

## Kinetic determination of As(III) in solution

SOFIJA M. RANČIĆ\*, RANGEL P IGOV and TODOR G. PECEV

Department of Chemistry, Faculty of Science, University of Niš, 18000 Niš, Serbia and Montenegro

(Received 7 July 2002, revised 7 May 2003)

**Abstract:** A new reaction is suggested and a new kinetic method is elaborated for the As(III) traces determination in solution, on the basis of their catalyzing effect on komplexon III (EDTA) oxidation by  $\text{KMnO}_4$  in a strong acid solution ( $\text{H}_2\text{SO}_4$ ). Using a spectrophotometric technique, a sensitivity of  $72 \text{ ng/cm}^3$  As(III) was achieved. The relative error of method varies from 5.5 to 13.9 % for As(III) concentration range from 83 to  $140 \text{ ng/cm}^3$ . Appropriate kinetic equations are formulated and the influence of some other ions, including the As(V), upon the reaction rate is tested.

**Keywords:** kinetic method, As(III) determination, EDTA, spectrophotometric technique.

### INTRODUCTION

There are only few methods for As(III) traces determination in solution by atomic spectrometry<sup>1</sup> and spectrophotometric method.<sup>2</sup> Between different kinetic methods for traces determination in solution, As(III) is mentioned for the first time in some Sandell and Kolthoff works. They used the reaction between As(III) and Ce(IV) which was catalyzed by  $\text{I}^-$  ions for determination of  $\text{I}^-$ .<sup>3,4</sup> Other authors examined the influence of reactant concentration, the type of acid ( $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) and the  $\text{Cl}^-$  ions presence in solution, upon the reaction rate of the same reaction using different laboratory techniques.<sup>5,6</sup> The study of As(III)–Ce(IV) reaction system was also done by Worthington and Pardue.<sup>7</sup> Mitić *et al.* developed two methods for kinetic determination of As(III) in solution. The first one is based on the catalytic effect of As(III) ions on the oxidation of sodium pyrogallol-5-sulphonate (Na-salt of sulfonated 1,2,3-trihydroxy benzene) by dichromate in acidic media,<sup>8</sup> while the other determines As(III) as the catalyst of the pyrogallol oxidation by dissolved oxygen.<sup>9</sup> Koukli and Calokerionos used variable-time method for determination of As(III) by monitoring the iodide product in reaction with iodate using the iodide-selective electrode.<sup>10</sup> Kinetic determination based on the direct dependence of the length of induction period on As(III) concentration in the periodate-bromide reaction, has been proposed by Alekseeva and Kurtova.<sup>11</sup> The reaction rate detection was accomplished amperometrically and detection limit of  $0.03 \text{ } \mu\text{g/cm}^3$  is reported. Garsia *et al.* determined arsenate as an inhibitor of the reaction between pyronine G and  $\text{H}_2\text{PO}_4^-$  ions which is catalyzed by Pd(II).<sup>12</sup>

## EXPERIMENTAL

*Apparatus*

Using spectrophotometric detection on Perkin-Elmer UV-VIS Lambda 15 spectrophotometer, kinetic measurements are performed at 525 nm. The cylindrical cells (10 cm) are thermostated at  $26 \pm 0.1$  °C using a thermocirculating bath (Thermostat Sutjeska). The pH measurements are performed using Radiometer PHM 29 b pH-meter and a combined glass-calomel electrode GK 2311 C.

*Reagents*

All solutions are prepared of p.a. quality reagents (Merck) using deionized water, and all of them are kept in appropriate polyethylene vessels.

The As(III) basic solution ( $1 \times 10^{-3}$  g/cm<sup>3</sup>) is prepared by dissolving exactly measured NaAsO<sub>2</sub>, and the precise concentration is verified volumetrically.<sup>13</sup> The KMnO<sub>4</sub> basic solution ( $2 \times 10^{-2}$  mol/dm<sup>3</sup>) and C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O basic solution are prepared of exactly measured dry substances and the final concentrations are verified volumetrically. The H<sub>2</sub>SO<sub>4</sub> working solution is made of original concentrated solution and adequate volume of deionized water.

