Determination of Silver Traces in Pure Metallic Copper and Zinc by a Catalytic Photometric Method

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Determination of silver traces in the presence of copper, zinc and sulphate ions by a catalytic method was studied. The highly sensitive method of silver determination is based on the catalytic effect of silver ions on the oxidation of salicylic acid by persulphate in the presence of 2,2'-dipyridyl as an activator. The reaction was followed spectrophotometrically by measuring the rate of change in absorbance with time at 420 nm after 10 min of reagents mixing. The sensitivity, precision and accuracy of the determination of silver traces were investigated in solutions containing excesses of interfering ions. The studied range of interfering ions concentrations was 8×10^{-6} to 2.4×10^{-2} mol dm^{-3} and corresponds to an amount ratio of interfering to silver ions from 50 to 150 000. The performed analyses showed that the accuracy and precision of silver trace determination by the proposed method is high even in the presence of a huge amount excess of interfering ions. The method was used for quantitative determination of silver contents in a copper foil and in a zinc rod. The obtained results were compared with the analyses performed by FAAS.

INTRODUCTION

The ultra-pure copper foil produced by electrorefining usually contains a few µg g^{-1} of silver. This content of silver modifies significantly the physical properties of metallic copper, *e.g*., electrical and thermal conductivity, resistance to corrosion, plastic behaviour.[1] Hence, the development of a simple method for determination of silver in copper or other metallic materials is highly desirable.

Trace amounts of silver can be directly determined in various matrices by inductively coupled plasma mass spectrometry (ICP-MS),[2,3] inductively coupled plasma atomic emission spectrometry (ICP-AES)[4] or electrothermal atomic absorption spectrometry (ETAAS).[5,6] These methods, however, require expensive analytical instrumentation. Flame atomic absorption spectrometry (FAAS)

is effectively used for quantitative determination of silver, but its detection limit is only about 0.1 mg dm^{-3} in the presence of a huge excess of matrices. A very sensitive spectrophotometric method used for silver determination in the trace range of concentrations (several ng cm^{-3}) is described in our paper.[7] The method is based on the catalytic action of Ag$^+$ ion in the oxidation of salicylic acid by ammonium persulphate in the presence of 2,2'-dipyridyl as an activator.

The aim of this paper is to study the effects of copper, zinc and sulphate ions concentrations on silver trace determination in samples containing a large excess of interfering ions. Special emphasis is laid on the accuracy, precision and sensitivity of silver determination in the presence on interfering ions.

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EXPERIMENTAL

The procedure of glassware pre-treatment before use and preparation of basic solutions were described in our previous paper.[7] Solutions used for the interference study of copper or zinc ions were prepared on the base of copper or zinc sulphates. The interfering effect of SO_4^{2-} ion was investigated in a sulphuric acid solution.

Basic solutions used for the preparation of the sample were kept at (40 ± 0.1) °C. The sample for the study was prepared in the following manner: 2 cm^3 of a solution containing the interfering ion was added into a 25 cm^3 measuring flask, then 0.5 – 4.5 cm^3 of 2×10^{-6} mol dm^{-3} AgNO$_3$ (only for the calibration curve), 0.8 cm^3 of 8×10^{-3} mol dm^{-3} 2,2'-dipyridyl, 3 cm^3 of 0.44 mol dm^{-3} ammonium persulphate and 3 cm^3 of 0.03 mol dm^{-3} salicylic acid were added. The mixture was filled up to 25 cm^3 with the buffer solution to adjust pH to 5.0, mixed and placed in a thermostatic bath for 10 min at a temperature of (40 ± 0.1) °C. The solution was then cooled in a water-ice mixture for 5 min and absorbance was measured at 420 nm using the buffer solution as a reference. Five cm path length quartz cells were used. In the interference study, copper or zinc ions were quantitatively masked with EDTA before putting them into the reaction flask. Optionally, for samples with the highest concentration of Cu^{2+} or Zn^{2+} ion (0.2 mol dm^{-3}), an additional volume of 0.1 mol dm^{-3} EDTA was introduced to mask completely the interfering ions.

