

# Application of environmentally friendly ligands for alkaline electroless copper plating systems: electroless copper deposition using trisodium salt of 2-hydroxy-1,2,3-propanetricarboxylic acid as Cu(II) ligand

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Trisodium salt of 2-hydroxy-1,2,3-propanetricarboxylic acid (citric acid) forming sufficiently stable complexes with copper(II) ions in alkaline solutions was found to be a suitable ligand for copper(II) chelating in alkaline (pH > 12) electroless copper deposition solutions. The reduction of copper(II)-citrate complexes by hydrated formaldehyde was investigated and the copper deposits formed were characterized. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 3 μm at ambient temperature. The plating solutions were stable and no signs of Cu(II) reduction in the bulk solution were observed. The results were compared to those for systems operating with other copper(II) ligands. Solution equilibria were discussed and itemized.

**Key words:** copper(II), ligand, 2-hydroxy-1,2,3-propanetricarboxylic acid, citrate, electroless copper deposition, copper coatings, surface roughness

## INTRODUCTION

Many chemical compounds used in technological processes are hazardous for total environment, therefore, efforts are made to displace those substances with less hazardous or purely harmless compounds.

Currently ethylenediaminetetraacetic acid (EDTA) is the most widely used ligand in alkaline electroless copper plating baths due to its perfect chelating properties. On the other hand, these excellent complexing properties of EDTA create environmental hazards because of the binding of heavy metal ions into soluble, very stable and hardly decomposable complexes in a wide pH range. In addition, EDTA is very weakly biodegradable. Therefore,

there are attempts to replace EDTA in alkaline electroless copper plating systems. Xylitol, D-mannitol and D-sorbitol were proposed as environmentally friendly alternate copper(II) ligands for electroless copper plating solutions [1]. The mentioned alditols showed good chelating properties for copper(II) ions in alkaline media (pH > 11.5). Electroless copper plating solutions containing the chelators xylitol, D-mannitol and D-sorbitol are stable, and under optimal conditions copper coatings up to 3 μm thick can be obtained in 1 hour at ambient temperatures [1]. Saccharose, which forms sufficiently stable complexes with copper(II) ions in alkaline solutions has been recently found to be also a suitable ligand for copper(II) chelating in alkaline (pH > 12) electroless copper deposition solutions allowing to obtain 2 μm thick compact copper coatings in 1 hour [2].

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Hydroxypolycarboxylic acids are also environmentally friendly Cu(II) ligands alternative to EDTA. The use of tartaric acid in electroless copper plating is well-documented [3, 4], and peculiarities of electroless copper deposition from such kind of system are investigated [5]. However, there are no data on the application of 2-hydroxy-1,2,3-propanetricarboxylic acid (citric acid) as a ligand for alkaline electroless copper baths, whereas it is rather widely used in copper or copper alloys electroplating baths [6–8] and nonformaldehyde electroless copper plating solutions [10].

Since it is known that Cu(II) ions form soluble complexes with citrate anions in alkaline medium [11, 12], the aim of this study is to evaluate the electroless copper deposition process in solutions containing citrate as the Cu(II) ligand.

## EXPERIMENTAL

### Chemicals and solutions

Analytical grade reagents were used, and the formaldehyde source was formalin (37% HCHO) solution. Formaldehyde concentration in the stock solution was determined iodometrically. The measurements of pH and pH-metric titrations were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode.

### Spectrophotometric measurements

The visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrometer at  $20 \pm 1$  °C in 1.0 cm path length quartz cells. The optical blank solution was pure water.

### Copper surface formation

The substrate was a smooth Pt sheet ( $1 \times 1$  cm) electroplated with Cu for 20 min from acid copper solution ( $1.0$  M  $\text{CuSO}_4 + 0.5$  M  $\text{H}_2\text{SO}_4$ ) at  $1.5$  A  $\text{dm}^{-2}$ . Before the electroless plating the electroplated substrate was activated for 30 seconds in acid  $\text{PdCl}_2$  solution ( $1$  g  $\text{l}^{-1}$ ). The main electroless copper plating experiments were carried out for 30 or 60 min at  $20$  °C in 50 ml of the solution containing (M):  $\text{CuSO}_4 \times 5\text{H}_2\text{O} - 0.05$ ; trisodium citrate – from 0.10 to 0.30; formaldehyde – 0.15; NaOH – up to pH needed. The amount of copper deposited was determined by the mass difference. All the measurements were repeated at least three times and the mean value was calculated.

### Determination of the real surface area of the Cu coatings obtained

The copper surface determination method is based on the underpotential deposition of the thallium monolayer on the Cu electrode surface. The method is described in [5, 13, 14]. The measurements were carried out at  $25$  °C in  $1$  M  $\text{Na}_2\text{SO}_4$  solution containing  $1$  mM  $\text{TlNO}_3$ . Before the measurements, copper oxides were removed from the surface: the working Cu electrode was kept at

$-0.80$  V for 5 seconds. Then the electrode was kept at  $+0.15$  V for 5 seconds (for dissolving the bulk Tl deposit). A Tl monolayer was formed at  $-0.49$  V for 200 seconds. Then the Tl monolayer was dissolved using anodic scanning of the potential up to  $-0.1$  V (scanning rate  $50$  mV  $\text{s}^{-1}$ ). By integrating the obtained potentiodynamic curve (in the range from  $-0.39$  to  $-0.10$  V), the quantity of electricity ( $Q$ ,  $\mu\text{C}$ ) used for the anodic dissolution of the Tl monolayer was calculated.

The real surface area (in nano-scale dimensions) of the Cu electrode ( $S_R$ ,  $\text{cm}^2$ ) was calculated using the Tl monolayer capacity  $Q_{\text{Tl}}$  (the quantity of electricity necessary to form a monolayer on  $1$   $\text{cm}^2$  of electrode), which was equal in this case to  $112$   $\mu\text{C cm}^{-2}$  [14]:

$$S_R = Q/Q_{\text{Tl}} \quad (1)$$

The surface nano-scale roughness factor  $R_f$  is calculated as a ratio of real and geometric surface areas:

$$R_f = S_R/S_G \quad (2)$$

### Voltammetric measurements

Open-circuit potential of the copper electrode during the process of electroless copper deposition was measured by means of an xy-recorder H-307 (Russia) using the Ag/AgCl reference electrode with a saturated KCl solution. All potentials are presented in reference to SHE.

