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DETERMINATION OF SUBMICROGRAM QUANTITIES OF OSMIUM BASED ON ITS CATALYTIC EFFECT ON THE Ce(IV)–As(III) REACTION *

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ABSTRACT

A new kinetic-thermometric method for the determination of subtraces of osmium (0.23–33 ppb) is proposed with a relative standard deviation of 2.99%. The method is based on the catalytic effect of this element in the Ce(IV)–As(III) reaction. The elimination of iodide and ruthenium interferences is also dealt with.

INTRODUCTION

It is well known that traces of osmium, ruthenium and iodide catalyse the Ce(IV)–As(III) reaction. Different analytical methods have been established based on this catalytic effect in order to determine these three species.

Most of these methods are based on the decrease in absorbance of the yellow Ce(IV) solution [1–4] due to the reductive effect of As(III).

The aim of this work is to monitor the reaction during the stage of temperature change when the catalyst is added. This method has been used successfully in previous work [5,6] in order to determine iodide (5–20 μg l^{-1}) and ruthenium (0.7–7.2 μg l^{-1}). The thermometric technique has the advantage that coloured solutions or suspensions can be easily analysed.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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EXPERIMENTAL

Apparatus

The thermometric system is similar to that used previously [5,6], constituting a nylon titration adiabatic cell, a thermistor (100 kΩ at 25 °C), a 1 ml syringe in order to add the catalyst, a conventional stirrer, a register and a stabilized voltage source. A scheme of the cell is shown in Fig. 1.

Reagents

Stock solutions of 0.1 M Ce(IV) (ceric ammonium sulphate, Merck) and 0.1 M As(III) (sodium arsenite, Merck) were prepared and standardized using conventional procedures.

The stock solution of osmium was prepared by dissolving 0.76 mg of OsO_4 (Carlo-Erba) in 1000 ml of 1 M sulphuric acid. This solution was standardized by liberation of iodine from excess potassium iodide and subsequent titration with thiosulphate.

All of these solutions were prepared in 1 M sulphuric acid media. The different osmium solutions were prepared daily from the concentrated stock solution.

Procedure

As(III) and Ce(IV) solutions (30 ml each) were placed in the thermomet-

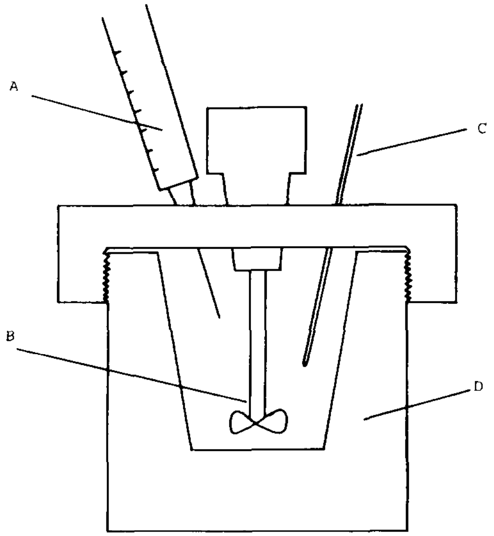

Fig. 1. Adiabatic cell. (A) Syringe, (B) stirrer, (C) thermistor, (D) nylon thermometric cell.

ric cell. After 5 min of homogenization, different quantities of a 2.84 ppm osmium solution were injected into the cell.

RESULTS AND DISCUSSION

Examples of the thermometric curves are shown in Fig. 2, where tg α values are plotted against Os concentration (tg $\alpha = \Delta T/t$).

These curves present very good linearity and the slopes increase with the osmium concentration. Therefore, the catalytic effect is maintained with no passivation of metal throughout the reaction, in contrast to other cases [7,8].

It is convenient to add the catalyst after a fixed time (5 min) due to the slow reaction between As and Ce once they are mixed.

In order to optimize the analytical conditions, the effect of As, Ce and H_2SO_4 concentrations was studied. Results are shown in Figs. 3–5.

Reproducibility of the method was determined using 2.34 ppb of osmium. Results are given in Table 1, and a relative standard deviation of 2.99% was obtained.

The response linearity of the method was determined over a wide concentration range by changing the register sensitivity (Table 2). Results obtained in the 0.47–4.67 ppb range are presented in Fig. 6.