A few 0.5 g samples of a copper foil and a zinc rod were dissolved in 100 cm^3 hot 1:1 HNO$_3$. Solutions were analyzed by the proposed and FAAS methods after proper dilutions.

RESULTS AND DISCUSSION

Characteristics of the Analytical Method

Corrected molar absorptivity, (ε_c), and molar absorptivity, (ε), for silver traces determination by the proposed method were calculated on the basis of seven identical measurements in the solution containing 1.6×10^{-7} mol dm^{-3} of Ag$^+$ ion. The estimated values of molar apsorption coefficients ε and ε_c were $(6.95 \pm 0.31) \times 10^5$ and $(6.83 \pm 0.34) \times 10^5$ dm^3 mol^{-1} cm^{-1}, respectively. It is worth noticing that ε and ε_c were calculated for the fixed time method and cannot be identified with real molar absorptivity. However, experimental values of ε and ε_c are consistent with molar absorptivities for a reaction based on the catalytic effect.[8] Moreover, they are also one order of magnitude higher than the ones observed for reactions based on the formation of binary or ternary complexes.[9–11] The relative absorbance of 7–9 samples was plotted against silver ion concentrations (mol dm^{-3}) and used as a calibration curve. The average slope of calibration curves over the range of silver ion concentrations from 4.3 to 38.8 ng dm^{-3} was calculated in order to express the sensitivity of the method. The obtained value was $(3377 \pm 74) \times 10^3$. To characterize the precision of the method, analyses of
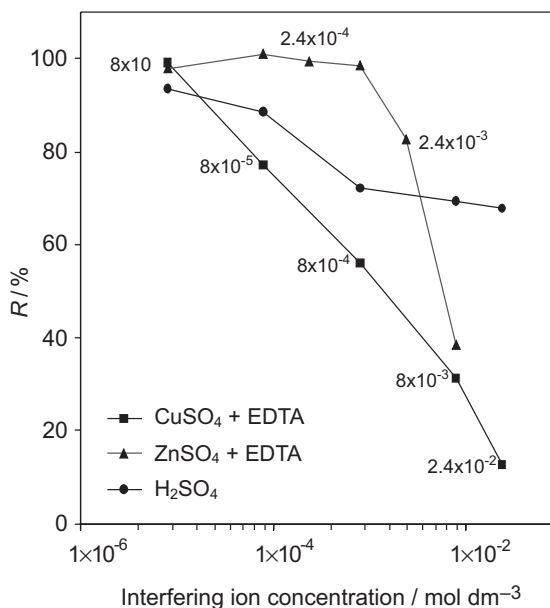

Figure 1. Reduced coefficient of sensitivity for various concentrations of interfering ions.

silver content in a standard silver solution containing 1.6×10^{-7} mol dm^{-3} Ag$^+$ were performed. The results of eight independent analyses gave the value of 1.67×10^{-7} ($\pm 8.22 \times 10^{-10}$) mol dm^{-3} of Ag$^+$ ion. The error of accuracy calculated from eight independent analyses performed for the standard silver solution was 4.4 %. The established detection and determination limits were 3.56×10^{-9} mol dm^{-3} and 7.12×10^{-9} mol dm^{-3} of Ag$^+$, respectively.[7]

Interference Study and Real Samples Analyses

The sensitivity, precision and accuracy of the analytical method were examined in the presence of copper, zinc or sulphate ions masked with EDTA. The studied range of the interfering ion concentration ranged from 8×10^{-6} to 2.4×10^{-2} mol dm^{-3} and corresponds to the amount excess ("molar excess") of the interfering ion from 50 to 150 000. Amount excess of the interfering ion, (E), was defined as the ratio of amount concentrations of interfering and silver ions. For each interfering ion concentration, five calibration curves, plotted as absorbance $vs.$ Ag$^+$ ion concentration, were examined.