*Procedure*

Selected volumes of the reactants and deionized water, are measured separately in the Budarin vessel,<sup>14</sup> up to the predetermined volume. The vessel is thermostated for ten minutes period on the working temperature. After that, it is stirred and the chronometer is turned on simultaneously. The properly rinsed cell is filled by solution and the absorbance is measured starting as 30th second within the first five minutes of reaction. Between the measurements the vessels are washed using hydrochloric acid (1:1) and alcoholic KOH solution, and rinsed properly and repeatedly with tap, distilled and deionized water.

## RESULTS AND DISCUSSION

*Kinetic studies*

Until the reaction goes on, the initial violet color of solution disappears and the colourless reaction product is forming. Kinetic results are treated by the differential variant of the fixed time method or constant concentration method.<sup>15</sup>

The reaction is tested by examining the influence of each component of the reaction mixture upon the reaction rate by consecutive changing the concentration of each component until the concentrations of other components are kept constant. So, the optimum conditions for reaction are found : pH 1.16;  $c(\text{KMnO}_4) = 4.44 \times 10^{-5}$  mol/dm<sup>3</sup>,  $c(\text{EDTA}) = 1.4 \times 10^{-4}$  mol/dm<sup>3</sup>.

Keeping the other experimental parameters constant, the sulfuric acid dependence of the system was studied in the concentration range  $3 \times 10^{-2}$  to  $22 \times 10^{-2}$  mol/dm<sup>3</sup>. There is a complicated relationship of H<sup>+</sup> ions concentration for both catalytic and non-catalytic reaction. In the range of about 1.0 to 1.2 both reactions show the first order dependence (Fig. 1). So the pH value of 1.16 was chosen and kept constant in further investigations.

The similar observation can be used on the EDTA concentration dependence (Fig. 2). The concentration of  $1.4 \times 10^{-4}$  mol/dm<sup>3</sup> was selected because of the biggest reaction rate difference between the catalytic and non-catalytic reaction.

In the range of 1.11 to  $4.44 \times 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub> both reactions show the first order dependence (Fig. 3). The greatest difference between the reaction rates occurring at  $4.44 \times 10^{-5}$  mol/dm<sup>3</sup> and this concentration is used as optimal in our further work.

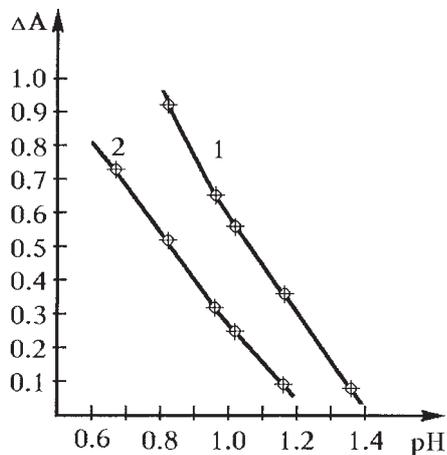


Fig. 1. Dependence of the reaction rate on pH. Initial conditions:  $4.4 \times 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>;  $1.4 \times 10^{-4}$  mol/dm<sup>3</sup> EDTA; 220 ng/cm<sup>3</sup> As(III); 1 – catalyzed reaction, 2 – non-catalyzed reaction.

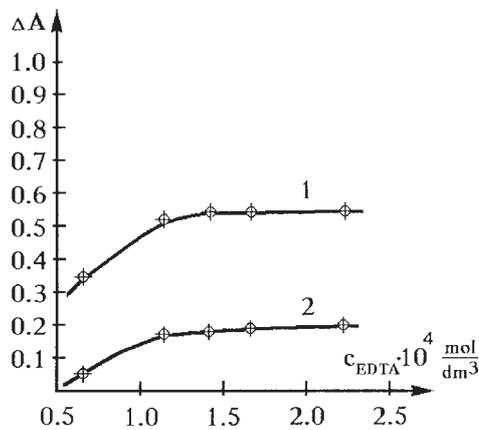


Fig. 2. Dependence of the reaction rate on EDTA concentration. Initial conditions:  $4.4 \times 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>; 220 ng/cm<sup>3</sup> As(III); pH = 1.16; 1 – catalyzed reaction, 2 – non-catalyzed reaction.

