

## **New indicator reaction for kinetic determination of micro amounts of Sn(II)**

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A new reaction is suggested and a new method is elaborated for determination of micro amounts of Sn(II) based on its inhibiting effect on the oxidation of {4-bis[*n*-(dimethylamino) phenyl ]methylene-2,5-cyclohexadiene-1-ilydene} dimethyl-ammonium chloride (crystal violet CV) by H<sub>2</sub>O<sub>2</sub>. The method sensibility is 0.4 µg/cm<sup>3</sup>. The probable relative error is 2.8–12.8 % for Sn(II) in the concentration interval of 3 to 0.8 µg/cm<sup>3</sup>. The kinetic equation for this process is given. The influence of some other ions on the reaction rate was tested. The method was applied to the determination of Sn(II) in a sample of microalloy.

*Keywords:* tin, kinetic determination, crystal violet.

### INTRODUCTION

As is known, there are not many indicator reactions for the kinetic determination of Sn(II).<sup>1–3</sup> There are only a few methods for the determination of Sn(II) using spectrophotometric method or atomic spectrometry.<sup>4–6</sup> We have observed that the oxidation of crystal violet with H<sub>2</sub>O<sub>2</sub> is strongly inhibited by small amounts of Sn(II). The rate of the reaction decreases proportionally with increasing concentration of Sn(II). This was used as the kinetic method for the determination of micro amounts of Sn(II).

### EXPERIMENTAL

#### *Aparatus*

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±0.1 °C before the beginning of the reaction. The kinetic measurements were performed at a wavelength of 584 nm.

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### Reagents

The hydrogen peroxide solution was  $0.010 \text{ mol/dm}^3$ , its exact concentration being determined by  $\text{KMnO}_4$ .<sup>7</sup> Solutions of  $\text{NaOH}$  ( $0.100 \text{ mol/dm}^3$ ) and  $\text{Na}_2\text{B}_4\text{O}_7$  ( $0.050 \text{ mol/dm}^3$ ) were used for the preparation of the boric buffer.<sup>8</sup> Crystal violet is readily soluble in water and gives a violet blue solution, which remains stable for several weeks. The crystal violet solution ( $1 \times 10^{-3} \text{ mol/dm}^3$ ) was prepared by dissolving an exactly measured amount of the solid substance in deionized water. The basic  $\text{Sn(II)}$  solution ( $1000 \text{ } \mu\text{g/dm}^3$ ) was prepared by dissolving  $1.0000 \text{ g}$   $\text{Sn}$  p.a. purity in  $\text{HCl}$  (conc.), supplemented with deionized water, and standardized volumetrically.<sup>9</sup> Merck analytical grade reagents, deionized water and polyethylene vessels were used throughout.

### Procedure

Selected volumes of the reactants ( $\text{H}_2\text{O}_2$ ,  $\text{Sn(II)}$ , crystal violet, boric buffer and deionized water) were separately measured in a Budarin vessel.<sup>10</sup> The vessel was thermostated for ten minutes at  $25 \pm 0.1 \text{ }^\circ\text{C}$ , then the solution was stirred and the chronometer was put on for one minute during which time the cell was filled with the solution and the spectrophotometric analyse started. The absorbance ( $A$ ) was measured every 30 s within the first ten minutes of the reaction.

The vessels were washed with alcoholic potassium hydroxide and pure hydrochloric acid (1:1) then repeatedly with tap water, distilled water and finally with deionized water.

## RESULTS AND DISCUSSION

### Kinetic studies

A integral variant of the tangent<sup>11</sup> method was used for processing the kinetic data. The reaction rate was followed by the change in the values of the tangent of the angle ( $\tan \alpha$ ) of the slope of the linear part of the kinetic curve to the abscissa in the coordinates  $A-t$ , because  $\tan \alpha = dA/dt$ .

In order to determine the lowest possible determinable concentration of  $\text{Sn(II)}$ , the reaction conditions needed to be optimised. Therefore, the dependencies of the rates of both the indicating and inhibiting reactions on the concentration of each of the reactants were determined.

