)	300	Dy(III), Lu(III)	60
Gd(III)	200	Ca(II)	40
Er(III), Tb(III)	150	Tm(III), Zn(II), Fe(II)	30
Y(III)	120	Cr(III), Mg(II), Cu(II)	20
La(III), Eu(III)	100	Pb(II), Ho(III)	10
Pr(III), Sm(III), Yb(III)	80	Fe(III)	5*

*In presence of 0.3 mg EDTA.

Table 2. Analysis of rare-earth ore samples

Sample number*	%CeO_2 stated	%CeO_2 found†
1	49.21	48.32 ± 0.32
2	69.98	70.06 ± 0.21

*The standard samples were obtained from The Baotou Institute of Rare Earth, Baotou, China

†Mean ± Std. Dev ($n = 5$)

solution ($1.0 \times 10^{-5}M$) were added sequentially to a 10-ml volumetric flask. The contents of the flask were mixed, then the flask was placed in a boiling-bath for 10 min, after which it was cooled under tap water and diluted to the mark with water. The fluorescence intensity of the solution was measured in a 1 cm quartz cell at an excitation wavelength of 265 nm and an emission wavelength of 360 nm against the corresponding reagent blank, prepared concurrently.

RESULTS AND DISCUSSION

Fluorescence spectra

The excitation and emission spectra of the system were investigated. The fluorescent species has excitation and emission maxima at 265 and 360 nm, respectively.

Effect of paracetamol concentration

The effect of paracetamol concentration on the fluorescence intensity of the system was studied. When the concentration of paracetamol was $5.0 \times 10^{-4}M$, the fluorescence intensity reached a maximum. Therefore, a paracetamol concentration of $5.0 \times 10^{-4}M$ was selected

Effect of sulphuric acid concentration

Experiments indicated that maximum and constant fluorescence intensity was obtained for H_2SO_4 concentration in the range 0.3–0.5M. The fluorescence intensity decreased for values outside this range. A sulphuric acid concentration of 0.5M was chosen.

In addition, it was shown that the fluorescence intensity of the system reached maximum after heating at 100°C for 10 min and then remained stable for 2 hr.

Calibration graph

The calibration graph for the determination of cerium was constructed under the optimum conditions. Good linearity obtained over the range 2.0×10^{-7}–$8.0 \times 10^{-6}M$ Ce(IV). The detection limit is $1.0 \times 10^{-8}M$ with the signal to noise ratio (S/N) value of 3.

Effect of foreign ions

The effect of foreign ions on the determination of Ce(IV) is shown in Table 1. An error of 5% in the intensity values was considered tolerable. Table 1 shows that the method is of good selectivity. The high degree of selectivity is probably due to two factors: (1) The test is conducted in strong acidic solution. (2) Not all oxidizing reagents are sufficiently powerful to oxidize paracetamol to the fluorescent species. Only Fe(III) and Pb(II) caused severe interference. In a sulphuric acid media, Pb(II) precipitated as its sulphates. The Fe(III) ion can be masked by adding EDTA.

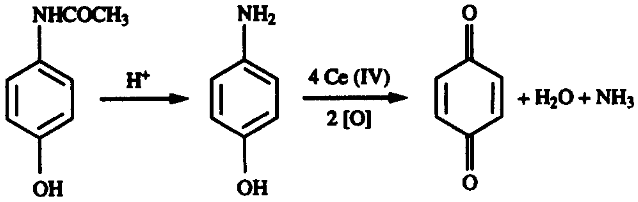
PRACTICAL APPLICATIONS

Treatment of ores

Dissolve the weighed ore sample in 20 ml of HCl (1:1), and heat gently on a hot plate. Add H_2O_2 dropwise until complete dissolution occurs. Cool the solution and add 5 ml of sulphuric acid (18M). The mixture was heated until white fumes were evolved. The solution was cooled. Add 20 ml of water and warm until the salts completely dissolve. Cool the solution to room temperature, transfer to a 250-ml flask and adjust to volume with sulphuric acid (0.5M). A suitable aliquot of the solution is then analyzed for Ce(IV) by the above procedure. The results are presented in Table 2. In addition, the method was tested on synthetic solution (Table 3). As can be seen, the results are very satisfactory.

Table 3 Analysis of synthetic mixtures

Sample number	Composition of solution (%)	%Ce present	%Ce found
1	Ce(IV) (0.72), La (14.20), Pr (14.40), Nd (14.71), Sm (15.32), Eu (15.52), Gd (16.04), Tb (5.24), Ho (1.09), Y (3.86)	0.720	0.712
2	As in 1 + Yb (10), Dy (10), Ca (5), Mg (5), Zn (5)	0.533	0.526



Scheme 1

Mechanism of the reaction

The mechanism of the reaction is similar to that proposed for the oxidation of paracetamol using Ce(IV) which has been used the basis for the spectrophotometric determination of paracetamol.[14]

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