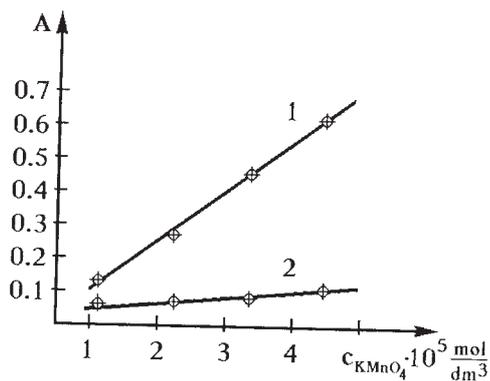


Fig. 3. Dependence of the reaction rate on KMnO<sub>4</sub> concentration. Initial conditions:  $1.4 \times 10^{-4}$  mol/dm<sup>3</sup> EDTA; 220 ng/cm<sup>3</sup> As(III); pH = 1.16; 1 – catalyzed reaction, 2 – non-catalyzed reaction.

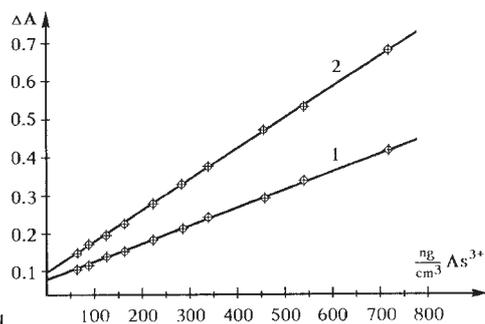


Fig. 4. Dependence of the reaction rate on As(III) concentration. Initial conditions:  $4.4 \times 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>;  $1.4 \times 10^{-4}$  mol/dm<sup>3</sup> EDTA; 1 – for 22 °C, 2 – for 26 °C.

The kinetic equations for the investigated process were deduced on the basis of the graphic correlations obtained for both catalytic (1) and non-catalytic (2) reaction for the following experimental conditions: pH from 1.0 to 1.2; EDTA concentration from 1.1 to  $2.3 \times 10^{-4}$  mol/dm<sup>3</sup>, KMnO<sub>4</sub> concentration from 1.11 to  $4.44 \times 10^{-5}$  mol/dm<sup>3</sup>

$$-dc_{\text{KMnO}_4}/dt = k_1 c_{\text{EDTA}} c_{\text{As(III)}} c_{\text{KMnO}_4} \quad (1)$$

$$-dc_{\text{KMnO}_4}/dt = k_0 c_{\text{EDTA}} c_{\text{KMnO}_4} \quad (2)$$

where:  $k_1$  is a constant proportional to the catalytic reaction rate constant and  $k_0$  is a constant proportional to the non-catalytic reaction rate constant.

The calibration curve was constructed (Fig. 4) and the calibration curve equation (3) was calculated:

$$\Delta A = 0.0008 c_{\text{As(III)}} + 0.100 \quad (3)$$

where:  $c$  is As(III) ng/cm<sup>3</sup> concentration.

According to this curve, it is possible to determine the As(III) concentration in the range from 72 to 720 ng/cm<sup>3</sup>.

In order to assess the accuracy and precision of the method, reaction rates were determined for the three different As(III) concentrations in five replicate determinations. The probable relative error varies from 5.5 to 13.9 % for the concentration range from 83 to 140 ng/cm<sup>3</sup> (Table I).

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

$\mu \times 10^8 \text{ g/cm}^3$	$x \times 10^8 \text{ g/cm}^3$	$n$	$(tS/xn^{1/2})100/\%$	$\frac{x - \mu}{\mu} 100 \%$
8.3	6.98	5	13.9	-15.9
11.1	11.7	5	5.5	+5.4
13.9	13.1	5	5.9	-5.8

where:  $x$  – mean value;  $\mu$  – true value;  $n$  – number of determinations;  $S$  – standard deviation;  $t$  – student's value for 95 % confidence;  $(tS/xn^{1/2})100/$  precision;  $\frac{x - \mu}{\mu} 100$  accuracy.

