KINETIC DETERMINATION
OF ULTRAMICRO AMOUNTS OF THIOCYANATE

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Abstract. *A kinetic method is suggested for determing traces of thiocyanate on the basis of their activating effect on the Fe(III) catalysis of oxidation of 4-amino-N,N-diethylaniline sulphate (ANNS) by hydrogen-peroxide. The sensitivity of the method is 50 ng/cm³. The probably relative error ranges beetwen 5,5-10,5% for concentration interval 300-70 ng/cm³ NCS⁻. Kinetic equation were proposed for the investigated process. The method has relatively good selectivity.*

Key words: *thiocyanate, kinetic determination, 4 – amino - N, N - diethylaniline sulphate*

INTRODUCTION

Only a small number of indicator reactions for the kinetic determination of thiocyanate by photometric method are known [1-3]. Their sensitivity ranges from about 0,2-6 ng/cm³. Bat, all these methods have relatively low selectivity.

Previously the kinetic method is suggested for the determination of ultramicro amounts of Fe(III) on the basis of its catalytic activity in oxidation of ANNS by hydrogen-peroxide[4]. We have observed that small amounts of thiocyanate activat the catalysis of this reaction by Fe(III). The rate of the reaction increases proportionally with increasing concentration of thiocyanate, and this is used as the basis of kinetic method for determination ultramicro amounts of thicyanate, in the range 50-500 ng/cm³.

EXPERIMENTAL

As the reaction product is colored the rate is followed photometrically. The dependence of the absorbance (A) on time (t) was measured using a Perkin-Elmer Lambda 15 spectrophotometer, equipped with a thermostat system. The pH was measured with a Radiometer PHM 29b pH-meter and combined glass-calomel electrode.

The solutions were thermostated at $22\pm0,1^oC$ before the beginning of the reaction. The kinetic measurements were performed at a wavelenght of 515 nm.

Hydrogen peroxide (1.000 mol/dm^3) was prepared from the 30% reagent. Acetic acid and sodium hydraxide were used for the preparation of acetate buffers[5]. ANNS solution ($1\cdot10^{-2}$ mol/dm^3) was made by direct weighing of the solid. Fe(III) solution (1 µg/cm^3) was prepared from a more concentrated $FeCl_3\cdot6H_2O$ solution and standardized volumetrically. NCS$^-$ solution (1 µg/cm^3) was prepared from a more concetrated KNCS solution and standardized volumetrically. Merck analytical grade reagents deionized water and polyethylene vessels were used throughout.

The selected volumes of reactants were put into a 50-cm^3 standard flask, in the order ANNS, pH 4,8 buffer (5cm^3), Fe(III), NCS$^-$, and water to make up a predetermined volume. The flask was kept in the thermostat for 5 min, then the solution was made up to the mark with hydrogen peroxide and water and vigorously shaken, and the stopwatch was started. The working cell of the colorimeter was first rinsed and then filled with the solution. The absorbance was measured every 30 sec over a period of 5-10 min after the hydrogen peroxide was added.

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

The initial concentration of the reagent solutions after the dilution to 50 cm^3 were: $1\cdot10^{-2}$ - $3,5\cdot10^{-2}$ mol/dm^3 H_2O_2, $1\cdot10^{-4}$ - $7\cdot10^{-4}$ mol/dm^3 ANNS, 50-500 ng/cm^3 NCS$^-$. The concentration of Fe(III) during all measurements was constant 50 ng/cm^3.

The measurements were made at $22\pm0,1^oC$ and also at $26\pm0,1^oC$.