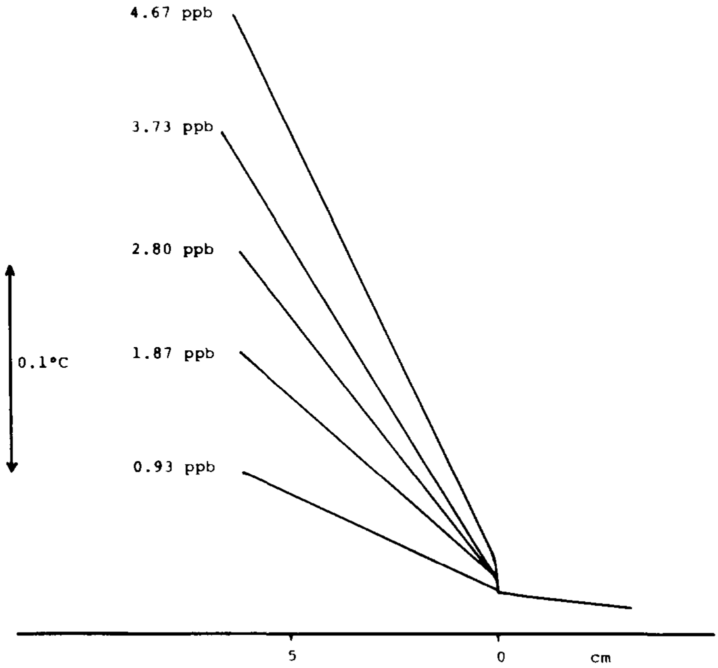

Fig. 2. Kinetic-thermometric curves of the Ce(IV)–As(III) solution.

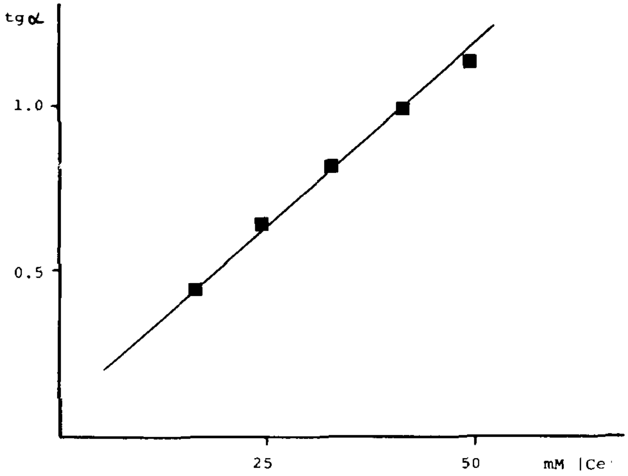

Fig. 3. Influence of the cerium concentration on the initial rate values. |As| = 50 mM, $S = 50$ mV, |Os| = 2.80 ppb.

TABLE 1

50 mM As(III), 50 mM Ce(IV), $V_0 = 60$ ml, $S = 50$ mV (0.02° C cm^{-1}), 2.34 ppb Os added

No. of detns.	1	2	3	4	5	6	X	σ
ppb found	2.30	2.27	2.33	2.40	2.45	2.35	2.35	0.07

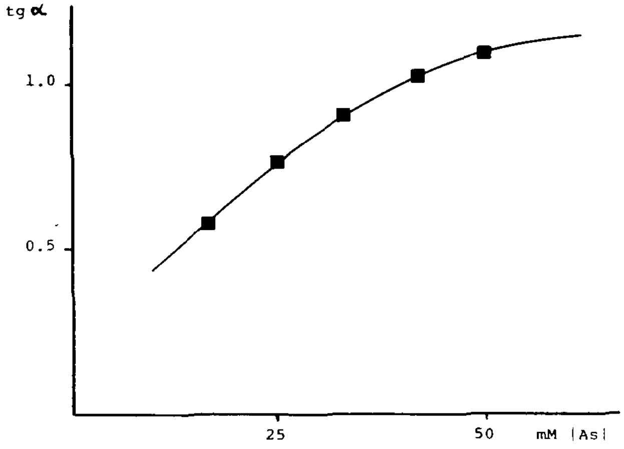

Fig. 4. Influence of the arsenic concentration on the initial rate values. |Ce| = 50 mM, $S = 50$ mV, |Os| = 2.80 ppb.