The reduced coefficient of sensitivity, (R), defined as the ratio of the average slope of calibration curves for the interfering ion masked with EDTA to the average slope of calibration curves for samples without the interfering ion, was calculated for each studied concentration of interfering ions. The results are presented in Figure 1. For solutions containing only H$_2$SO$_4$ as the interference agent, the sensitivity of the method decreases slightly with increasing concentration of the sulphate ion. This can be attributed to the effect of decreasing molar absorptivity with increasing ionic strength of the solution. In the case when copper ions are present in the solution, a

monotonic decrease in sensitivity of the method is observed with increasing concentration of the interfering ion. For zinc ions, the sensitivity of silver determination remains almost constant up to a zinc ion concentration of 8×10^{-4} mol dm^{-3}, but the sensitivity of the method decreases drastically for higher concentrations. This decrease is so sharp that at a concentration of 2.4×10^{-2} mol dm^{-3} ZnSO$_4$ calibration curves lose their linearity and determination of silver becomes impossible. Different interfering effects of copper and zinc ions in solutions containing the highest concentration of these ions can be explained by the lower masking efficiency of the zinc ion than the copper ion masked with EDTA at pH = 5.0.[12]

To evaluate the precision of silver determination at various interfering ion contents, five samples containing a constant concentration of silver ion (1.6×10^{-7} mol dm^{-3}) and varying excess of the interfering ion were assayed. For each amount excesses of interfering ions, at least 7 analyses of silver contents were performed and relative standard deviations were calculated (Table I). The data collected in Table I show that the average relative standard deviation ($\overline{RSD}$) increases with increasing concentration of the copper ion, with one exception at the concentration of 8×10^{-3} mol dm^{-3}. These results suggest that the precision of silver determination in the presence of copper ions decreases slightly with increasing concentration of the copper ion. The precision of silver determination is very good in the range of copper ion concentrations between 8×10^{-6} and 8×10^{-3} mol dm^{-3}. For higher copper ion contents, the precision of silver determination is significantly reduced. For the case when zinc or sulphate ions are present in the solution, the precision of silver determination is satisfactory for the whole range of interfering ion concentrations ($\overline{RSD}$ lower than 1 %). Note that for the zinc ion concentration (introduced as zinc sulphate) lower than 8×10^{-5} mol dm^{-3}, only sulphate ions are responsible for the precision of determination. For higher concentrations of zinc sulphate, both zinc and sulphate ions are responsible for reduced precision.

Determination of silver contents in the copper foil and zinc rod was performed in order to study the accuracy of the proposed analytical method. The data were compared with the results of FAAS analyses. The concentration of silver and copper ions in the solution prepared on the basis of the copper foil was 1.89×10^{-5} mol dm^{-3} (2.039 mg dm^{-3}) and 0.39 mol dm^{-3}, respectively. The amount excess of copper ion in the studied solution was about 20 600. The same analyses were performed for a solution containing 1.95×10^{-5} mol dm^{-3} (2.130 mg dm^{-3}) Ag$^+$ in the presence of 0.79 mol dm^{-3} Zn^{2+} ion. In the latter case, the excess of zinc ion amounted to 40 500. The results of four independent analyses are collected in Table II. The relative uncertainty in the silver determination, defined as $G = \dfrac{t \cdot S_x}{\bar{x} \cdot \sqrt{n}}$ where: t – Student's coeffi-

TABLE I. Average relative standard deviation ($\overline{RSD}$) for different amount excesses of interfering ions[(a)]

c (interf. ion)	$E^{(b)}$	$\overline{RSD}$ / %		
mol dm^{-3}		Cu^{2+}	Zn^{2+}	SO$_4^{2-}$
0	0	0.49	0.49	0.49
8×10^{-6}	50	0.73	0.42	0.52
8×10^{-5}	500	0.78	0.33	0.38
2.4×10^{-4}	1 500	–	0.29	–
8×10^{-4}	5 000	1.02	0.74	0.30
2.4×10^{-3}	15 000	–	0.47	–
8×10^{-3}	50 000	0.80	0.51	0.28
2.4×10^{-2}	150 000	2.22	–	0.59

[(a)] Silver ion concentration was 1.6×10^{-6} mol dm^{-3}.
[(b)] E – amount excess of the interfering ion, defined as the ratio of amount concentrations of interfering and silver ions, c(interf. ion) / c(Ag$^+$).