The effect of pH on the indicating and inhibiting reaction rates is shown in Fig. 1, from which it appears that there is a linear correlation between pH and reaction rate for both the inhibiting and the indicating reaction.

The correlation between  $\tan \alpha$  and crystal violet concentration is shown in Fig. 2. Both reactions are first order with respect to the crystal violet concentration. The optimal concentration of crystal violet was  $5.0 \times 10^{-5} \text{ mol/dm}^3$ . The difference of the reaction rates for both reactions in this range is almost the same. In the presence of  $5.0 \times 10^{-5} \text{ mol/dm}^3$  crystal violet all the measured values of the absorbance lay within the range 0.2 to 0.8, which is the range of highest accuracy for spectrophotometric determinations.<sup>12</sup>

The dependance of the reaction rate on the concentration of hydrogen peroxide is shown in Fig. 3, from which it can be seen that both reactions are first order with respect to the hydrogen peroxide concentration. For further work a hydrogen peroxide concentration of  $3.26 \times 10^{-3} \text{ mol/dm}^3$  was chosen for the same reasons as the concentration of crystal violet was chosen.

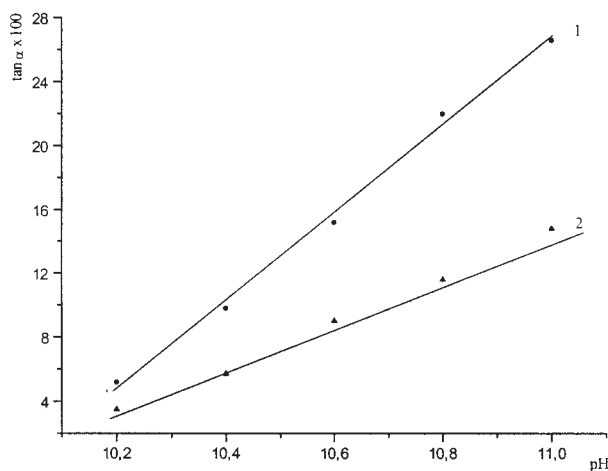


Fig. 1. Dependence of  $\tan \alpha$  on pH for the indicating (1) and inhibiting (2) reaction. Initial conditions:  $c(\text{CV}) = 5 \times 10^{-5} \text{ mol/dm}^3$ ;  $c(\text{H}_2\text{O}_2) = 3.26 \times 10^{-3} \text{ mol/dm}^3$ ;  $c(\text{Sn(II)}) = 2 \text{ } \mu\text{g/cm}^3$ ;  $t = 25 \pm 0.1 \text{ } ^\circ\text{C}$ .

In such a way, the optimal conditions for this reaction were found: pH 10.6,  $c(\text{H}_2\text{O}_2) = 3.26 \times 10^{-3} \text{ mol/dm}^3$ ,  $c(\text{CV}) = 5 \times 10^{-5} \text{ mol/dm}^3$ . Under these optimal conditions Sn(II) in the concentration intervals of 0.4 to  $3 \text{ } \mu\text{g/cm}^3$  could be determined.

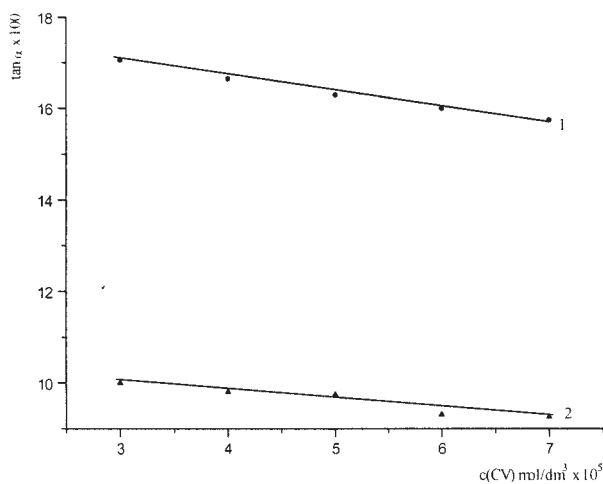


Fig. 2. Dependence of  $\tan \alpha$  on the crystal violet concentration for the indicating (1) and inhibiting (2) reaction. Initial conditions: pH 10.6;  $c(\text{H}_2\text{O}_2) = 3.26 \times 10^{-3} \text{ mol/dm}^3$ ;  $c(\text{Sn(II)}) = 2 \text{ } \mu\text{g/cm}^3$ ;  $t = 25 \pm 0.1 \text{ } ^\circ\text{C}$ .

