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SIMPLE KINETIC-THERMOMETRIC DETERMINATION OF SUBMICROGRAM QUANTITIES OF RUTHENIUM BASED ON ITS CATALYTIC EFFECT ON THE Ce(IV)-As(III) REACTION

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ABSTRACT

The study of different variables that affect the catalytic action of ruthenium on the Ce(IV)-As(III) reaction is carried out in order to select the best analytical conditions for its thermometric determination In the final solution 0 7-41 μg l^{-1} of Ru(III) or 0 1-2 5 μg l^{-1} of Ru(VIII) were determined, with very few interferences

The method was applied to determine ruthenium in the $K_4[Ru(CN)_6]$ $3H_2O$ complex and the results are compared with those obtained from a spectrophotometric method

INTRODUCTION

The determination of ruthenium, in amounts from 0 005 to 0 1 μg, can be carried out on its catalytic effect on the slow reaction between Ce(IV) and As(III) in sulphuric acid solution The catalysed reaction rate has been determined spectrophotometrically measuring the Ce(IV) concentration as a function of time [1]

In previous papers [2,3] we proposed a similar thermometrically monitored method for determination of traces of iodide and osmium based on its catalytic effect on the same reaction The optimum results obtained in the kinetic-thermometric methods for determination of iodide (5-20 μg l^{-1}) [2], osmium (0 23-33 μg l^{-1}) [3], vanadium [4] and other ions [5-9] encouraged us to select the best conditions for ruthenium determination by means of the same technique

We report here a new thermometric method to determine Ru traces based on its catalytic effect on the Ce(IV)-As(III) reaction

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EXPERIMENTAL

Apparatus

The temperature monitoring system consisted of a rapid response thermistor of the thermometer type with a nominal resistance value of 100 kΩ at 25 ° C, a Wheatstone bridge fed with 8.93 V from a stabilized source and a recorder, the sensitivity of which was 0.02 ° C cm^{-1} with a 50 mV full-scale deflection. This temperature monitoring system is a modification of the apparatus of Lumbiarres et al. [10].

Reagents

The stock solution 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 ruthenium was prepared by dissolving 0.1233 g of $RuCl_3 \cdot 3H_2O$ (Strem Chem. Inc.) in 50 ml of water. In the absence of interfering substances, the determination of ruthenium is simply carried out by mixing the sample solution of ruthenium with ceric sulphate solution, allowing it to stand for a few minutes if necessary to oxidize Ru(III) to Ru(VIII), adding the mixture rapidly to arsenious oxide solution, and noting the time for the absorbance of the solution to decrease to some specified value. The absorbance is measured at a wavelength that will allow the change in the concentration of cerium(IV) to be determined with adequate photometric precision.

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

$K_4[Ru(CN)_6] \cdot 3H_2O$ was prepared as described in the literature [11].

Procedure

Twenty millilitres of 0.1 M sodium arsenite solution and 20 ml of 0.1 M ceric sulphate solution and 30 ml of water were placed in the adiabatic cell. After a predetermined time of stirring, different quantities of a 0.9829×10^{-5} M ruthenium solution were added by means of a syringe into the thermometric cell.

RESULTS AND DISCUSSION

Examples of the temperature–time curves for different quantities of Ru(III) are shown in Fig. 1.

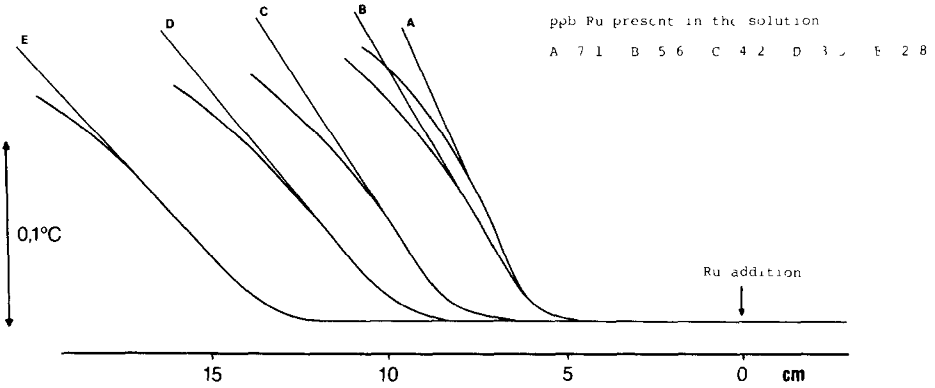

Fig 1 Kinetic–thermometric curves of the Ce(IV)–As(III) solution

As could be expected from previous studies, the slope of the curves (tg α) increase with the catalyst concentration due to the exothermic reaction The main difference from other systems is the presence of an induction time (t_1) This can be assigned to the previous oxidation of Ru(III) to Ru(VIII), which is the oxidation state that catalyses the As(III)–Ce(IV) reaction