### Electrochemical quartz crystal microbalance (EQCM) measurements

AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelemetrics Ltd., UK) sputtered by gold from both sides were used. They were connected to a home-built oscillator. Their electrochemically and piezoelectrically active geometric areas were  $0.636$  and  $0.283$   $\text{cm}^2$ , respectively. The quartz crystals were installed at the bottom of the cell of working volume ca. 2 ml. The upper part of the cell contained the Pt-wire counter electrode, joints for the electrolyte inlet and the Luggin capillaries and the electrolyte outlet tube. The construction of the cell allowed an exchange of the solution under the controlled electrode potential. The electrolytes in the supply bottles were constantly purged with Ar. Prior to carrying out the experiments, a copper layer was electrodeposited onto a gold sublayer on quartz crystal mounted in the cell from a solution containing  $1.0$  mol  $\text{l}^{-1}$   $\text{CuSO}_4$  and  $0.5$  mol  $\text{l}^{-1}$   $\text{H}_2\text{SO}_4$  at a current density of  $10$  mA  $\text{cm}^{-2}$  for 15–20 s.

EQCM measurements were carried out using a precision frequency counter Ch3-64 and two digital voltmeters B7-46 connected to a PC through an IEEE 488 interface (all the equipment was made in Russia). A programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia) were used to control the electrode potential. The potential has been measured with respect to the Ag/AgCl/KCl<sub>sat</sub> reference electrode and is given below versus the standard hydrogen electrode (SHE).

The measured electrode potential, the faradaic current and the frequency (counted with an accuracy of 0.01 Hz) were transferred to the PC every 1.3 s. A calibration constant  $33.5 \text{ Hz s}^{-1}$  per 1 mA was found in EQCM measurements of copper deposition from alkaline Cu(II) solutions containing trisodium citrate as a ligand.

## RESULTS AND DISCUSSION

### Equilibria in alkaline copper(II)–citrate solutions

#### *Deprotonation of citric acid*

2-hydroxy-1,2,3-propanetricarboxylic acid or citric acid ( $\text{H}_4\text{Cit}$ ) contains three carboxylic groups and a ternary hydroxyl group. The typical  $\text{p}K_{1-3}$  values given in literature [11, 12, 15, 16] show that at pH above 7, the triply deprotonated species  $\text{Cit}^{3-}$  dominate in solutions. The data on the deprotonation of ternary hydroxyl group in solutions of higher alkalinity and the formation of tetranegative anion  $\text{Cit}^{4-}$  are rather ambiguous, and the values of  $\text{p}K_4$  varies from 10.82 [17], 12.42 [18] to 16 [19, 20].

Since electroless copper plating systems using formaldehyde as a reducing agent are operating at pH above 12, it is essential to know specifically the speciation of citric acid in alkaline solutions, regarding the fact that the data given in the literature are contradictory. For this reason, we have performed a series of pH-metric titrations with the aim to examine the dissociation of ternary hydroxylic group of citric acid in solutions of different alkalinity. The applied procedure of titration (we have named it a “dry” titration) was as follows: the increments of solid trisodium citrate were added into a 50-ml beaker containing a fixed initial volume of  $1.0 \text{ mol l}^{-1}$  or  $0.5 \text{ mol l}^{-1}$  NaOH and pH, and the volume of the resulting solution was measured. The magnetic stirring was employed in the titrations. The addition of trisodium citrate to the solutions of NaOH did not lower the concentration of  $\text{OH}^-$  ions, i. e. pH values of the solutions did not decrease with an increase in the amount of trisodium citrate added (up to the solubility limit of trisodium citrate in the mentioned NaOH solutions). The obtained results are opposite to those when investigating deprotonation of D-mannitol in a similar manner [21] – in the case of D-mannitol significant pH changes (pH lowering) were observed after the addition of a solid substance to the solution of sodium hydroxide due to the neutralization reaction of the OH-groups of the mentioned alditol. It is worth noting that the determined value of  $\text{p}K_1$  of D-mannitol is 13.1 [21], therefore, we can conclude that  $\text{p}K_4$  value for the deprotonation of the ternary hydroxyl group of citric acid is much higher. Thus,  $\text{p}K_4$  value equal to 16 [19, 20] is most believable from the above-mentioned values.

#### *Cu(II) complex formation*

The interaction of citric acid with Cu(II) ions in alkaline solutions has been the subject of several studies [7, 8, 19, 22–26], but there is no definite answer about

Cu(II) complex speciation in those solutions. Mononuclear and dinuclear copper(II) complexes with trinegative ( $\text{Cit}^{3-}$ ) or tetranegative ( $\text{Cit}^{4-}$ ) anions of citric acid were considered, since in solutions with pH above 7–8, citric acid can exist only in the form of three- or fourfold deprotonated anions.

The major part of investigations was carried out by means of potentiometric (pH-metric) titration. The presented titration curves of the solutions containing equimolar quantities of citric acid and Cu(II) salt showed a steep inflection after four equivalents of base per mole of metal salt. This is interpreted to indicate that Cu(II) ions combine with citric acid through the dissociation of the total four protons from carboxylic acid groups and hydroxyl group of the ligand [19, 22, 23].

As a result of the potentiometric studies supported by spectrophotometric measurements, Warner and Weber have reported the formation of 1:1 Cu(II)-citrate complex where the four protons are displaced from citric acid; the stability constant ( $\beta$ ) of this  $\text{CuCit}^{2-}$  complex is about  $10^{18}$  [19]. The last value was calculated under the estimation of  $\text{p}K_4$  value of citric acid being 16.

On the basis of concentration dependence, Rajan and Martell concluded that Cu(II) interacts with fourfold deprotonated citric acid to form a dimer  $\text{Cu}_2\text{Cit}_2^{4-}$ . The formula of that complex indicating the arrangement of the coordinate bonds was also suggested [23].

Campi et al. reported on the formation of both mononuclear and dinuclear Cu(II)-citrate complexes. By assuming for  $\text{p}K_4$  constant of citric acid a value of the order 13, the stability constants of the complexes  $\text{CuCit}^{2-}$  and  $\text{Cu}_2\text{Cit}$  was calculated being of the order of  $10^{14}$  and  $10^{18}$ , respectively [22]. In the same work, when investigating the interaction of citric acid with other divalent cations such as Zn(II), Co(II), Cd(II), Mg(II), Ba(II), Ca(II) an interesting result was obtained. In the presence of these cations, citric acid exhibits different behaviour comparing with Cu(II) – no displacement of hydrogen ions from the alcoholic hydroxyl was observed, since the titration curves of the solutions containing equimolar quantities of citric acid and metal ions showed an inflection after three equivalents of base per mole of metal salt.

