

Binary co-deposited mixtures of silver and magnesium phosphates and silver and copper(II) phosphates

*O.P.Perepelytsia*¹, *V.I.Maksin*², *T.I.Ushchapivska*²,
*T.V.Petrenko*¹, *B.S.Khomenko*³

¹National University of Food Technologies, 68 Volodymyrska Str.,
01033 Kyiv, Ukraine

²National University of Life and Environmental Sciences of Ukraine,
17 Heroyiv Oborony Str., 03041 Kyiv, Ukraine

³V.Vernadsky Institute of General and Inorganic Chemistry,
32/33 Akademika Palladina Blvd., 02000 Kyiv, Ukraine

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Mixtures of silver magnesium phosphates or silver copper(II) phosphates have been obtained from aqueous solutions of silver and magnesium or copper(II) nitrates and sodium hydrogenphosphate at the basic mixture ratios of $[\text{AgNO}_3]:[\text{Me}(\text{NO}_3)_2]:[\text{Na}_2\text{HPO}_4] = 1:1:1.7$ (Me—Mg,Cu) and temperature of reacting solutions 80–90°C. The mixtures have been studied using chemical, thermogravimetric and X-ray diffraction analyses. The temperature ranges for dehydration and crystallization of X-ray amorphous phases and for interaction of silver and copper(II) phosphates with formation of double phosphate have been determined. The resulting mixtures have antimicrobial activity, thus may be applied for treatment of water. In addition, they act as catalysts of electrochemical processes (electrolytic water splitting, and anodic refinement of silver).

Keywords: mixtures, silver, magnesium, copper(II) phosphates, thermogravimetry, X-ray analysis.

Из водных растворов нитратов серебра и магния или меди(II) и натрий гидрофосфата, при исходном соотношении компонентов $[\text{AgNO}_3]:[\text{Me}(\text{NO}_3)_2]:[\text{Na}_2\text{HPO}_4] = 1:1:1.7$ (Me—Mg,Cu) и температурах реагирующих растворов 80–90°C получены смеси наноразмерных фосфатов магния или меди(II) и поликристаллического фосфата серебра. Смеси исследованы методами химического, термогравиметрического и рентгенофазового анализов. Установлены температурные интервалы обезвоживания, кристаллизации рентгеноаморфных фаз и взаимодействия фосфатов серебра и меди(II) с образованием двойного фосфата. Полученные смеси имеют антимикробное действие и могут найти применение для обработки воды. Они также являются катализаторами электрохимических процессов (электролиза воды, анодного рафинирования серебра).

Бінарні співосажені суміші фосфатів аргентума і магнію та аргентума і купрума(II). *О.П.Перепелиця, В.І.Максін, Т.І.Ущанівська, Т.В.Петренко, Б.С.Хоменко.*

Из водних розчинів аргентум і магній або купрум(II) нітратів і натрій гідроген фосфату, при вихідному співвідношенні компонентів $[\text{AgNO}_3]:[\text{Me}(\text{NO}_3)_2]:[\text{Na}_2\text{HPO}_4] = 1:1:1.7$ (Me—Mg,Cu) і температурах реагуючих розчинів 80–90°C одержано суміші нанорозмірних магній або купрум(II) фосфатів та полікристалічного аргентум фосфату. Суміші досліджено методами хімічного, термогравіметричного та рентгенофазового аналізів. Встановлено температурні інтервали зневоднення, кристалізації рентгеноаморфних фаз та взаємодії аргентум та купрум(II) фосфатів з утворенням подвійного фосфату. Одержані суміші проявляють антимікробну дію, тому можуть знайти використання для обробки води. Вони також є катализаторами електрохімічних процесів (електролізу води, анодного рафінування срібла).

1. Introduction

It is known that silver or copper(II) phosphates have antimicrobial activity [1, 2], silver or copper(II) phosphates act as catalysts of alcohol oxidation to aldehydes [3–5], while double phosphates of silver and magnesium (or copper(II)) are advanced materials for functional use [6]. The potential for cobalt phosphate application as catalyst in electrochemical process of hydrogen production from water were demonstrated in [7], which is of practical importance for hydrogen energetics.

The conditions for production of individual silver, magnesium, copper(II) phosphates have been described. For the catalysts, it is also important to be produced as part of mixtures, since often this ensures their increased activity. Among many ways to derive these compounds, the technique of deposition from aqueous solutions is rather well-known.