A study was carried out to determine the induction time (t_1) and the tg α value with respect to the reagents' mixing time The results are shown in Fig 2 From Fig 2 the tangent values (tg α) decrease when the mixing time is deduced, probably caused by the presence of some impurities [1] For this reason in the next experiments we chose a mixing time of 10 min

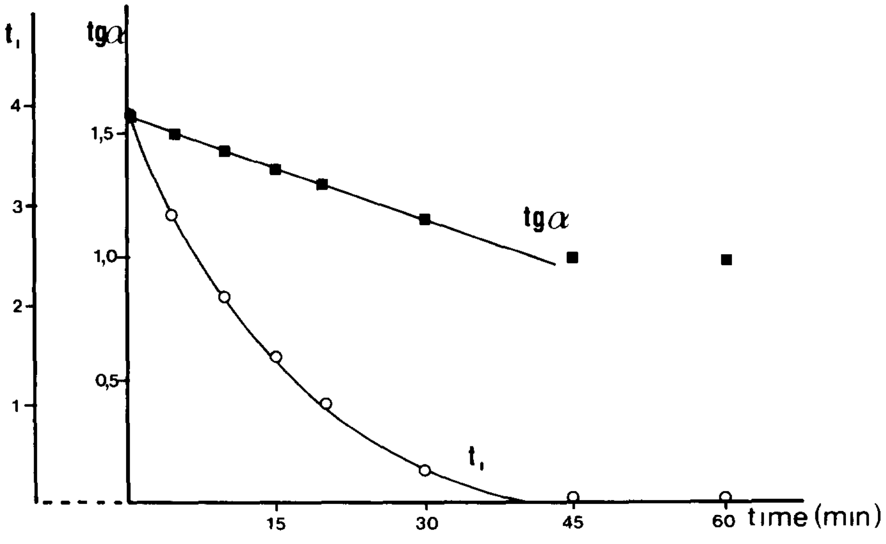

Fig 2 The influence of mixing time of reagents on the tg α and induction time (t_1) values

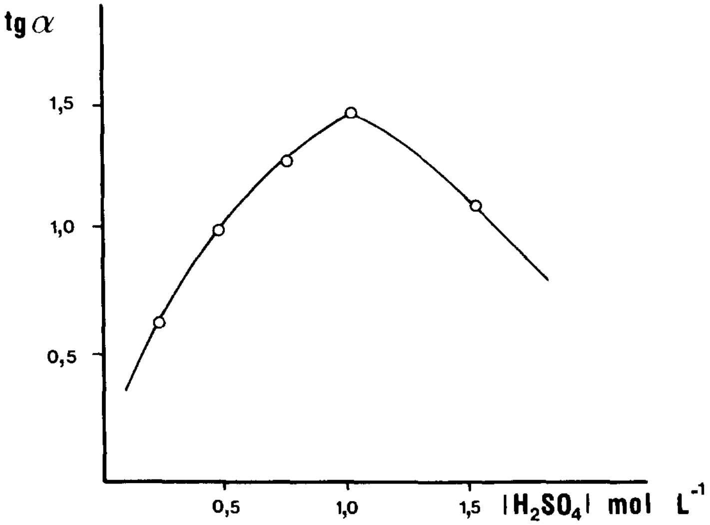

Fig 3 The influence of sulphuric acid concentration on the initial rate values Concentrations [Ce(IV)] = 0 0285 M, [As(III)] = 0 0285 M, [Ru(III)] = 4 76 ppb

The effect of the sulphuric acid, arsenite and ceric sulphate concentrations on the reaction rate are studied in order to optimize the conditions for determination of ruthenium (Figs 3 and 4) When the order of reaction with respect to these concentrations is as near zero as possible they are considered to be optimum, as their slight variation will not affect the initial reaction rate Thus the sulphuric acid concentration of 1 M was optimum (Fig 3)