RESULTS AND DISCUSSION

The differential variant of the tangent method was used for processing the kinetic data, because there is a linear relation between the absorbance and time during the first 5-10 min[6].
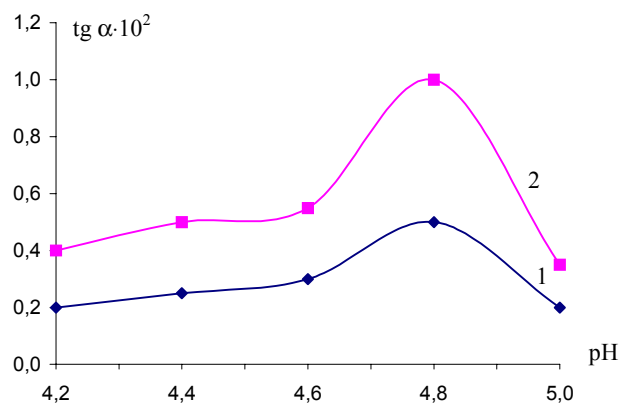

Fig. 1. Dependence of the reaction rate on pH. Initial conditions: $5\cdot10^{-4}$mol/dm^3 ANNS; 0,03 mol/dm^3 H_2O_2; 50ng/cm^3 Fe(III); 500 ng/cm^3 NCS$^-$; 1 – inactivated reaction, 2 – activated reaction.

The effect of pH on the activated and inactivated reaction rates is shown in Fig.1. From Fig.1, it appears that there is a complicated relationships between pH and reaction rate, i.e., the order reaction is variable with respect to hydrogen-ion concentration for the range of concentrations studied. For further work pH of 4,8 was chosen for quantitative applications.
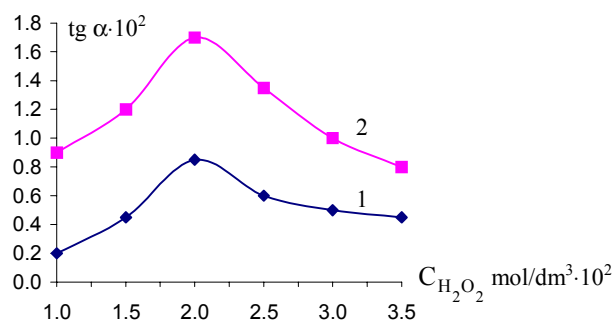

Fig. 2. Dependence of the reaction rate on H_2O_2 concentration. Initial conditions:
$5 \cdot 10^{-4}$mol/dm^3 ANNS; pH = 4,8; 50 ng/cm^3 Fe(III); 500 ng/cm^3 NCS$^-$;
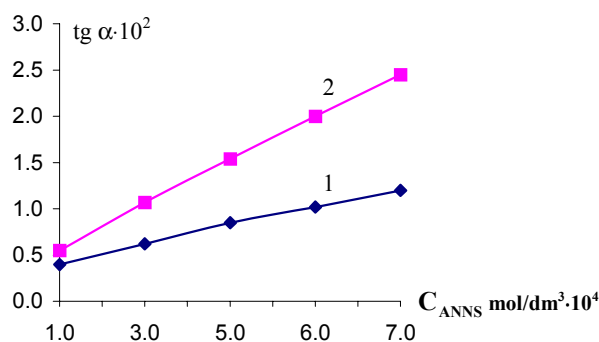1 – inactivated reaction, 2 – activated reaction

Fig.3. Dependence of the reaction rate on ANNS concentration. Initial conditions:
0,02 mol/dm^3 H_2O_2; pH = 4,8; 50 ng/cm^3 Fe(III); 500 ng/cm^3 NCS$^-$;
1 – inactivated reaction, 2 – activated reaction

The dependence of the reaction rates on concentration of H_2O_2 is shown in Fig. 2. From Fig. 2. it appears that there is a complicated relationships between $C(H_2O_2)$ and reaction rate, i.e., the reaction order is variable with respect to H_2O_2 concentration for the ranges of concentrations studied. For further the concentrations of 0,02 mol/dm^3 H_2O_2 was chosen.

The dependence of tg α on ANNS concentration is shown in Fig. 3, which shows that with increasing ANNS concentration the difference in the rates of the activated and inactivated reaction increases.

Both reactions are of first order with respect to the ANNS concentration. For further work an ANNS concentration of $6 \cdot 10^{-4}$ mol/dm^3 was selected, because with higher concentrations the linear part of the kinetic curve (A – t) is rather shortened.