According to the potentiometric titration data of Daniele et al.,  $\text{Cu}_2\text{Cit}_2^{4-}$  is the predominating Cu(II) species in alkaline solutions of citric acid [24]. The stability of this complex was calculated using the  $\text{p}K_4$  value of citric acid equal to 16, the stability constant logarithm ( $\log\beta$ ) was 38.2 [9].

It is worth mentioning that the above investigations were carried out in solutions of relatively low alkalinity – up to 7.5 [19], 8.5 [22], 9.0 [24] and 11.5 [23].

L. Meits has investigated Cu(II)-citrate system in a wide pH range ( $2 < \text{pH} < 14$ ) by means of d.c. polarography [25]. The polarographic waves of Cu(II) reduction in citrate solutions were thermodynamically reversible in all pH regions mentioned. Therefore, the

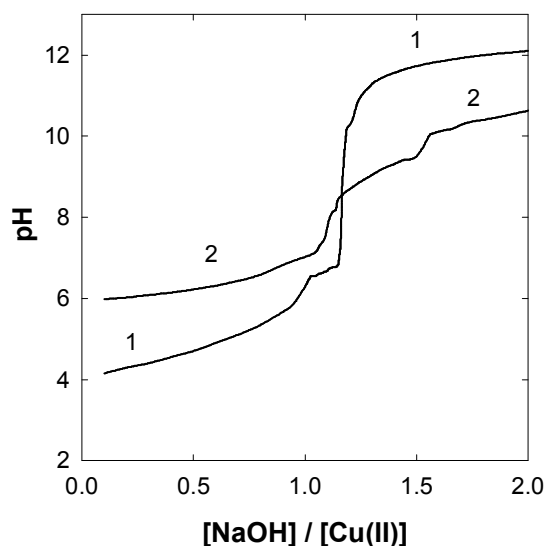
obtained data do not raise doubts. The half-wave potential of Cu(II) reduction was found independent of pH above about 8.5 and remained constant up to pH of about 12.0. From the dependence of the half-wave potential on the citrate concentration ( $8.5 < \text{pH} < 12.0$ ), it was concluded that one citrate anion ( $\text{Cit}^{3-}$ ) is coordinated with one Cu(II) cation in the complex, the stability constant logarithm being 14.2. In more strongly alkaline solutions, the half-wave potential shifts to more negative potentials by ca. 68 mV per one pH unit, and by 41 mV when the concentration of potassium tartrate increases from  $0.046 \text{ mol L}^{-1}$  to  $0.395 \text{ mol L}^{-1}$ . On the basis of the values mentioned, the author concluded that one copper(II) ion combines with two hydroxyl anions and two citrate anions ( $\text{Cit}^{3-}$ ) forming the  $\text{CuCit}_2(\text{OH})_2^{6-}$  complex with the stability constant logarithm value of 19.3.

The formation of hydroxycomplexes was also proposed when investigating Cu(II)– $\text{K}_3\text{Cit}$  system using pH-metric titration and a method of solubility of  $\text{Cu}(\text{OH})_2$  [26]. On the basis of the experiments mentioned, the authors reported the formation of  $\text{CuCit}(\text{OH})_2^{2-}$  ( $\log\beta = 17$ ) and  $\text{CuCit}(\text{OH})_3^{3-}$  ( $\log\beta = 19$ ) complexes at pH's 7.0–11.5 and pH higher than 12.0, respectively.

Although citrate complexes of Cu(II) were the subject of numerous studies, the literature data disagree with each other and, however, are sometimes contradictory.

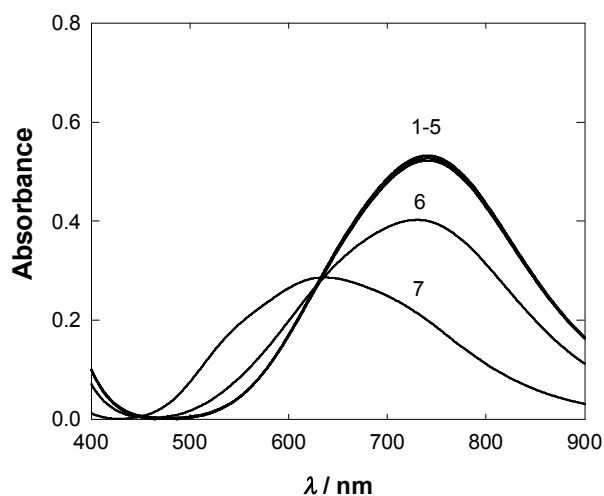
Therefore, we have made titrimetric (pH-metric) and spectrophotometric investigations under conditions approximate to those of electroless copper plating.

The titration curves of the solutions containing equimolar quantities of trisodium citrate and Cu(II) salt as well as fivefold excess of trisodium citrate showed an inflection after the addition of ca. one equivalent of base per mole of copper(II) salt (Fig. 1). This confirms without dispute that in the case of Cu(II) complex for-



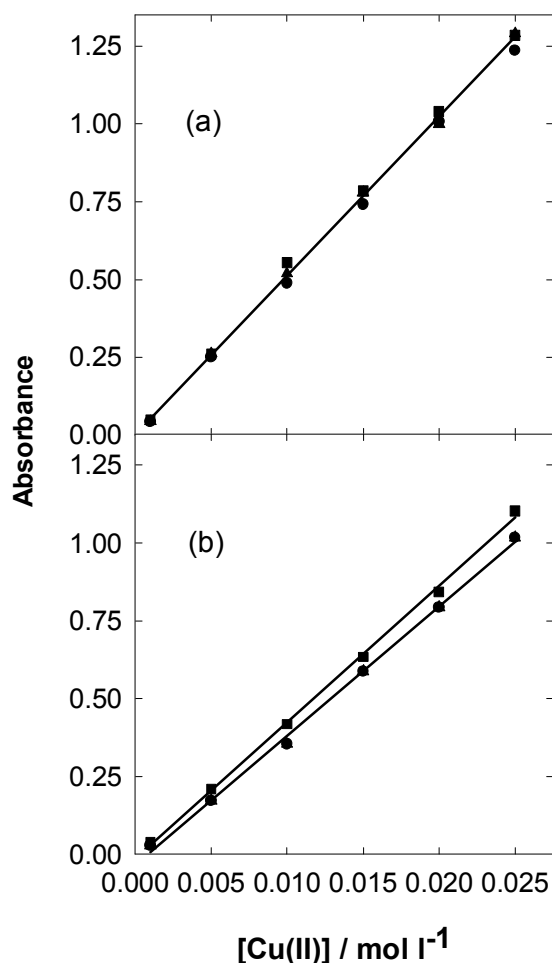
**Fig. 1.** Titrations curves of the solutions of copper(II) sulphate and trisodium acetate with  $1 \text{ mol L}^{-1}$  sodium hydroxide. Initial concentrations ( $\text{mol L}^{-1}$ ):  $[\text{Cu}(\text{II})] = 0.05$ ,  $[\text{Na}_3\text{Cit}] = 0.05$  (1) and  $0.25$  (2)

