

Kinetic determination of ultramicro amounts of As(III) in solution

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Abstract: A new catalytic reaction is proposed and a kinetic method developed for the determination of ultramicro amounts of As(III) on the basis of its catalytic activity in the oxidation of ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid (EAP) by KMnO_4 in the presence of hydrochloric acid. Under optimal conditions, the sensitivity of the method is 20 ng/cm^3 . The probable relative error is 7.6 – 14.5 % for the concentration range 50 – 200 ng/cm^3 As(III). The effect of certain foreign ions upon the reaction rate were determined for the assessment of the selectivity of the method. The method has relatively good selectivity. Kinetic equations were proposed for the investigated process.

Keywords: kinetic method, As(III) determination, ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid.

INTRODUCTION

Only a small number of indicator reactions for the kinetic determination of As(III) by photometric or amperometric method are known.^{1–3} Their sensitivity ranges from about 6.2 ng/cm^3 to $5 \text{ } \mu\text{g/cm}^3$. However, all these methods have relatively low selectivity.

The oxidation of ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid (EAP) by KMnO_4 in the presence of hydrochloric acid is catalysed by small amounts of As(III). On the basis of this reaction, a kinetic method was elaborated for the determination of trace amounts of As(III) in the range 20 – 200 ng/cm^3 . Diminution of the color intensity of the oxidant (KMnO_4) was followed spectrophotometrically as the change of absorbance (A) with time (t).

EXPERIMENTAL

Apparatus

A spectrophotometric method was used for following the investigated reaction rate. The dependence of the absorbance (A) on time (t) was measured using a Perkin-Elmer Lambda 15 spectrophotometer, connected to a thermocirculating bath. The pH was measured by means of a Radiometer PHM 29b pH meter and a combined glass – calomel electrode, GK 2311C. The solutions were thermostated at $25 \pm 0.1 \text{ }^\circ\text{C}$ before the beginning of the reaction. The kinetic measurements were performed at a wavelength of 525 nm.

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Reagents

The KMnO_4 solution (0.02 mol/dm^3) was prepared from an ampule, produced by Merck. The EAP solution ($1 \times 10^{-3} \text{ mol/dm}^3$) was made by direct weighing of the solid. The HCl solution (1.000 mol/dm^3) was prepared from a 37 % concentrated HCl solution. The basic As(III) solution ($1 \times 10^{-3} \text{ mol/dm}^3$) was prepared by dissolving a weighed amount of NaAsO_2 in deionized water. The exact concentration was determined volumetrically. Analytical-grade reagents, deionized water and polyethylene vessels were used throughout.

Procedure

The initial concentration of each of the reactants was in turn varied systematically, the initial concentrations of the other reactants being kept constant.

The selected volumes of the reactants were put into a 20 cm^3 standard flask, in the order EAP, HCl, catalyst and water to make up exactly the predetermined volume. The flask was kept in the thermostat for 10 min, then the solution was made up to the mark with KMnO_4 and water and vigorously shaken. The cell of the photometer was rinsed well and filled with the solution. The absorbance was measured every 15 s, for 3–6 min, the timing being started at the moment of KMnO_4 addition.

The initial concentrations of the reagent solutions after dilution to 20 cm^3 were: $1 \times 10^{-5} - 3.5 \times 10^{-5} \text{ mol/dm}^3$ EAP; $1 \times 10^{-5} - 4.5 \times 10^{-5} \text{ mol/dm}^3$ KMnO_4 ; $1.5 \times 10^{-2} - 4.5 \times 10^{-2} \text{ mol/dm}^3$ HCl; $20 - 200 \text{ ng/cm}^3$ As(III). The measurements were made at $25 \pm 0.1 \text{ }^\circ\text{C}$. A calibration curve was also plotted for the temperature $30 \pm 0.1 \text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

The differential variant of the fixed time method or constant-concentration method was used for processing the kinetic data.⁴

The effect of pH on the catalysed and uncatalysed reaction rates is shown in Fig. 1. From Fig. 1, it appears that there is a complicated relationship between pH and reaction rate, *i.e.*, the reaction order is variable with respect to hydrogen-ion concentration in the range of concentrations studied. For further work a pH of 1.6 was chosen for quantitative applications.

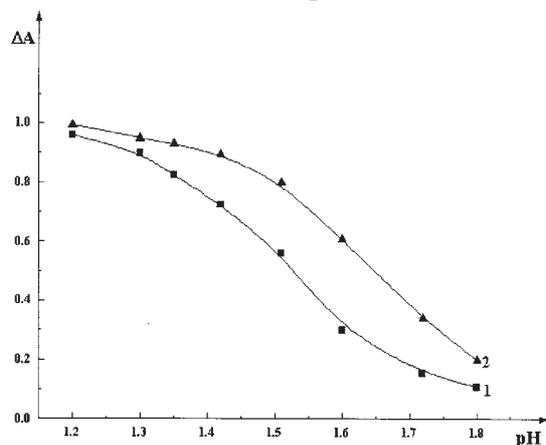


Fig. 1. Dependence of the reaction rate on pH. Initial conditions: $4.5 \times 10^{-5} \text{ mol/dm}^3$ KMnO_4 ; $1.5 \times 10^{-5} \text{ mol/dm}^3$ EAP; 100 ng/cm^3 As(III); 1—uncatalysed reaction, 2—catalysed reaction.