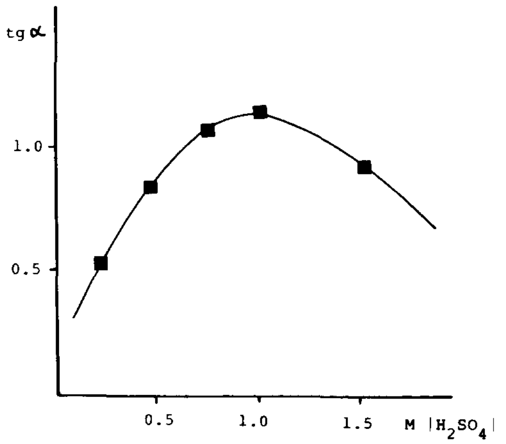

Fig. 5. Influence of the sulphuric acid concentration on the initial rate values. |As| = 50 mM, |Ce| = 50 mM, |Os| = 2.80 ppb.

TABLE 2

50 mM As(III) and 50 mM Ce(IV); C is concentration in ppb

S (mV)	Range (ppb)	Calibration (ppb)	r
20	0.23–2.35	tg $\alpha = 0.0168 + 0.6096C$	0.9965
50	0.47–4.67	tg $\alpha = 0.0799 + 0.3399C$	0.9988
100	2.34–8.01	tg $\alpha = 0.2162 + 0.1477C$	0.9999
200	4.73–33.12	tg $\alpha = 0.1637 + 0.0979C$	0.9991

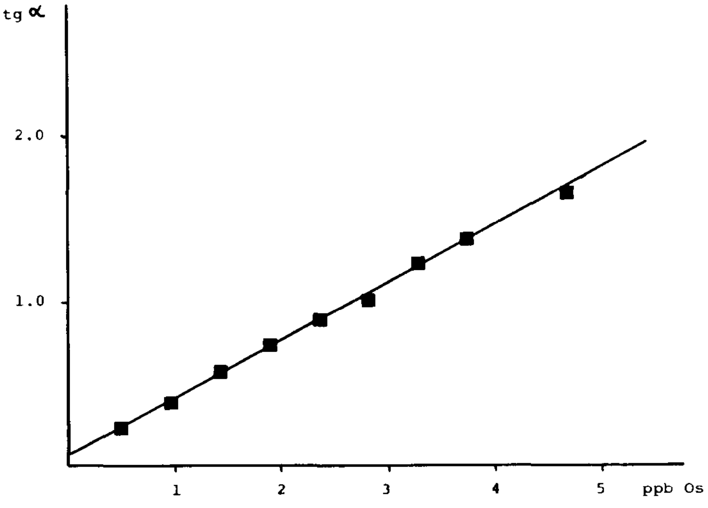

Fig. 6. Calibration curve. Range, 0.47–4.67 ppb.

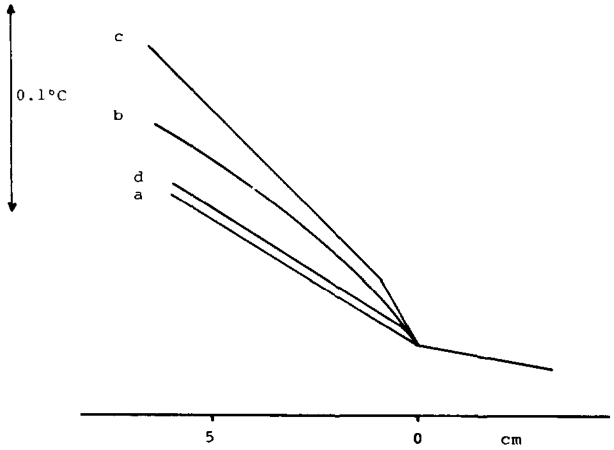

Fig. 7. Iodide interference elimination. |As| = 50 mM, |Ce| = 50 mM, $S = 50$ mV. (a) Addition of 0.2 ml of Os (0.28 ppm), (b) addition of 0.1 ml of $|I^-|$ (3.3 ppm), (c) addition of 0.1 ml of $|I^-|$ (3.3 ppm) + 0.2 ml of |Os| (0.28 ppm), (d) addition of 0.1 ml of $|I^-|$ (3.3 ppm) + 0.2 ml of |Os| (0.28 ppm) + 0.2 ml $|Ag^+|$ (10 ppm).

From Table 2 we deduced that osmium can be determined from 0.23 to 33 ppb, using the appropriate sensitivity range.

Finally, we have studied how to eliminate the iodide and ruthenium interferences. Iodide interference is easily overcome by a small addition of silver (Fig. 7). With the objective of eliminating the ruthenium interference, its separation was carried out by a redox process followed by extraction, as reported in the literature [2].

Chlorides can also interfere due to the formation of $OsCl_6^{2-}$, a compound which does not cause any catalytic effect. This interference can be eliminated by evaporation of the sample to dryness with H_2SO_4.

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