Under conditions of reaction, $C(H_2O_2) = 0,02$ mol/dm^3, $C(ANNS) = 6 \cdot 10^{-4}$ mol/dm^3, pH = 4,8 the NCS-concentration was varied from 50 to 500 ng/cm^3. Fig. 4. shows the two calibration lines which can be used for determination of NCS$^-$ concentration in the interval mentioned. The detection limit is 12 ng/cm^3 NCS$^-$.
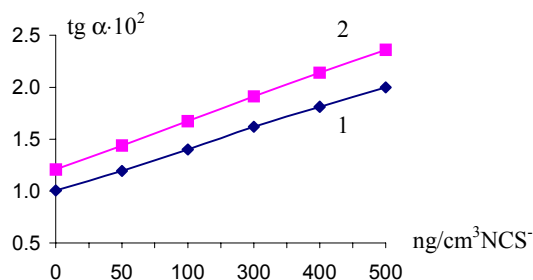

Fig. 4. Dependence of the reaction rate on NCS$^-$ concentration. Initial conditions:
    $6 \cdot 10^{-4}$ mol/dm^3 ANNS; 0,02 mol/dm^3 H$_2$O$_2$; pH = 4,8; 50 ng/cm^3 Fe(III);
    1 – for 22°C, 2 – for 26°C

The relationship between the reaction rates and the concentrations of the reacting components can be explained by the following equations (at constant pH).
For the activated reaction,

$$\frac{dC}{dt} = k \cdot C_{H_2O_2}^x \cdot C_{ANNS} \cdot C_{NCS^-} \tag{1}$$

where x is a variable and k is constant proportional to the rate constant of the activated reaction.

For the inactivated reaction,

$$\frac{dC}{dt} = k_0 \cdot C_{H_2O_2}^y \cdot C_{ANNS} \tag{2}$$

where y is a variable and k_0 is constant proportional to the rate constant of the inactivated reaction.

The accuracy a precision are presented in Table 1. The probably relative error ranges from 5,5-10,5% for NCS$^-$ concentrations from 300-70 ng/cm^3. The method has relatively good accuracy.

The assess selectivity of the method, the influence of several foreign ions on the activated reaction rate was investigated, at constant NCS$^-$ concentration of 400 ng/cm^3. The presence (individually, in the ratio to NCS$^-$ that is given in brackets) of NH_4^+, K^+, Cl$^-$, SO_4^{2-} (10^3:1), Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, y$^-$ (1:1) has practically no influence on the reaction rate. Cu^{2+} (0,1:1) catalyse the reaction and Hg^{2+}, Sn^{2+}, PO_4^{3-}, $C_2O_4^{2-}$, $H_4C_4O_6^{2-}$, citrate, EDTA (0,1:1) have a inhibiting effect.

Table 1. Accuracy and precision of NCS⁻ determination

Taken (ng/cm^3)	Found (ng/cm^3)	n	$\dfrac{100 \cdot t \cdot s}{\bar{x} \cdot \sqrt{n}}\,(\%)$	$\dfrac{\bar{x} - \mu}{\mu} \cdot 100\,(\%)$
300	305	5	5,5	+1,7
200	194	5	10,2	−3,0
70	74	5	10,5	+5,7

$\bar{x}$ - mean value; μ - true value; s – standard deviation;
t – Student's for 95% confidence; n – number of determination.

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KINETIČKO ODREĐIVANJE
ULTRAMIKRO KOLIČINA TIOCIJANATA

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Predložena je nova kinetička metoda za određivanje tragova tiocijanata na bazi njegovog aktivatorskog dejstva na reakciju oksidacije 4-amino-N, N-dimetilanilin sulfata vodonikperoksidom u prisustvu Fe(III) kao katalizatora. Osetljivost metode iznosi 50 ng/cm^3 NCS⁻.

Verovatna relativna greška se kreće od 5,5 – 10,5% za interval koncentracija od 300 – 70 ng/cm^3 NCS⁻. Predložene su kinetičke jednačine za proučavani proces. Metoda ima relativno dobru selektivnost.

Ključne reči: *tiocijanat, kinetičko određivanje, 4-amino-N,N-dimetilanilin sulfat*