Photometric Determination of Copper(II) by the Catalytic Action on the Reaction of Iron(III) Reduction with Thiosulfate Ion

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Abstract—A procedure is proposed for the kinetic determination of copper(II) by its catalytic effect on the reduction of iron(III) with thiosulfate ion, followed by the photometric detection of the destruction of iron(III) thiocyanate. The optimal reaction conditions were selected. The limit of determination of copper(II) is 0.06 $\mu g/cm^3$; and the relative error of determination is 4%. The results are characterized by good convergence and accuracy. The procedure is applicable for the quantitative determination of copper(II) in water.

Among the pollutants entering the environment, heavy metals, including copper, are the most dangerous [1]. Possible sources of pollution of the biosphere with copper compounds are, first, nonferrous metallurgy enterprises (aerosol emissions, industrial effluents, polluting surface waters) and mechanical engineering (galvanic copper plating baths). Therefore, environmental protection assumes constant analytical monitoring of environmental objects. Chronic poisoning with copper salts is accompanied by disorders of the nervous system, liver, and kidneys. An excess of copper leads to a deficiency of zinc and molybdenum [2, 3]. Copper not only has a negative effect, it is also involved in cellular respiration and the absorption of iron [4]. Copper deficiency leads to the development of diseases of the respiratory system, musculoskeletal system, blood, and pathologies of the immune system [5].

For the determination of copper(II), spectrophotometric methods of analysis using organic reagents [6] are widely used in combination with the preconcentration of the element to be determined [7]. A decrease in the detection limit and an increase in selectivity can be achieved using kinetic-catalytic methods [8].

This study aims to study the optimal conditions for determining trace amounts of copper(II) without preliminary isolation and preconcentration and find the range of determined concentrations and metrological characteristics of the procedure.

EXPERIMENTAL

Reagents and solutions. To obtain a stock copper solution (1250 $\mu g/cm^3$), 0.4860 g of $CuSO_4 \cdot 5H_2O$ was dissolved in a 100-cm^3 volumetric flask and diluted up to the mark with distilled water. An iron(III) chloride solution (0.23 mol/dm^3) was prepared by dissolving 31.1080 g of $FeCl_3 \cdot 6H_2O$ in distilled water acidified with hydrochloric acid in a 500-cm^3 volumetric flask. To prepare a sodium thiosulfate solution (0.004 mol/dm^3), 0.4690 g of $Na_2S_2O_3 \cdot 5H_2O$ was dissolved in distilled water (with the addition of 0.1 g of sodium carbonate for stabilization) in a 500-cm^3 volumetric flask. A potassium thiocyanate solution (0.145 mol/dm^3) was prepared by dissolving 3.5160 g of KSCN in distilled water in a 250-cm^3 volumetric flask. A potassium bromide solution (0.2 M in a 0.1 M solution of H_2SO_4) and solutions of sodium hydroxide (1 mol/dm^3) and hydrochloric acid (1 : 2) were prepared using distilled water. Working solutions with a lower concentration were prepared by the appropriate dilution of the stock solutions with distilled water. All the reagents were of analytical grade or cp grade.

Equipment. A PE-5300V spectrophotometer was used for the photometric monitoring of the reaction; a pH-150MI pH meter was used to control the acidity of solutions. Coulometric titration was performed using a P-5827 M potentiostat.

RESULTS AND DISCUSSION

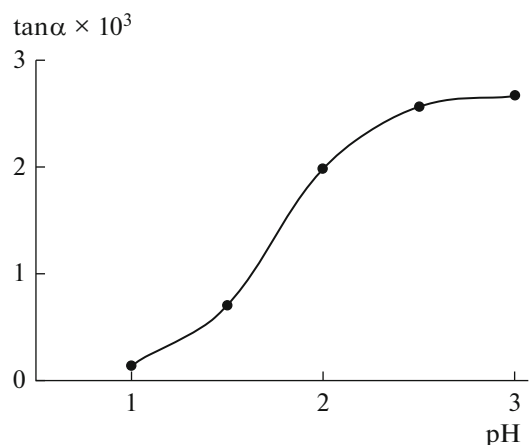The reaction between iron(III) and thiosulfate ions, catalyzed by copper salts, proceeds according to the equation

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{2+} + S_4O_6^{2-}.$$
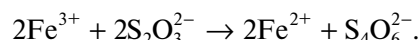
Fig. 1. Dependence of the slope of the kinetic curves on pH; $c(Cu^{2+}) = 1.5$ Mg/cm^3; $c(Na_2S_2O_3) = 8.0 \times 10^{-4}$ M; $c(FeCl_3) = 6.9 \times 10^{-3}$ M; $c(KSCN) = 1.45 \times 10^{-2}$ M; $\lambda = 450$ nm; $l = 10$ mm, pH 1.0–3.5.

Iron ions are indicated by adding potassium thiocyanate to the solution. In the reaction time, the colored complex of iron(III) with thiocyanate ion is destroyed. The reaction rate is determined by the decrease in the absorbance of the solution.

Effect of acidity. To study the effect of the medium on the reaction rate, kinetic curves $A = f(t)$ were plotted at different pH values, where A is the absorbance, t is the time; $c(Cu^{2+}) = 1.5$ µg/cm^3; $c(Na_2S_2O_3) = 8.0 \times 10^{-4}$ M; $c(FeCl_3) = 6.9 \times 10^{-3}$ M; $c(KSCN) = 1.45 \times 10^{-2}$ M; $\lambda = 450$ nm; and $l = 10$ mm, pH 1.0–3.5. The pH of the medium was adjusted with solutions of hydrochloric acid (1 : 2) and sodium hydroxide (1 M). A graph of the dependence of the slope of the kinetic curves on the medium pH was constructed (Fig. 1).