mation with trianion of citric acid with pH's higher than 6–8, the dissociation of the proton from the hydroxyl group takes place and Cu(II) ions additionally combined with citrate trianion through the deprotonated OH-group. The constancy of Cu(II)-trisodium citrate light absorbance spectra in wide pH range from 8 to 12 (Fig. 2) is also in good agreement with the above-mentioned conclusion. It can be noted that formation of the above mentioned copper(II)-citrate-hydroxycomplexes (i. e. an incorporation of the OH-groups from the solution bulk into the complex) is much less presumable, since the bulk concentration of OH-ions is in the range from  $10^{-6}$  to  $10^{-3} \text{ mol L}^{-1}$  (pH from 8 to 11), i. e. much lower than the concentration of Cu(II) in solutions under titration ( $0.05 \text{ mol L}^{-1}$ ). It is rather surprising how the dissociation of the OH-group of citrate trianion occurs at relatively low pH values, whereas the  $\text{p}K_4$  value is rather high and equal to 16 (see above). This phenomenon could be explained by the known metal-ion promoted deprotonation of alcoholic OH-groups in aqueous solutions of low pH, and the issue is given in a more extended treatment in [27–29].



**Fig. 2.** Light absorbance spectra of Cu(II) in alkaline solutions of trisodium acetate ( $\text{Na}_3\text{Cit}$ ). Solution composition ( $\text{mol L}^{-1}$ ):  $[\text{Cu}(\text{II})] = 0.05$ ,  $[\text{Na}_3\text{Cit}] = 0.10$ ; pH: 1 – 8.0, 2 – 9.0, 3 – 10.0, 4 – 11.0, 5 – 12.0, 6 – 13.0, 7 – 14.0

With the aim to explore a possible composition of Cu(II)-citrate complexes formed, a series of spectra of solutions with different Cu(II) concentrations but a constant metal-to-ligand ratio were recorded (Fig. 3). The linear dependence of light absorbance on Cu(II) concentration was observed for solutions with pH value equal to 12 (Fig. 3a), the light absorbance being practically independent on metal-to-ligand ratio (from 1:1 to 1:5). Two inferences can be drawn from the obtained results: 1) that the linear dependence on Cu(II) concentration does not confirm the formation of polynuclear copper(II) complexes, i. e. only mononuclear complexes are formed under experimental conditions; and 2) that the stoichiometry of the Cu(II) complex formed is 1:1,



**Fig. 3.** Dependence of light absorbance on Cu(II) concentration in alkaline solutions of trisodium acetate. Molar ratio  $[Cu(II)]/[Na_3Cit]$ : (●) – 1:1, (▲) – 1:2, (■) – 1:5. (a) – pH = 12.0,  $\lambda = 748$  nm; (b) – pH = 13.0,  $\lambda = 737$  nm

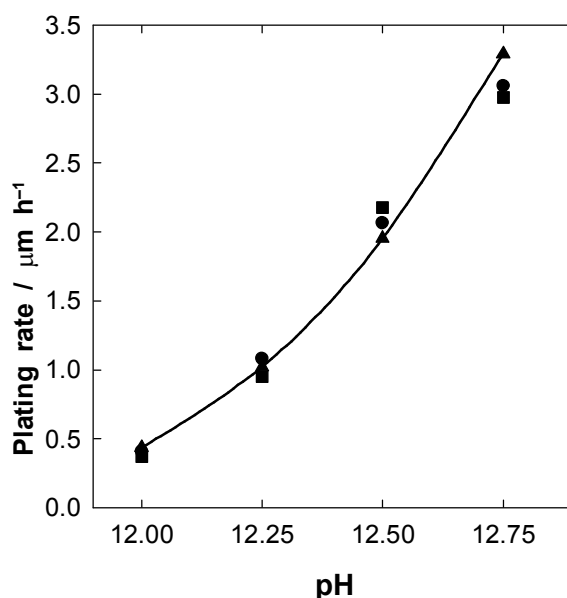
since the light absorbance does not depend on ligand concentration beginning from the metal-to-ligand ratio equal to 1:1. Taking into account that Cu(II) is combined with the tetraanion of citric acid (see above), the composition of the complex formed with pH=12 is  $CuCit^{2-}$ .

When analyzing the dependence of light absorption spectra of Cu(II) in alkaline solutions of trisodium citrate at pH's over 12 (Fig. 2), it is seen that the light absorbance decreases (the light absorbance maximum shifting to shorter wavelengths) with an increase in the solution pH. This indicates that the  $CuCit^{2-}$  complex is in an equilibrium with an additional Cu(II) complex compound, which appears when pH value is higher than 12. Possible expectants for such kind newly appearing complexes could be the above-mentioned copper(II)-citrate-hydroxycomplexes, because the concentration of OH<sup>-</sup> ions rises dramatically at higher pH values, or even – tetrahydroxycuprate(II) complex  $Cu(OH)_4^{2-}$ , since the decomposition of sufficiently stable copper(II) complexes and their transformation into  $Cu(OH)_4^{2-}$  was documented in alkaline and strongly alkaline solutions [30, 31].

From the obtained data, we are not yet able to determine full Cu(II) equilibria in citrate solutions with pH value over 12, some additional experiments are needed. The only thing that can be confirmed is that no formation of polynuclear Cu(II) complexes was observed at pH = 13, since the linear dependence of light absorbance on Cu(II) concentration was observed, the light absorbance being practically independent of metal-to-ligand ratio (from 1:1 to 1:2) and being slightly higher at the ratio 1:5 (Fig. 3b).