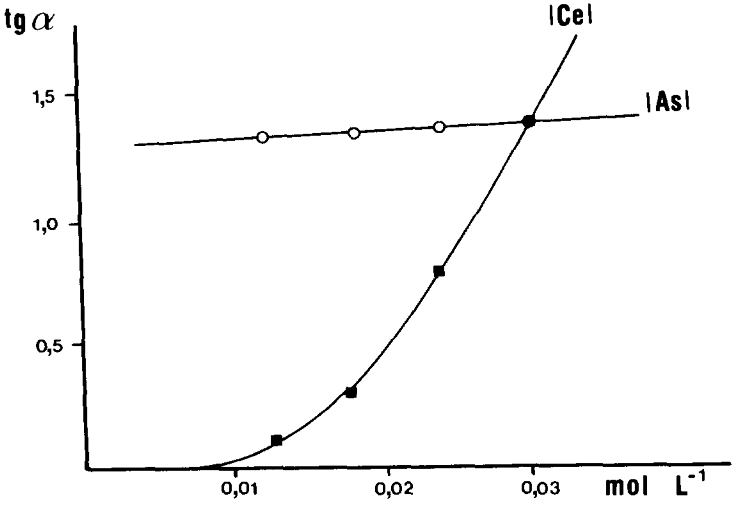

Fig 4 The influence of Ce(IV) and As(III) concentration on the initial rate values Concentrations [Ru(III)] = 5 7 ppb, $[H_2SO_4] = 1$ M

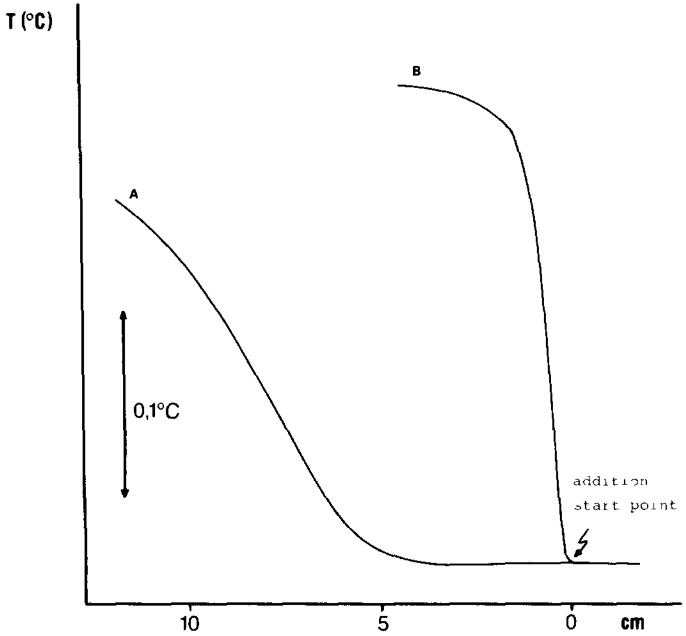

Fig 5 Kinetic–thermometric curves (A) Ru(III) added to Ce(IV)–As(III) solution Concentrations [As(III)] = 0 0285 M, [Ce(IV)] = 0 0285 M, [Ru(III)] = 4 76 ppb (B) Previous oxidation to Ru(III) by means of a small addition of Ce(IV) (4 25 × 10^{-5} M) to the Ru(III) solution Concentrations [As(III)] = 0 0285 M, [Ce(IV)] = 0 0285 M, [Ru(VIII)] = 4 76 ppb

The rate of the reaction is independent from the As(III) concentration, whereas it continuously increases with Ce(IV) content, confirming literature data [1] Ceric sulphate and arsenite concentrations were both 0 03 M, which is considered the most convenient (Fig 4)

The experiments were repeated first adding a small quantity of Ce(IV) to the Ru(III) solution and then the oxidized Ru(VIII) to the cell mixture, in order to verify that the induction time was due only to this oxidation process, and showed that the induction time disappeared in the kinetic curves when Ru(III) was previously oxidized (Fig 5) One can appreciate the

TABLE 1

Calibration curves for ruthenium determination by means of the kinetic–thermometric method

S (mV)	Calibration (ppb)	r	Range (ppb)
Concentration of Ru(III)			
50	tg α = 0 2275 + 0 1969C	0 9961	0 7– 7 2
100	tg α = 0 3487 + 0 0471C	0 9964	6 8–41 0
Concentration of Ru(VIII)			
50	tg α = 0 5295 + 1 2453C	0 9974	0 1–2 5

TABLE 2

Accuracy and precision of the kinetic–thermometric method (mean of five determinations)

	S (mV)	Theoretical (ppb)	Experimental (ppb)
Ru(III)	50	5.6	5.8±0.5
		4.9	5.1±0.4
		2.8	3.2±0.3
	100	5.6	5.8±0.5
		9.8	9.9±0.7
		11.2	11.6±0.5
Ru(VIII)	50	2.47	2.5±0.2
		1.24	1.4±0.1
		0.37	0.4±0.1

increase of the slope of the kinetic curve with preoxidation. However, the induction time reappears when the ruthenium(VIII) concentration decreases, showing that this period depends not only on the oxidation state, but also on other factors.

