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KINETIC-THERMOMETRIC DETERMINATION OF SUBMICROGRAM QUANTITIES OF Pd(II)

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ABSTRACT

A new kinetic–thermometric method for the submicrogram determination of Pd(II) is proposed. The method is based on the inhibitory effect of this element on the iodide-catalysed Ce(IV)–As(III) reaction. Microamounts of Pd(II) within the range 5–20 ng ml^{-1} were determined with a relative standard deviation of 1.5%. The proposed method was used for Pd(II) determination in palladimized active carbon (organic catalyst).

INTRODUCTION

One of the most popular methods for trace iodide determination is based on its catalytic effect in the Ce(IV)–As(III) redox reaction. This well known process, studied by Sandell and Kolthoff [1,2], is also catalysed by osmium [3,4] and ruthenium [5]. Although spectrophotometry has been used to monitor the reaction development, thermometry has also proved to be very useful in the catalytic–kinetic methods [6–8]. The Kolthoff–Sandell reaction has also been applied to determin other elements [Hg(II), Ag(I) and Pd(II)], based on their inhibitory effects.

The Kolthoff–Sandell reaction has been used in catalytic titrations [9–13]. The end-point can be detected by different methods: spectrophotometrically, potentiometrically [10,14], biamperometrically [15] or thermometrically [13]. Using this last method, several authors determined Ag(I) and Hg(II) within the range 1000–0.1 ppm [11] or Ag(I) (50–550 μg), Hg(II) (100–1000μg) and Pd(II) (50–550μg) [13] by direct titration. Moreover, several anions (Cl^-, Br^-, I^-, SCN^-CN^-, S^{2-} and $[Fe(CN)_6]^{4-}$) were determined by back titration with iodide standard solution [13].

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In previous papers [6], Hg(II) and Ag(I) were determined by thermometric methods. This paper describes a procedure for determining Pd(II) in the range 5–20 ng ml^{-1}.

EXPERIMENTAL

Apparatus

The thermometric system, described elsewhere [16,17], constitutes a nylon titration adiabatic cell, a rapid response thermistor of the thermometer type (with a nominal resistance value of 100 kΩ at 25°C), a 1 ml syringe for adding the catalyst, a conventional stirrer, a register and a stabilized voltage source (9.35 V). This temperature monitor is a modification of the apparatus of Lumbiarres et al. [18].

Reagents

Cerium(IV) solution (0.1 M) was prepared by dissolving ceric suphate in 1 M sulphuric acid. Arsenic(III) solution (0.1 M) was prepared by dissolving sodium arsenite in 1 M sulphuric acid. Stock solutions of potassium iodide (7.8995 mM) and palladium chloride (0.9362) were prepared. More dilute solutions containing iodide and palladium were prepared daily.

Procedure

The procedure used was similar to those described in a previous paper on Hg(II) and Ag(I) [6]. Ceric sulphate (10 ml, 0.1 M), sodium arsenite (10 ml, 0.1 M) and sulphuric acid (40 ml of 1 M) were placed in the adiabatic cell. Different quantities of Pd(II) were introduced and, after 10 min, a pre-fixed quantity of iodide was added into the thermometric cell by means of a syringe.

Mineralization method

The kinetic method was used to determine the Pd(II) concentration in palladimized active carbon (hydrogenation catalyst). The sample (0.1000 g) was treated first with aqua regia, then with HNO_3–H_2SO_4 mixture. The product was evaporated to dryness, dissolved in dilute HCl, and transferred to a 250 ml flask and diluted with H_2SO_4(1 M) to the mark.

RESULTS AND DISCUSSION

In a previous paper the effect of sulphuric acid, ceric sulphate and arsenite concentration on the initial rate were reported [6]. Concentrations

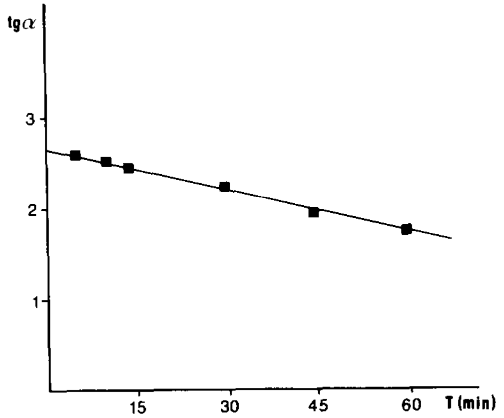

Fig. 1. Influence of the time elapsed between reagents, mixture and catalyst injection. [As] = 0.017 M, [Ce] = 0.017 M, $[H_2SO_4]$ = 1M. Injection of 0.5 ml of iodide of 5 ppm. $S = 20$ mV (0.008°C cm^{-1}), $V_r = 3$ cm min^{-1}.

of 1 M sulphuric acid, 0.02 M ceric sulphate and 0.2 M arsenite were considered optimum. Figure 1 illustrates the influence of the time elapse between reagent mixture and catalyst injection. The decrease of tangent values is probably due to the presence of some impurities [5]. An interval of 10 min was chosen for further experiments.