TABLE II. Silver ion concentration in solutions, determined by the proposed method and the FAAS method[(a),(b)]

Proposed method		FAAS method	
$(\bar{\gamma}_{Ag} \pm S_\gamma)$ / mg dm^{-3}	G / %	$(\bar{\gamma}_{Ag} \pm S_\gamma)$ / mg dm^{-3}	G / %
Cu^{2+} excess (E = 20 600)			
1.954 ± 0.030	2.82	1.801 ± 0.010	1.02
1.838 ± 0.006	0.60	1.795 ± 0.006	0.58
1.989 ± 0.049	4.52	1.903 ± 0.011	0.90
1.887 ± 0.040	3.89	1.843 ± 0.009	1.06
Zn^{2+} excess (E = 40 500)			
1.972 ± 0.053	4.92	1.968 ± 0.008	0.74
2.078 ± 0.053	4.68	1.935 ± 0.008	0.76
1.761 ± 0.026	2.71	1.959 ± 0.030	2.81
1.932 ± 0.009	0.85	1.912 ± 0.012	1.15
2.025 ± 0.017	1.54	1.964 ± 0.018	1.68
1.946 ± 0.041	3.87	1.939 ± 0.014	1.32

[(a)] The exact silver ion concentration in the presence of accompanying Cu^{2+} or Zn^{2+} ions was 2.039 and 2.130 mg dm^{-3}, respectively.

[(b)] $G = \dfrac{t \cdot S_x}{\bar{x} \cdot \sqrt{n}}$, t – Student's coefficient for the confidence level 0.95 and n equals 3.

cient for the confidence level 0.95 and n equals 3, was calculated and is given in Table II. From the comparison of G values it can be seen that the precision of FAAS analyses was slightly better than the proposed method. This can be explained in terms of the total error of dilutions, which were made for silver determination by the proposed method. Silver determination by the proposed method requires additional dilutions of samples prepared from the copper foil or zinc rod whereas in the FAAS method the basic samples prepared from the copper foil

or zinc rod can be directly analyzed. Still, the precision and accuracy of silver determination by the proposed method are satisfactory for a large amount excess of copper or zinc ions present in the studied solutions.

CONCLUSIONS

The sensitivity and precision of the catalytic method monotonically decrease with increasing concentration of the copper ion, but they are still satisfactory even at a very high amount excess of the interfering ion (about 150 000). Silver ion determination in solutions containing more than 8×10^{-3} mol dm^{-3} of Zn^{2+}, corresponding to the amount excess of 50 000, can be performed with low sensitivity. The precision of the method is almost independent of the zinc and/or sulphate ion concentration in the range of concentrations from 8×10^{-6} to 2.4×10^{-2} mol dm^{-3}. These concentrations correspond to the range of amount excess of the interfering ion from 50 to 150 000. However, the accuracy of the proposed method is slightly worse than the FAAS method but is still satisfactory for the trace determination. The proposed method allows determining a much lower concentration of the silver ion than the FAAS method. The proposed method can be used for determination of silver contents in metallic and nontypical samples containing very low silver contents. The great advantages of the proposed method are its simplicity and the low cost of analysis.

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SAŽETAK

Određivanje tragova srebra u metalnom bakru i cinku visoke čistoće katalitičkom fotometrijskom metodom

Grzegorz D. Sulka i Marian Jaskula

Istraživan je katalitički postupak određivanja tragova srebra u prisutnosti bakrovih, cinkovih te sulfatnih iona. Visoko osjetljiva metoda određivanja srebra temelji se na katalitičkom učinku srebrovih iona na oksidaciju salicilne kiseline persulfatom u prisustvu 2,2'-bipiridila kao aktivatora. Reakcija je praćena spektrofotometrij-ski mjerenjem brzine promjene apsorbancije s vremenom pri 420 nm 10 minuta nakon miješanja reaktanata. Osjetljivost, preciznost i točnost određivanja tragova srebra ispitivane su u otopini koja je sadržavala višak bakrovih odnosno cinkovih iona. Istraživano područje koncentracija bakrovih odnosno cinkovih iona bilo je od 8×10^{-6} do $2,4 \times 10^{-2}$ mol dm^{-3}, što je odgovaralo omjeru koncentracija $c(\text{Cu}^{2+})$ / $c(\text{Ag}^+)$ odnosno $c(\text{Zn}^{2+})$ / $c(\text{Ag}^+)$ od 50 do 150 000. Provedene analize pokazale su veliku točnost i preciznost određivanja tragova srebra korištenom metodom čak i kad su bakrovi odnosno cinkovi ioni prisutni u velikom suvišku. Postupak je korišten za kvantitativno određivanje sadržaja srebra u bakrenom listiću odnosno cinkovom štapiću. Postignuti rezultati uspoređeni su s rezultatima FAAS analize.