#### Electroless copper deposition from solutions containing citrate as Cu(II) ion ligand

In solutions with an excess of trisodium citrate, autocatalytic reduction of Cu(II) by formaldehyde starts at pH 12 (Fig. 4). The plating rate near the lower pH limit (pH 12) is ca.  $0.5 \mu m h^{-1}$ . With the further increase in solution pH, the plating rate rises sharply reaching maximum values at a pH near 12.75 (Fig. 4), and then decreases sharply as pH is further elevated (Table). The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca.  $3 \mu m$  (Fig. 4). It is worth noting that the plating rate practically does not depend on the excess of ligand, i. e. the plating rate remains constant even if a sixfold excess of trisodium citrate is used, comparing with a two-fold starting-excess (Fig. 5). It should be emphasized that the plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed at least during one hour.



**Fig. 4.** Dependence of copper plating rate on pH. Solution composition ( $mol l^{-1}$ ):  $[Cu(II)] = 0.05$ ,  $[CH_2O] = 0.15$ ,  $[Na_3Cit]$ : (●) – 0.10, (▲) – 0.20, (■) – 0.30

Dependencies of copper deposit mass on electroless copper plating solution pH obtained in 0.5 and 1 hour (Fig. 5, curve (a) and curve (b), respectively) have the same exponential shape. At the same pH values the mass of copper deposited in 1 hour is practically two

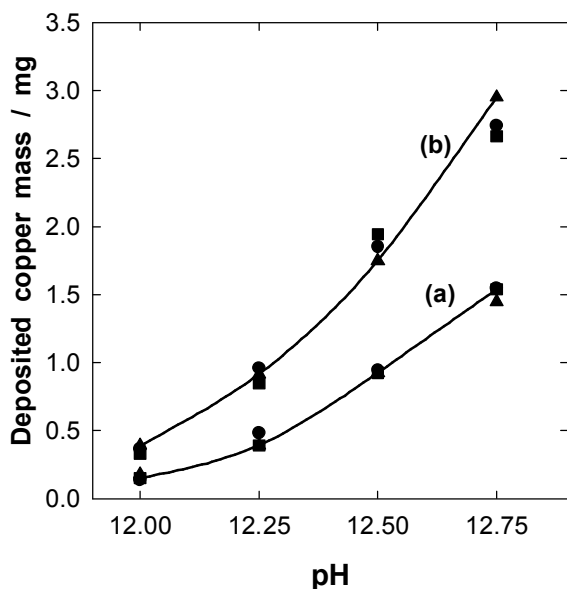


Fig. 5. Dependence of electrolessly deposited copper mass on pH. Solution composition (mol l<sup>-1</sup>): [Cu(II)] – 0.05, [CH<sub>2</sub>O] – 0.15, [Na<sub>3</sub>Cit]: (●) – 0.10, (▲) – 0.20, (■) – 0.30. Plating time: (a) – 0.5 hour, (b) – 1 hour

times higher than that obtained in 0.5 h. It can be predicted from the obtained results that the process of electroless copper deposition starts without a long induction period, and quasi-stationary plating conditions are reached after a relatively short time at the investigated pH values (i. e. pH 12–12.75). The measurements of the mixed potential ( $E_{\text{mix}}$ ), i. e. the potential of copper electrode under open circuit conditions confirm the above-mentioned assumption during electroless copper deposition process (Fig. 6).

The open-circuit potential of copper in the course of electroless deposition at pH 12.0–12.75 varies over a rather wide range of values depending on solution pH (Fig. 6). As the process of the autocatalytic copper(II) reduction (electroless metal deposition) is generally accepted to be electrochemical by nature (the electrons appearing in formaldehyde anodic oxidation are transferred through metallic copper to copper(II) ions), the open-circuit potential in this case is a mixed one ( $E_{\text{mix}}$ ). The potential is established as a result of two reactions occurring simultaneously on the same copper surface – cathodic reduction of Cu(II) ions and anodic oxidation of formaldehyde [32–34]. The time-dependence curves

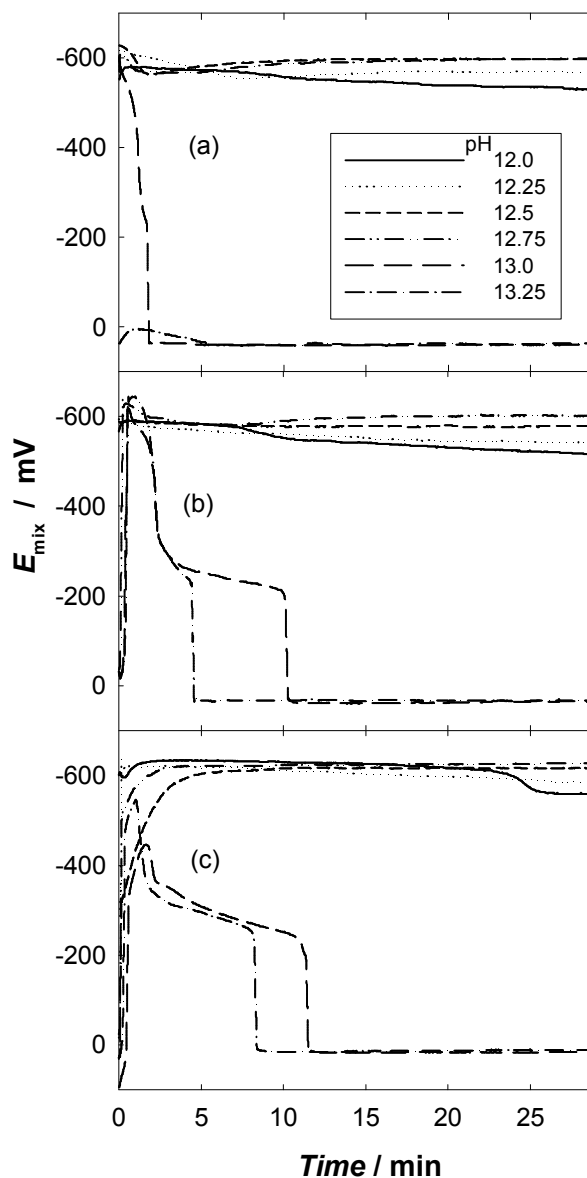


Fig. 6. Time dependence of mixed potential ( $E_{\text{mix}}$ ) of copper electrode during the electroless copper plating. Solution composition (mol l<sup>-1</sup>): [Cu(II)] – 0.05, [CH<sub>2</sub>O] – 0.15, [Na<sub>3</sub>Cit]: (a) – 0.10, (b) – 0.20, (c) – 0.30. Denotation of pH values is given in Fig. 6a

of  $E_{\text{mix}}$  are typical for alkaline formaldehyde-containing electroless copper plating solutions [35, 36]. During the initial period (i. e. in the first 1–2 minutes),  $E_{\text{mix}}$  reaches its most negative value, later shifting to more