The dependence of ΔA ($\Delta A = 1 - A$) on the EAP concentration is shown in Fig. 2. The maximum difference between the rates of the catalysed and uncatalysed reaction was observed for concentrations of EAP greater than $2.5 \times 10^{-5} \text{ mol/dm}^3$. At lower concentrations, as already mentioned, both reactions are first order with respect to EAP. For further work, an EAP concentration of $2.5 \times 10^{-5} \text{ mol/dm}^3$ was selected.

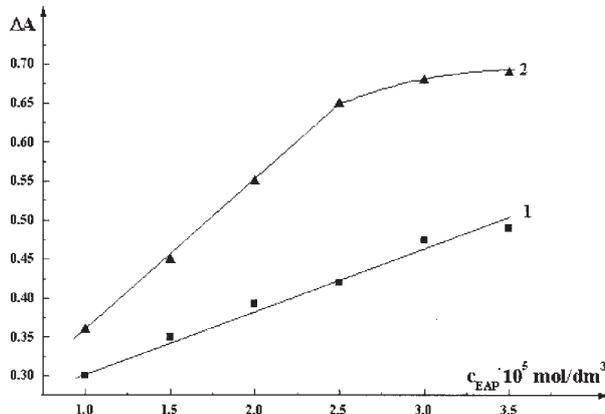


Fig. 2. Dependence of the reaction rate on the EAP concentration. Initial conditions: $4.5 \times 10^{-5} \text{ mol/dm}^3 \text{ KMnO}_4$; $100 \text{ ng/cm}^3 \text{ As(III)}$; pH 1.6; 1–uncatalysed reaction, 2– catalysed reaction.

The dependence of the reaction rates on the concentration of KMnO_4 is shown in Fig. 3. Both reactions are first order with respect to the KMnO_4 concentration. For further work a KMnO_4 concentration of $4.5 \times 10^{-5} \text{ mol/dm}^3$ was selected.

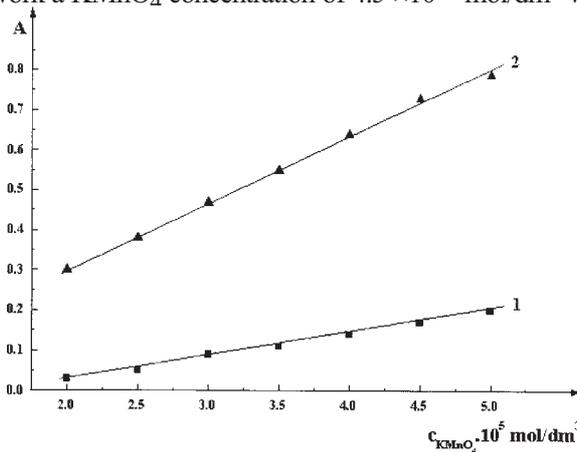


Fig. 3. Dependence of the reaction rate on the KMnO_4 concentration. Initial conditions: $4.5 \times 10^{-5} \text{ mol/dm}^3 \text{ EAP}$; $100 \text{ ng/cm}^3 \text{ As(III)}$; pH 1.6; 1–catalysed reaction, 2– uncatalysed.

Under optimal conditions ($c_{EAP} = 2.5 \times 10^{-5} \text{ mol/dm}^3$, $c_{KMnO_4} = 4.5 \times 10^{-5} \text{ mol/dm}^3$, pH = 1.6), the As(III) concentration was varied from 20 to 200 ng/cm^3 . Figure 4 shows the two calibration lines which can be used for the determination of the As(III) concentration in the mentioned interval. Line 2, measured at 30 °C, is steeper and more suitable for use than line 1, measured at 25 °C.

The relationship between the reaction rates and the concentrations of the reacting components can be described by the following kinetic equations (at constant pH).