BOOK REVIEW

Mladen Mintas, Silvana Raić-Malić,
Nenad Raos

Načela dizajniranja lijekova
[Principles of Drug Design]

HINUS d.o.o., Zagreb, 2000,
pages 202
ISBN 953-97716-6-8

Mladen Mintas, Silvana Raić-Malić,
Nenad Raos

*Lijekovi u prostoru – farmakofori i
receptori*
[Drugs in the space – pharmacophores
and receptors]

Školska knjiga d.d., Zagreb, 2005,
pages 230
ISBN 953-0-31566-X

A very productive group of authors, headed by Professor Mladen Mintas, produced these two topical books, but they have also announced that the third book in the series on medicinal chemistry is ready for print. It should be pointed out that such an activity is rare in Croatian science.

The first book *Načela dizajniranja lijekova* (Principles of Drug Design) consists of an introduction, two parts, dictionary of less-known terms and index. The first part (pp. 10–96), entitled *Prediction and Interpretation of Drug Action*, contains a presentation of current methods used for predicting drug action. The following approaches are discussed: the qualitative approach, the heuristic approach (QSAR) and the molecular modeling approach (based on molecular mechanics, quantum chemistry), indirect methods (such as pharmacophore analysis) and direct methods (such as docking). The second part (pp. 97–193), entitled *Retrosynthetic Analysis and Synthesis of Drugs*, presents fundamental concepts of retrosynthetic analysis, synthesis strategy and planning, and examples of multistep-syntheses. Each section in the book is followed by a set of per-

tinent references. The book is well-written and nicely illustrated.

The second book *Lijekovi u prostoru – farmakofori i receptori* (Drugs in the space – pharmacophores and receptors) consists of four chapters, a glossary and index. The first chapter (pp. 9–36), entitled *The Theory of Pharmacophores*, presents the key-and-lock idea of Erhlich in the contemporary research of pharmacophores and receptors and discusses the receptors in the space. The second chapter (pp. 39–132), entitled *Stereochemical Basis of Drug Action*, discusses the concepts of stereoisomers, symmetry and asymmetry, chirality, pseudosymmetry, prochirality, chiral drugs, pharmacophores and their analysis, and search of databases such as the *Cambridge Structural Database*. The third chapter (pp. 135–174), entitled *Preparation of Enantiomeric Pure Compounds*, presents natural chiral building blocks, chromatographic separation of enantiomers on the chiral stationary phase, separation of enantiomers by fractional crystallization of racemic mixtures, kinetic differentiation of enantiomers, biological synthetic methods of chiral compounds and stereoselective organic synthesis. The fourth chapter (pp. 177–220), entitled *Examples of Holistic Stereochemical Approach*, consists of sections on stereochemistry of sugar-based drugs, stereochemistry of nucleic acids building blocks, and three sections on cytostatics and antitumor drugs. Each is followed by selected references. The whole book is clearly written and nicely illustrated.

Both books are intended for graduate students and for organic and pharmaceutical chemists, but I believe that undergraduate students will also find them useful in their studies. It should be also noted that both books are listed as University of Zagreb textbooks. The publisher of the first book, HINUS d.o.o, publishes a series of books on topical subjects in science and technology whilst Školska knjiga d.d. is a well-known Croatian publishing house of textbooks, monographs, literary masterpieces, dictionaries, *etc*.

Finally, I wish to stress that I greatly enjoyed reading these two books and am looking forward to the authors' other books that I was told will follow. It is a pity that other distinguished Croatian chemists do not follow the example set by this diligent trio: Mladen Mintas, Silvana Raić-Malić and Nenad Raos.

Nenad Trinajstić