Table. Dependence of increment of copper electrode mass ( $\Delta m$ ) after immersion in solution for electroless copper plating on time and pH. Solution composition (mol l<sup>-1</sup>): [Cu(II)] – 0.05, [CH<sub>2</sub>O] – 0.15, and excess of trisodium citrate (Na<sub>3</sub>Cit) is itemized in Table captions.

| pH    | [Cu(II)]/[Na <sub>3</sub> Cit] = 1:2 |                              | [Cu(II)]/[Na <sub>3</sub> Cit] = 1:4 |                              | [Cu(II)]/[Na <sub>3</sub> Cit] = 1:6 |                              |
|-------|--------------------------------------|------------------------------|--------------------------------------|------------------------------|--------------------------------------|------------------------------|
|       | $\Delta m$ (mg) after 0.5 hour       | $\Delta m$ (mg) after 1 hour | $\Delta m$ (mg) after 0.5 hour       | $\Delta m$ (mg) after 1 hour | $\Delta m$ (mg) after 0.5 hour       | $\Delta m$ (mg) after 1 hour |
| 13.0  | 0.25                                 | 0.35                         | 0.90                                 | 1.10                         | 0.80                                 | 1.00                         |
| 13.25 | 0.20                                 | 0.30                         | 0.60                                 | 0.85                         | 0.70                                 | 0.80                         |

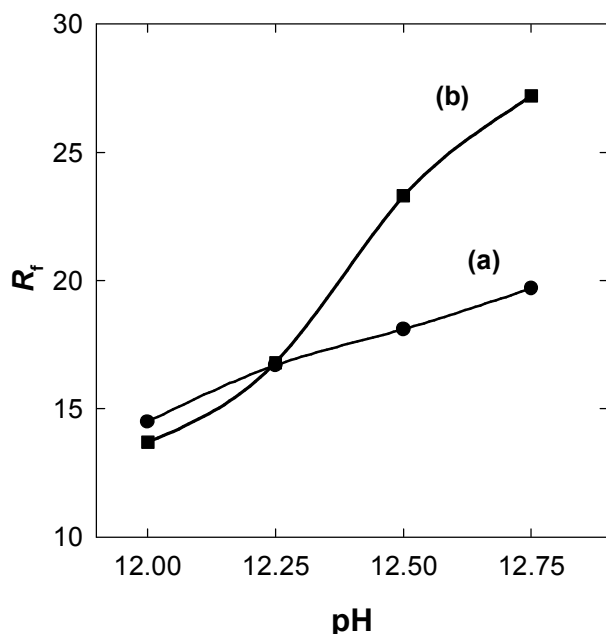


Fig. 7. Dependence of the copper surface roughness factor of electrolessly deposited copper coatings on pH. Solution composition (mol l<sup>-1</sup>): [Cu(II)] – 0.05, [CH<sub>2</sub>O] – 0.15, [Na<sub>3</sub>Cit]: (a) – 0.10, (b) – 0.20. Plating time – 1 hour.

positive potentials and after ca. 15 min it remains practically constant (or shifts negligible to more positive potentials) due to the establishment of quasi-stationary plating conditions (Fig. 6). After establishing the quasi-stationary conditions, the mixed potential shifts continuously to more negative values with the rise in the solution pH (Fig. 6), corresponding to the shift of the potential regions in both electrochemical half-reactions of the catalytic process. One difference from the other investigated electroless copper plating systems using different ligands is observed – the difference between the most positive and the most negative values of  $E_{\text{mix}}$  in the Cu(II)–citrate–formaldehyde system is quite small and does not exceed ca. 70–100 mV (Fig. 7), whereas in other systems this difference can reach ca. 200 [2] or even 300 mV [37].

As mentioned, the obtained copper coatings are compact, but differ in colour depending on the solution pH – from brown (pH 12.0) to dark brown (pH 12.75). Such colour of copper coatings is typical of electrolessly deposited copper coatings with a developed surface [2, 37]. Thus, the changes in colour of copper coatings obtained at different pH's might be connected with the development of the real surface area of copper in the process of electroless plating.

The real surface areas (nano-scale roughness) of the obtained copper coatings were characterized using the thallium underpotential deposition method described below. The roughness factor ( $R_f$ ) of the electroplated copper electrode (which was used as the substrate for electroless plating) was found to be relatively low – 2.2, whereas the copper coatings deposited by the electroless technique have more developed surfaces and  $R_f$  va-

lues that vary widely, from ca. 14 up to 28 (Fig. 7). If one observes the pH-dependence in the  $R_f$  of the copper deposits, the interrelationship among  $R_f$  and copper plating rates is evident (cf. Figs. 4 and 7), the trend being more expressed for the solutions with a higher excess of trisodium citrate (Fig. 7, curve b). This correlation could correspond to the known general trend, e. g., electroplating when the formation of smoother metal deposits occurs at lower deposition rates.