The optimum value of the medium acidity for the quantitative determination of copper(II) ions is 2.5–3.0. In strongly acidic media (pH 1.0–1.5), the reduction reaction rate decreases due to the instability of the thiosulfate ion. At pH 3.5, the iron(III) thiocyanate complex is destroyed, and iron is precipitated in the form of hydroxide.

Effect of the concentrations of reagents. To find out the optimal values of the concentration of reagents, we recorded the change in absorbance over time upon varying their concentrations. The obtained kinetic data were presented in the form of kinetic curves in the coordinates log $(A_0/A) - t$, where A_0 is the absorbance at the initial moment. The optimal concentrations of the reagents after dilution were as follows: 8×10^{-4} M for sodium thiosulfate, 3.45×10^{-3} M for iron(III) chloride, and 1.16×10^{-2} M for potassium thiosulfate. The reaction rate strongly depends on the concentration of Fe^{3+} ions; therefore, when analyzing real objects, it is necessary to determine the concentration of iron(III) and take into account its concentration in the sample with the addition of iron(III) chloride.

Calibration curves. Kinetic analysis methods are based on the correlation between the analytical signal and the concentration of the analyte. There are four methods of kinetic data processing: the tangent method, fixed time method, fixed concentration method (or any other proportional value), and the method based on the duration of the induction period [8]. The latter method cannot be applied under the conditions of this procedure. We performed a series of measurements to select the most optimal method for constructing the calibration graphs. Analysis of the results (Table 1) allows us to conclude that it is preferable to use the tangent method since the range of linearity of the copper concentration is wider (0.06–3.50 µg of copper(II)/cm^3) in comparison with the results of other methods.

Study of the interfering effect of foreign ions. To study the interfering effect of some ions contained in water on the determination of copper, we recorded the kinetic curves and determined the known amount of copper in the presence of an interfering ion by the tangent method. If the introduced amount of a foreign ion does not lead to a determination error of more than 5%, then we can assume that this ion does not interfere. The results are presented in Table 2. Ions Ca^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, Cr^{3+}, and Cr^{6+} are interfering, as they violate the accuracy of the copper determination. Aqua complexes of nickel(II), cobalt(II), and chromium(III) have their own color; chromium(VI) oxidizes thiosulfate ions. The rest of the ions participate in competing reactions with anions in water.

Assessment of performance of the procedure. To assess the metrological characteristics of the proposed technique, we analyzed a series of solutions with the same concentration of copper(II) ions. The detection limit is 0.06 µg/cm^3, the relative error is 4%, the accuracy is 0.074 µg/cm^3, and the repeatability is 0.195 µg/cm^3 ($n = 6$, $P = 0.95$).

Table 1. Comparison of the methods for constructing the calibration graph

Method	Approximation coefficient	Concentration linearity range, µg/cm^3
Tangent method	0.995	0.06–3.50
Fixed time method	0.953	0.06–0.75
Fixed value method	0.951	0.35–2.00

Table 2. Amount of foreign ions interfering with the determination of copper(II)

Salt	Ion	$C(\text{ion})/C(\text{Cu}^{2+})_{\text{added}}$
KCl	K^+	640
NaCl	Na^+	420
$CaCl_2$	Ca^{2+}	50
$MnCl_2 \cdot 4\,H_2O$	Mn^{2+}	25
$Pb(NO_3)_2$	Pb^{2+}	25
$ZnSO_4 \cdot 7\,H_2O$	Zn^{2+}	20
$MgSO_4 \cdot 7\,H_2O$	Mg^{2+}	20
$Al_2(SO_4)_3 \cdot 18\,H_2O$	Al^{3+}	20
$NiSO_4 \cdot 7\,H_2O$	Ni^{2+}	12
$CoCl_2 \cdot 6\,H_2O$	Co^{2+}	10
$CrCl_3 \cdot 6\,H_2O$	Cr^{3+}	10
$K_2Cr_2O_7$	Cr^{6+}	9

Table 3. Results of the determination of copper(II) by various methods in the water of the Argazinsky reservoir ($n = 5$; $P = 0.95$)

Method used and amount of copper found (mg/L)		
kinetic method	coulometry	photometry
1.97 ± 0.06	2.05 ± 0.07	1.93 ± 0.12

Proposed procedure. In a 50-cm^3 volumetric flask, 10.0 cm^3 of a 0.004 M sodium thiosulfate solution, 2.5 cm^3 of a 0.0069 M solution of iron(III) chloride, and 4.0 cm^3 of a 0.145 M potassium thiosulfate solution are placed; and the pH value is adjusted to 2.5−3.0 upon control of a pH meter. Then, 25 cm^3 of the test water is added, and the total volume of the solution is brought to the mark with distilled water. After stirring, the solution is transferred to the spectrophotometer cuvette, and its absorbance is measured at regular 10-min intervals at a wavelength of 450 nm against a solution containing distilled water. The measurement data yielded a graph plotted in coordinates $\log(A_0/A) - t$ (time in s), where A_0 is the absorbance at the initial moment, and the slope of the straight line is measured. The concentration of copper is determined by the calibration graph plotted in the coordinates of the straight line's slope−the copper concentration. To build a calibration graph, several measurements are carried out with different volumes of a standard solution of copper sulfate (the copper concentration in the solution after all dilutions should be in the range from 0.06 to 3.5 µg/cm^3).

The technique was used to analyze water from the Argazinsky reservoir (Chelyabinsk region). The data obtained are compared with the results obtained using photometry and coulometry (Table 3). The results obtained by different methods agree well with each other.

Thus, the proposed procedure has a sufficient detection limit and good accuracy and repeatability for the kinetic determination of copper(II) in the water of various origins.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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