The calibration curves were obtained both with and without Ru(III) preoxidation to Ru(VIII). The results are included in Table 1. Experiments have shown that the method is reproducible with a relative standard deviation of 2.5% ($n = 8$, 4.2 ppb of Ru(III)).

By using several solutions of different ruthenium concentrations, the accuracy and precision of the kinetic method was obtained. The results are shown in Table 2.

Interferences

Finally, a study was performed in order to eliminate the interferences in this method.

It is well known that osmium [12,13] and iodide [2] also catalyse this reaction. Surasiti et al. [1] have proposed two procedures for ruthenium and osmium separation, one based on a ferrous sulphate reduction–nitric acid oxidation, the other on boiling the sample with hydrogen peroxide.

We have achieved iodide interference elimination by the addition of silver. In Fig. 6 the kinetic curves obtained with Ru(III) (curve B), with Ru(III) and iodide (curve A) or Ru(III), iodide and silver (curve C) are presented.

Application

The thermometric method has been used to determine the content of Ru in the $K_4[Ru(CN)_6]\cdot 3H_2O$ complex, and the results have been fairly concordant with those obtained by a spectrophotometric method [14] The theoretical value was 21 6%, the thermometric method result was 21 2 ± 0 1%, whilst the spectrophotometric method gave a value of 21 1 ± 0 1% (mean of three determinations)

The thermometric method has been applied to determine the ruthenium content of the modified γ-Al_2O_3 samples as a function of time during impregnation of the latter with solutions of $K_4[Ru(CN)_6]$, to prepare ruthenium supported catalysts active in the ammonia synthesis [15,16] This determination has not been possible by the spectrophotometric method, since the variation of the ruthenium content in the solution is smaller than the relative standard deviation of the spectrophotometric method

The procedure for the spectrophotometric method is long and tedious, because the $[Ru(CN)_6]^{4-}$ complex is more stable than the $[RuCl_4]^{2-}$ blue complex used in the spectrophotometric determination [14,17], and the sample must be previously calcined For the thermometric method, it is not necessary to pretreat the sample, since the $[Ru(CN)_6]^{4-}$ solution, after its oxidation by Ce(IV) addition, activates the catalytic reaction

The thermometric method has the following advantages over the spectrophotometric method fast analyses, low cost of equipment and greater sensitivity (0 1 ppb compared with 0 5 ppm [14])

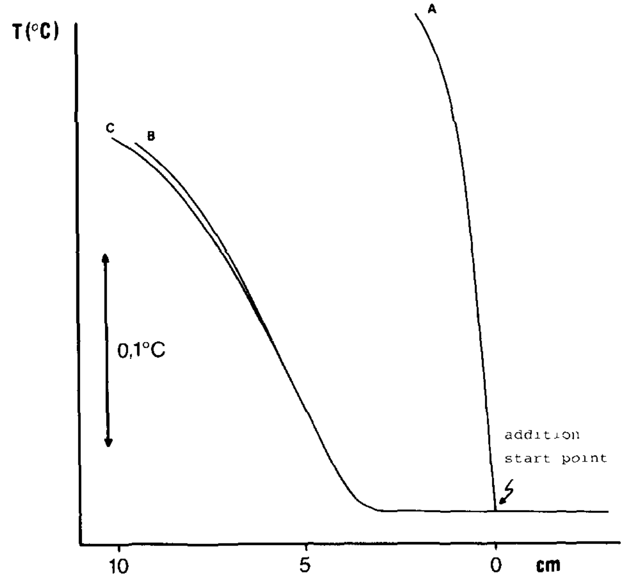

Fig 6 Kinetic–thermometric curves (A) Catalysed by Ru(III) (5 6 ppb) and iodide (1 ppm) (B) Catalysed by Ru(III) (5 6 ppb) (C) Catalysed by Ru(III) (5 6 ppb), iodide (1 ppm) and Ag(I) (5 ppm)

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