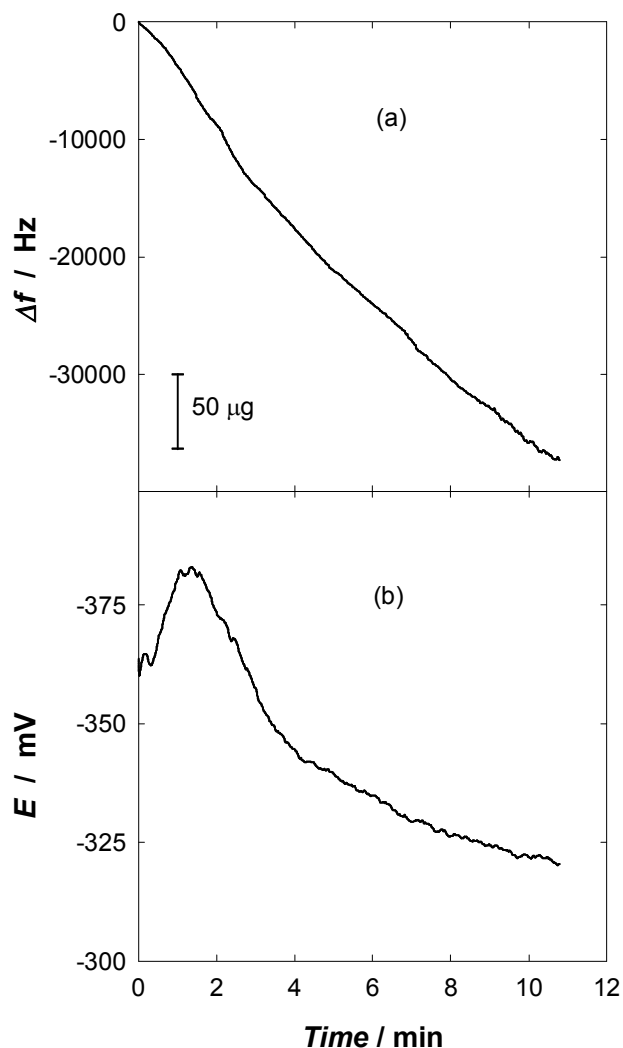
A particular discussion is needed concerning the data obtained on the electroless copper plating at higher pH values, namely at pH 13.0–13.25, where a dramatical decrease in the process rate was observed (cf. Fig. 5 and Table). The decrease in the plating rate could be caused by the changes in the catalytic surface state and characteristics of the Cu surface obtained at higher pH values may be important. For example, the surface may be less catalytically active due to the formation of Cu(I) species. The formation of Cu(I) species during the electroless copper deposition processes is documented [35, 38]. The Cu(I) species slow down the autocatalytic reduction of Cu(II) by formaldehyde through retardation of anodic formaldehyde oxidation on the Cu surface [39].

The fact of Cu surface passivation at higher pH's, i. e. the formation of Cu<sub>2</sub>O, confirms the measurements of  $E_{\text{mix}}$ , showing that at pH 13.0–13.25 the values of  $E_{\text{mix}}$  become relatively positive and reach a constant value equal to ca. from 0 to +20 mV (Fig. 6). It is well known from the standard redox potential values that at the mentioned potentials Cu(II) can be thermodynamically reduced only to Cu(I), but not to the metallic state. It can be noted that the time of reaching of the most positive potentials depends on the solution pH and the excess of citrate, and it is in the range from tens of seconds to minutes (Fig. 6). It is worth indicating that such kind of passivation at potentials close to zero mV was documented for the electroless copper plating solutions containing glycerol and saccharose as Cu(II) ligands, and the passivation film formed was identified by X-ray diffraction investigations as Cu<sub>2</sub>O [35].

In solutions containing a two-fold excess of citrate, the passivation of the copper electrode occurs practically immediately after the immersion of electrode into the solution, when the solution pH value is the highest, i. e. 13.25, whereas at pH = 13.0, the copper plating process starts (the potential of the electrode becomes negative like at lower pHs when electroless copper deposition was observed), but in a couple of minutes it stops. The  $E_{\text{mix}}$  shifts continually (with a short stop at ca. –250 mV) to more positive potentials and reaches a constant value at ca. +20 mV after about 2–2.5 minutes, and later the value of  $E_{\text{mix}}$  remains constant (Fig. 6 a). It is interesting that we have observed the increase in the electrode mass after its exposure to the solution for 0.5 and 1 hour. The mass increment is quite moderate and is in the range from 0.2 to 0.35 mg (Table). It is clear that the mass increment cannot be connected

with the deposition of metallic copper at the mentioned potential values and can be accounted for the formation of  $\text{Cu}_2\text{O}$  film. It can be noted that the formation of  $\text{Cu}_2\text{O}$  films in the electroless copper plating systems is not trivial, i. e. the growth of  $\text{Cu}_2\text{O}$  film in time is observed, the process is autocatalytic and consisting of the reduction of  $\text{Cu(II)}$  from the solution bulk by formaldehyde on the surface to be plated [38].

Quite unexpected results were obtained when using a higher (fourfold or sixfold) excess of citrate. The increase in the electrode mass is much higher comparing with that obtained in solutions with a two-fold excess of citrate and could reach 1.1 mg per hour (Table). A comparison of time dependencies of  $E_{\text{mix}}$  in solutions with various concentrations of citrate (Fig. 6) shows that additional process occurs after ca. 2–3 min after immersion of the copper electrode into solution – the shift of  $E_{\text{mix}}$  stops at ca.  $-300$  mV. The duration of this stop depends on the solution pH and the concentration of citrate, being longer at higher pHs and citrate concentrations and reaching maximum in ca. 10 min (Figs.



**Fig. 8.** The change in quartz crystal frequency and mixed potential ( $E_{\text{mix}}$ ) of copper electrode during electroless copper plating. The solution contained (mol  $\text{l}^{-1}$ ):  $[\text{Cu(II)}] - 0.05$ ,  $[\text{CH}_2\text{O}] - 0.15$ ,  $[\text{Na}_3\text{Cit}] - 0.20$ ; pH  $- 13.0$ .

6a and 6b). Later  $E_{\text{mix}}$  shifts sharply to the most positive potentials and remains constant (Figs. 6a and 6b).

Since the ordinary mass of electrode was determined only after 0.5 or 1 hour, the measurements were performed using electrochemical quartz crystal microbalance (EQCM) during the period of the initial eleven minutes, i. e. during the period of the observed potential stop. Fig. 8 represents the time-dependent decrease in quartz crystal frequency (corresponding to mass increase) and simultaneously measured values of  $E_{\text{mix}}$ . A conversion of the decrease in quartz crystal frequency during ca. 11 minutes (Fig. 8 a) gives the mass increase equal to 0.3 mg. The active surface area of the electrode used in EQCM measurements is ca. three times lower than that used in ordinary experiments, therefore, the recalculated mass for the electrode with the surface area of  $2 \text{ cm}^2$  would be ca. 0.9 mg. When comparing this value with the data given in Table, it can be seen that the main increase in the electrode mass is obtained at ca.  $-300$  mV, i. e. during the initial period.