For the catalysed reaction:

$$-\left(\frac{dc}{dt}\right) = k \times c_{EAP} \times c_{KMnO_4} \times c_{As}$$

for $c_{EAP} \leq 2.5 \times 10^{-5} \text{ mol/dm}^3$, $2.5 \times 10^{-5} \text{ mol/dm}^3 \leq c_{KMnO_4} \leq 5 \times 10^{-5} \text{ mol/dm}^3$, 20 ng/cm^3

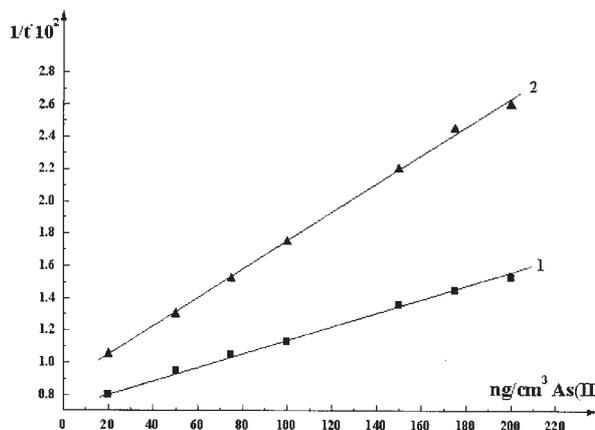


Fig. 4. Dependence of the reaction rate on the As(III) concentration. Initial conditions: 2.5×10^{-5} mol/dm³ EAP; 4.5×10^{-5} mol/dm³ KMnO₄; pH 1.6; 1— for 25 °C, 2—for 30 °C.

$\leq c_{\text{As(III)}} \leq 200$ ng/cm³ where k is a constant proportional to the rate constant of the catalysed reaction.

For the uncatalysed reaction:

$$-\left(\frac{dc}{dt}\right) = k_0 \times c_{\text{EAP}} \times c_{\text{KMnO}_4}$$

for $c_{\text{EAP}} \leq 2.5 \times 10^{-5}$ mol/dm³, 2.5×10^{-5} mol/dm³ $\leq c_{\text{KMnO}_4} \leq 5 \times 10^{-5}$ mol/dm³, where k_0 is a constant proportional to the rate constant of the uncatalysed reaction

The accuracy and precision are presented in Table I. The probable relative error ranges from 14.5 % to 7.6 % for As(III) concentrations from 50 to 200 ng/cm³. The method has relatively good accuracy.

TABLE I. Accuracy and precision of the As(III) determination

Taken/(ng/cm ³)	Found(\bar{x})/(ng/cm ³)	n	$\frac{100 \cdot t \cdot s}{\bar{x} \cdot \sqrt{n}}/\%$	$\frac{\bar{x} - \mu}{\mu} \cdot 100/\%$
200	197	5	7.6	-1.5
100	106	5	10.5	6.0
50	56	5	14.5	12.0

\bar{x} – Mean value; μ – true value; s – standard deviation; n – number determination; t – Student's for 95 % confidence; $\frac{100 \cdot t \cdot s}{\bar{x} \cdot \sqrt{n}}$ – precision; $\frac{\bar{x} - \mu}{\mu} \cdot 100$ – accuracy

The detection limit is 5 ng/cm³ As(III).⁴

The proposed method was applied for determining As(III) in the presence of As(V) in an artificially prepared mixture in which the ratio of As(III) and As(V) was 1:10³. The exact value of the concentration As(III) was 100 ng/cm³ while a value of 100 ± 8 ng/cm³ was obtained by the proposed analytical method.

To assess the selectivity of the method, the influence of several foreign ions on the catalysed reaction rate was investigated, at a constant As(III) concentration of 150 ng/cm³.

The presence of (individually, in the ratio to As(III) given in brackets) Na^+ , NO_3^- , ($10^4:1$), NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} ($10^3:1$), Zn^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Fe^{3+} , AsO_4^{3-} ($10^2:1$), Al^{3+} , Co^{2+} , Cd^{2+} , SCN^- , SO_4^{2-} , CH_3COO^- , PO_4^{3-} , F^- , WO_4^{2-} ($10:1$) has practically no influence on the reaction rate. $\text{Mo}_7\text{O}_{24}^{6-}$ ($10^{-1}:1$), VO_3^- ($1:1$), strongly inhibit the reaction. Fe^{2+} ($10^{-1}:1$), Sn^{2+} ($1:1$), Mn^{2+} ($10^{-2}:1$) further catalyse the reaction.

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ИЗВОД

КИНЕТИЧКО ОДРЕЂИВАЊЕ УЛТРАМИКРО КОЛИЧИНА As(III) У РАСТВОРУ

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Предложена је нова каталитичка реакција и разрађена нова кинетичка метода за одређивање ултрамикро количина As(III) на бази његове каталитичке активности на реакцију оксидације етилендиамин-*N,N'*-диацетат-*N,N'*-дипропионске киселине калијум-перманганатом у присуству хлоридне киселине. При оптималним условима осетљивост методе је 20 ng/cm^3 . Вероватна релативна грешка се креће од 7,6–14,5 % за интервал концентрације од $50\text{--}200 \text{ ng/cm}^3$ As(III). Ради оцене селективности методе испитан је утицај извесног броја страних јона на брзину реакције. Метода има релативно добру селективност. Предложене су кинетичке једначине за проучавани процес.

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