Two calibration lines, obtained at different temperatures, are shown in Fig. 4, which can be used for the determination of Sn(II) in the above-mentioned concentration interval.

The kinetic equations for the investigated process were deduced on the basis of the graphic correlations obtained. They refer to the investigated concentration of  $\text{H}_2\text{O}_2$  from  $1.63 \times 10^{-3}$  to  $3.26 \times 10^{-3} \text{ mol/dm}^3$ ,  $c(\text{CV})$  from  $3.0 \times 10^{-5}$  to  $7.0 \times 10^{-5} \text{ mol/dm}^3$ , pH from 10.2 to 10.6 and  $c(\text{Sn(II)})$  from 0.4 to  $3 \text{ } \mu\text{g/cm}^3$ .

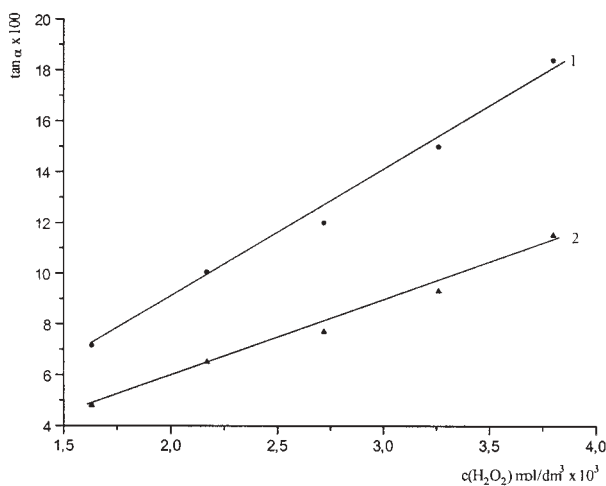


Fig. 3. Dependence of  $\tan \alpha$  on the  $\text{H}_2\text{O}_2$  concentration for the indicating (1) and inhibiting (2) reactions. Initial conditions:  $c(\text{CV}) = 5 \times 10^{-5} \text{ mol/dm}^3$ ; pH 10.6;  $c(\text{Sn(II)}) = 2 \text{ } \mu\text{g/cm}^3$ ;  $t = 25 \pm 0.1 \text{ } ^\circ\text{C}$ .

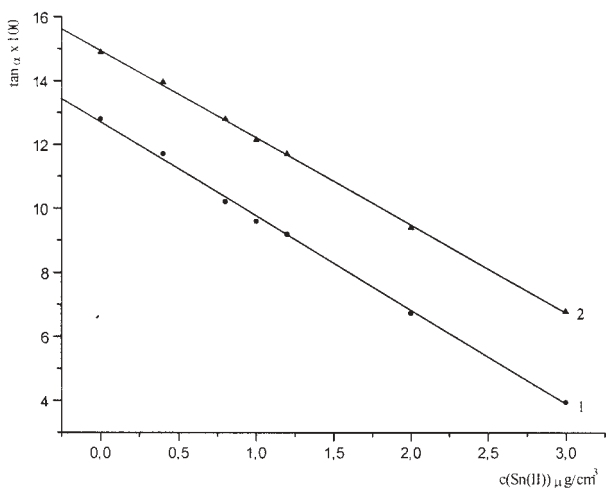


Fig. 4. Dependence of  $\tan \alpha$  on the  $\text{Sn(II)}$  concentration for the inhibiting reaction. Initial conditions:  $c(\text{CV}) = 5 \times 10^{-5} \text{ mol/dm}^3$ ;  $c(\text{H}_2\text{O}_2) = 3.26 \times 10^{-3} \text{ mol/dm}^3$ ; pH 10.6; 1.  $t = 20 \pm 0.1 \text{ } ^\circ\text{C}$ ; 2.  $t = 25 \pm 0.1 \text{ } ^\circ\text{C}$ .