It is known from the literature that spontaneous potential oscillations were observed during a galvanostatic deposition of layers of Cu and  $\text{Cu}_2\text{O}$  in alkaline copper(II)-citrate solutions [40]. The oscillations observed were in a potential range from  $-550$  to  $-250$  [40]. In our case no oscillations were observed, but the potential range is rather similar. At the moment we can not explain the processes occurring at ca.  $-300$  mV in our systems under investigation. Additional EQCM and X-ray diffraction experiments are needed for a further clarification of the occurring processes.

#### Comparison of citrate-containing electroless copper plating system with systems operating with other $\text{Cu(II)}$ ligands

For comparative purposes, we have selected literature data for electroless Cu plating rates obtained under similar experimental conditions (20 °C temperature, 1 hour plating time, concentrations of copper(II) salt and formaldehyde equal to  $0.05 \text{ mol l}^{-1}$  and  $0.15 \text{ mol l}^{-1}$ , respectively), but using different ligands.

The rate of copper deposition in citrate-containing electroless copper solutions under optimal operating conditions (pH 12.75) reaches about  $3 \mu\text{m h}^{-1}$  (Fig. 4). Similar or slightly lower rates ( $2\text{--}2.5 \mu\text{m h}^{-1}$ ) were determined using other environmentally friendly compounds such as saccharose ( $2 \mu\text{m h}^{-1}$  at pH 12.75) [2], xylitol, D-mannitol and D-sorbitol as  $\text{Cu(II)}$  ligands, but for the three last ligands the required pH values were much higher and reached 13.5–13.8 [1]. The plating rates that were slightly higher (ca.  $4 \mu\text{m h}^{-1}$  at pH 13.0) were obtained from solutions with Quadrol ( $N,N,N',N'$ -tetrakis(2-hydroxypropyl)ethylenediamine) as the  $\text{Cu(II)}$  ligand [5]. Besides, rather high plating rates were documented recently using novel ligands such as 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the  $\text{Cu(II)}$  ligands. The copper plating rates with these ligands reached  $2.8 \mu\text{m h}^{-1}$  (pH 13.0) and



3.9  $\mu\text{m h}^{-1}$  (pH 12.7) [37]. The use of L-tartrate and DL-tartrate gave interesting results: maximum plating rate of only about 1  $\mu\text{m h}^{-1}$  (pH 13.0) was observed in solutions with L-tartrate, whereas it reached ca. 3.5  $\mu\text{m h}^{-1}$  (pH 12.5) when using the racemic mixture of DL-tartrate [5]. Thus, the citrate-containing electroless copper plating solutions give the rates of copper deposition that are comparable to other ligands.

It should be noted that the process of the electroless copper deposition from citrate-containing solutions occurs at  $-600$  mV, i. e. at relatively negative open-circuit potentials ( $E_{\text{mix}}$ ). Similarly, negative or more negative values of  $E_{\text{mix}}$  were observed only in the systems with saccharose [2] or 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the Cu(II) ligands [37]. Usually the values of  $E_{\text{mix}}$  are in the range from  $-300$  to  $-500$  mV for systems with other ligands [36].

Copper is an effective catalyst for anodic reduction of small organic molecules in alkaline solutions as well as for other catalytic processes. Since catalytic activity depends critically on real catalytic surface area, the formation of copper surfaces with a high degree of roughness is of interest for practical purposes. Usually the surface roughness factor ( $R_f$ ) of the electrolessly deposited copper coatings exceeds those of Cu electroplated from an acid copper(II) sulfate bath ( $R_f \sim 2.2$ ). Previously, copper coatings with the highest  $R_f$  values were obtained from solutions containing the following Cu(II) ligands: pyridine-2,6-dicarboxylic acid ( $R_f = 124$ ) [37], 4-hydroxypyridine-2,6-dicarboxylic acid ( $R_f = 350$ ) [37], Quadrol ( $R_f = 23$ ) [5] and saccharose ( $R_f = 25$ ) [2]. In the case when EDTA, L-tartrate and DL-tartrate were used, the values of  $R_f$  were lower and did not exceed 18 [39]. Our experiments show that rather high surface roughness values ( $R_f = 28$ ) are obtained for copper deposition using trisodium citrate as the Cu(II) ligand.

Finally, it is worth noting that copper recovery from the used electroless copper plating solutions containing trisodium citrate as the Cu(II) ligand is much less complicated than for the solutions using conventional ligands such as EDTA, tartrates or Quadrol, since the Cu(II) complexes with citrate can be decomposed by simply lowering the solution pH down to acidic conditions. The remaining citric acid is environmentally benign, i. e. it does not form stable complexes with heavy metals under natural conditions and it is easily biodegraded.

## CONCLUSIONS

This study has shown the possibility of using trisodium citrate as a Cu(II) ligand in electroless copper plating systems. The autocatalytic reduction of Cu(II) by formaldehyde from solutions containing trisodium citrate as ligand begins at pH above 12, accelerates with a further increase in pH, reaches a maximum value at pH 12.75, then slows at higher pH values.

The process of electroless copper deposition from saccharose-containing solutions occurs at relatively negative

open-circuit potentials (ca.  $-600$  mV). A correlation among copper plating rates and surface roughness values of the formed copper deposits has been established.

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**EKOLOGIŠKŲ LIGANDŲ PANAUDOJIMAS  
CHEMINIO VARIAVIMO SISTEMOSE: CHEMINIS  
VARIAVIMAS CU(II) LIGANDU NAUDOJANT  
2-HIDROKSI-1,2,3-PROPANTRIKARBOKSIRŪGŠTIES  
TRINATRIO DRUSKĄ**

**S a n t r a u k a**

Nustatyta, kad 2-hidroksi-1,2,3-propantrikarboksirūgšties (citrinų rūgšties) trinatrio druska, šarminėje terpėje sudaranti pakankamai patvarius kompleksus su vario(II) jonais, yra tinkamas ligandas vario(II) kompleksinimui šarminiuose (pH > 12) cheminio variavimo tirpaluose. Ištirta vario(II)-citrato kompleksų redukcija hidratuotu formaldehidu, apibūdintos gautosios vario dangos. Optimaliomis proceso vykdymo sąlygomis kambario temperatūroje per vieną valandą gali būti nusodintos kompaktiškos iki ~3 mm storio vario dangos. Cheminio variavimo tirpalai buvo stabilūs – jokių Cu(II) redukcijos tirpalo tūryje požymių nepastebėta. Gauti rezultatai palyginti su duomenimis, gautais sistemose su kitokiais ligandais. Aptartos ir patikslintos galimos pusiausvyros tirtuose tirpaluose.