Figures 2 and 3 show the effect of the iodide concentration on the *tgα* values, under the selected conditions.

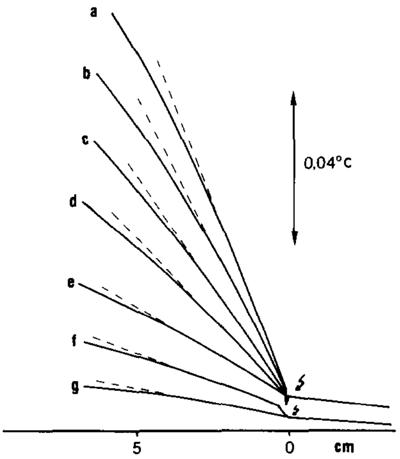

Fig. 2. Kinetic–thermometric curves of the Ce(IV)–As(III) solution, catalysed by iodide. [As] = 0.017 M, [Ce] = 0.017 M, $[H_2SO_4]$ = 1 M. Iodide concentration (ppb): (a) 41.7, (b) 33.3, (c) 25.0, (d) 16.7, (e) 8.3, (f) 5.0, (g) 1.7. (⇝) Iodide addition.

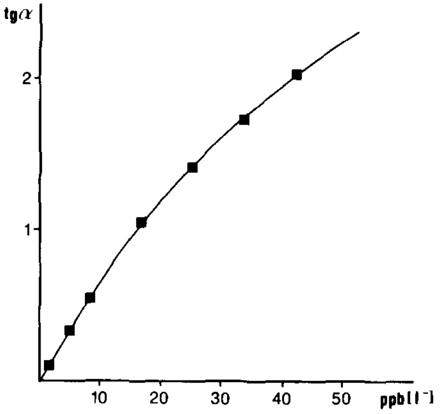

Fig. 3. Iodide calibration curve.

Pd(II) determination

The inhibitory effect of Pd(II) was applied to the iodide catalysis of the As(III)–Ce(IV) system to develop a reaction-rate method for Pd(II) determination.

A constant iodide concentration (41.7 ng ml^{-1}), 10 ml of ceric solution, 10 ml of arsenite solution, 40 ml of sulphuric acid solution and different quantities of Pd(II) solution were introduced into the adiabatic cell. The decrease in initial reaction rate, caused by the presence of the inibitor, was measured. Results are shown in Fig. 4. When an iodide concentration of 41.7 mg ml^{-1} was used, the calibration graph was steep and linear for 5–20 ng ml^{-1} of palladium. The relative standard deviation (7 determinations) was 1.5%.

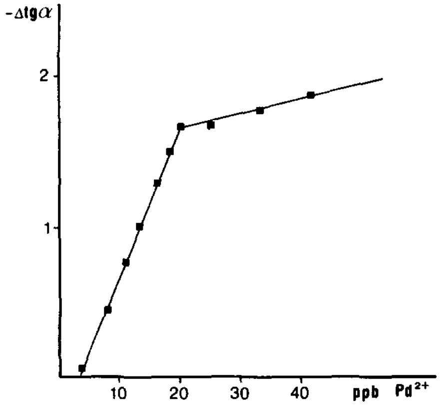

Fig. 4. Pd(II) calibration curve.

Study of the interferences

A study of the interferences has been performed. Thirty ions were tested: Ag(I), Hg(II), Pb(II), Cu(II), Cd(II), Bi(III), Sn(II), Sb(III), Fe(III), Al(III), Cr(III), Co(II), Ni(II), Zn(II), Mn(II), Ca(II), Sr(II), Ba(II), Mg(II), Mo(VI), Os(VIII), Ru(VIII), V(V), Cl^-, F^-, Br^-, CN^-, AcO^-, SCN^- and PO_4^{3-}. Only 6 ions interfered: 1 ng ml^{-1} of Hg(II) or Ag(I) due to their precipitation with iodide; 1 ng ml^{-1} of Os(VIII) or Ru(VIII) due to their catalytic effect on the As(III)–Ce(IV); reaction; and 2 ppm of Mn(II) and Fe(III).

Determination of palladium in the organic catalyst

The sample was first mineralized as previously described and then diluted. $4.7 \pm 0.1\%$ of palladium was found (the palladium concentration in the palladimized active carbon was 5%).

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