For the indicating reaction the kinetic equation is:

$$-dc(\text{CV})/dt = k c(\text{H}_2\text{O}_2) c(\text{CV})$$

and for the inhibiting reaction:

$$-dc(\text{CV})/dt = k_1 c(\text{H}_2\text{O}_2) c(\text{CV}) c(\text{Sn(II)})^{-1}$$

where  $k$  is a constant proportional to the rate constant of the indicating reaction and  $k_1$  is a constant proportional to the rate constant of the inhibiting reaction.

The accuracy and precision of the determination of  $\text{Sn(II)}$  were examined. The results, shown in Table I, were calculated using calibration line 2 (Fig. 4). It can be seen that the relative error was 2.8 to 12.8 % for  $\text{Sn(II)}$  in the concentration range from 0.8 to  $3 \text{ } \mu\text{g/cm}^3$ .

TABLE I. Accuracy and precision of Sn(II) determination

Taken $\mu/(\mu\text{g}/\text{cm}^3)$	Found $x/(\mu\text{g}/\text{cm}^3)$	$n$	$s \times t \times 100 / (x \times \sqrt{n})$	$[(x - \mu/\mu)] \times 100 \%$
3.00	3.02	5	2.8	0.7
2.00	1.90	5	4.4	-4.8
0.80	0.78	5	12.8	-2.1

$x$  – mean value;  $\mu$  – true value;  $n$  – number of determination;  $s$  – standard deviation;  $t$  – Student's  $t$  for 95 % confidence

To assess the selectivity of the method, the influence of a large number of extraneous ions on the inhibiting reaction rate was examined. At a constant Sn(II) concentration of  $1.0 \mu\text{g}/\text{cm}^3$ , the presence of 100-fold amounts of:  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , and 10-fold amounts of:  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$  and the equal amounts of  $\text{Bi}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Cu}^{2+}$  has no practical influence on the inhibiting reaction.  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Sb}^{3+}$  (1:1 ratio) inhibits the reaction very strongly.

The method was directly applied to the determination of Sn(II) in a sample of microalloy. A sample of microalloy (0.1000 g) was added in  $10.00 \text{ cm}^3$  HCl (1:1), and the solution was heated. After the microalloy had completely dissolved, the solution was diluted with distilled water if necessary depending on the Sn(II) content.

TABLE II. Determination of Sn(II) in a sample of microalloy

Sn(II) Proposed method/%	Sn(II) AAS method/%	$[(x - \mu/\mu)] \times 100 \%$
0.31		
0.27		
0.33	0.32	-5.00
0.32		
0.29		

$x$  – mean value;  $\mu$  – AAS value

The tangent method was applied for the determination of Sn(II) in the solution specified above, and the results are shown in Table II.

## ИЗВОД

### НОВА ИНДИКАТОРСКА РЕАКЦИЈА ЗА КИНЕТИЧКО ОДРЕЂИВАЊЕ МИКРО КОЛИЧИНА Sn(II)

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Предложена је нова реакција и дата нова кинетичка метода за одређивање ултра-микро количина Sn(II) на бази њиховог инхибиторског дејства на оксидацију {4-бис[ $n$ -(диметиламино) фенил]метиле-2,5-циклохексадиен-1- $n$ -илиден} диметиламонијум-хлорида (кристал виолет) водоник-пероксидом. Осетљивост методе је  $0,4 \mu\text{g}/\text{cm}^3$ . Вероватна

релативна грешка је 2,8–12,8 % за интервал концентрација Sn(II) од 0,8–3  $\mu\text{g}/\text{cm}^3$ . Изведене су одговарајуће кинетичке једначине. Испитан је утицај већег броја страних јона на брзину реакције. Метода је примењена за анализу узорка микролегура.

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