To assess the selectivity of the method, the influence of the presence of some other ions in the reaction mixture upon the reaction rate under the constant As(III) concentration (111 ng/cm<sup>3</sup>) was investigated. The presence of 100-fold amount of Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Pd(II), Co(II), Ni(II), Al(III), Au(III), As(V), Br<sup>-</sup>, F<sup>-</sup>, I<sup>-</sup>, 10-fold amount of Ca(II), Sr(II), Cu(II), Pb(II), Zn(II), Hg(II), Cd(II), Pt(IV) and phosphates and an equal amount of acetates, has no practical influence on the catalyzed reaction rate. Only the presence of Mn(II) (in the ratio 1:10 to the As(III) concentration) catalyze, while the Mo(VI) (in the ratio 1:10) disturb and Sn(II) (1:10<sup>2</sup>) inhibit this reaction.

#### ИЗВОД

#### КИНЕТИЧКО ОДРЕЂИВАЊЕ As(III) У РАСТВОРУ

СОФИЈА М. РАНЧИЋ\*, РАНГЕЛ П. ИГОВ и ТОДОР Г. ПЕЦЕВ

*Одсек за хемију, ПМФ, Универзитет у Нишу, 18000 Ниш*

Предложена је нова реакција и описана нова кинетичка метода за одређивање трагова As(III) у раствору, на основу њиховог каталитичког дејства на реакцију оксидације комплекса III (КОМ) калијум перманганатом у јако киселој средини (H<sub>2</sub>SO<sub>4</sub>). Применом спектрофотометријске методе, под оптималним условима, постигнута је осетљивост одређивања

од  $7.2 \times 10^{-8}$  g/cm<sup>3</sup> As(III). Релативна грешка методе, за испитивани интервал концентрација, креће се од 5.5 до 13.9 %. Формулисане су одговарајуће кинетичке једначине, а испитан је и утицај присуства других јона у реакционој смеси на брзину основне реакције. Присуство As(V) јона у реакционој смеси не омета одређивање As(III) овом реакцијом.

(Примљено 7. јула 2002, ревидирано 7. маја 2003)

## REFERENCES

1. I. Bano, *Atomic Absorption Spectrometry*, Science, Amsterdam, 1982
2. D. C. Harris, *Quantitative Chemical Analysis*, W. H. Freeman and Co., New York, 1987
3. E. B. Sandell, I. M. Kolthoff, *J. Am. Chem. Soc.* **56** (1934) 1426
4. E. B. Sandell, I. M. Kolthoff, *Microchim. Acta* **9** (1937)
5. A. Lein, N. Schwartz, *Anal. Chem.* **23** (1951) 1507
6. W. Quingzhang, C. Dechang, *Fenxi Huaxue* **9** (1981) 686
7. L. B. Worthington, H. L. Pardue, *Anal. Chem.* **42** (1970) 1157
8. S. S. Mitić, M. V. Obradović, D. S. Veselinović, G. Ž. Miletić, *Latvijas kimijas Žurn.* **1** (1997) 125
9. S. S. Mitić, V. V. Živanović, M. V. Obradović, *J. Serb. Chem. Soc.* **62** (1997) 1011
10. I. I. Koukli, A. C. Calokerionos, *Anal. Chem. Acta* **192** (1988) 333
11. I. I. Alekseeva, L. V. Kurotva, *Zh. Anal. Khim.* **43** (1988) 1449
12. M. S. Garcia, A. Garre, M. I. Albero, C. Sanchez-Pedreno, *Anal. Quim.* **84** (1988) 247
13. E. B. Sandell, M. I. Kolthoff, *Anorganska kvantitativna analiza*, Naučna kwiga, Beograd, 1972 (in Serbian)
14. L. J. Budarin, K. E. Prik, *Zavodskaya Laboratoriya* **26** (1960) 1018
15. K. B. Yatsimirskii, *Kineticheskie metody analiza*, Khimiya, Moskva, 1967 (in Russian).