In [8] authors described silver phosphate Ag_3PO_4 derived from the aqueous solutions of silver nitrate and sodium hydrogenphosphate as a result of a ion-exchange reaction. It is a yellow substance, poorly water-soluble (solubility product is $1.8 \cdot 10^{-16}$; according to [9], the solubility product of Ag_3PO_4 is $1.3 \cdot 10^{-20}$); this belongs to a cubic system with $Pm\bar{3}n$ space group, lattice parameter is $a = 0.599$ nm, $z = 2$, density is $d = 6.370 \cdot 10^3$ kg/m³, melting point is 849°C; under exposure to light, the silver compound partially recovers to unbound metal. Magnesium phosphate is obtained in the form of a poorly soluble precipitate as a result of interaction of solutions containing magnesium sulfate, sodium hydrogen phosphate and sodium hydrogencarbonate with mole ratios of 1:1:1 [10], the solubility product of $\text{Mg}_3(\text{PO}_4)_2 = 1 \cdot 10^{-13}$ [9], melting point is 1357°C. Magnesium phosphate anhydrous crystallizes within the monoclinic system with the following lattice parameters: $a = 0.7596$ nm, $b = 0.8230$ nm, $c = 0.5077$ nm, $\alpha = 94.05^\circ$, $z = 2$ [11]. Copper(II) phosphate is derived in the form of monohydrate as a result of interaction of copper(II) hydroxide or copper(II) nitrate with phosphoric acid. The compound belongs to a monoclinic system with $C2/c$ space group; the lattice parameters are as follows: $a = 1.805$ nm, $b = 0.620$ nm, $c = 1.226$ nm, $\beta = 105.50^\circ$, $z = 8$ [12]. Copper(II) phosphate anhydrous is a poorly soluble compound, which crystallizes in a triclinic system, space group $P\bar{1}$, $a = 0.48537$ nm, $b = 0.52855$ nm, $c = 0.61821$ nm, $\alpha = 72.35^\circ$,

$\beta = 86.99^\circ$, $\gamma = 68.54^\circ$, $z = 1$, $d = 4.503 \cdot 10^3$ kg/m³ [13]. Authors of [14] described double phosphates of silver and magnesium, manganese, cobalt, and zinc, produced as a result of mixing of mono- and bivalent metal chlorides with phosphoric acid, with subsequent drying of the mixtures at 80°C and heating, first at 600°C and then at 700°C, for 24 h. There are available data on the precipitation of $\text{KMgPO}_4 \cdot 2,5\text{H}_2\text{O}$ from aqueous solutions of potassium and magnesium chlorides and phosphoric acid as a result of the action of potassium hydroxide solution on the mixture. The derived compound belongs to a rhombic system with the following unit cell parameters: $a = 0.5676$, $b = 0.8712$, $c = 0.4753$ nm [15].

Currently, there are absent available data on double phosphates of silver and magnesium or silver and copper(II) derived from solutions, as well as on the composition and properties of co-deposited mixtures of silver and magnesium phosphates or silver and copper(II) phosphates.

Therefore, the purpose of this work was to obtain precipitates of these phosphates from aqueous solutions, and determine their composition, nature and properties.

2. Experimental

In this study the following substances have been used as starting materials: magnesium carbonate or nitrate, copper(II) nitrate, silver nitrate, sodium hydrogen phosphate — all of AR-grade; sodium hydroxide, nitric acid and sodium nitrate — all of CP-grade.

To perform the co-deposition of silver and magnesium or silver and copper(II) phosphates, the calculated quantities of nitrates of these metals with their molar ratios of $[\text{AgNO}_3]:[\text{M}(\text{NO}_3)_2] = 1:1$, $M = \text{Mg}^{2+}$, Cu^{2+} , were used.

With magnesium as a starter compound, its carbonate has been used after conversion to nitrate by nitric acid, with subsequent pH-adjustment to 3.5 with a sodium hydroxide solution.

The content of oxides in magnesium carbonate or nitrate, in copper(II) nitrate and content of $\text{Na}_4\text{P}_2\text{O}_7$ in dehydrated sodium hydrogenphosphate crystalhydrate were determined after careful drying and heating of the starting substances at optimum temperatures until a stationary mass was reached. The weight analysis was performed for two parallel samples; the deviations from obtained mean values for weight form content were below 0.2 %; according to the

obtained data, the content of magnesium oxide was 86.7 % in magnesium carbonate and 15.5 % in magnesium nitrate; copper(II) nitrate contained 28.4 % of copper(II) oxide and sodium hydrogen phosphate crystallohydrate contained 20.2 % of water. Silver nitrate was an anhydrous compound.

During the study of co-deposition of silver phosphate and magnesium or copper(II) phosphate the influence of the following factors was identified, namely: pH of the solutions of mixtures of mono- and bivalent metal nitrates, and the sodium hydrogen phosphate solution. At pH levels below 3.5 for the solutions of mixtures of mono- and bivalent metal nitrates, the deposition of Ag^+ and Mg^{2+} or Cu^{2+} ions was incomplete. Similarly, the incomplete deposition of these ions was observed with the original ratios of $[\text{Ag}^+]:[\text{Me}^{2+}]:[\text{PO}_4^{3-}] = 1:1:1$ or $1:1:1.2$. The complete deposition of these ions was observed only with $[\text{Ag}^+]:[\text{Me}^{2+}]:[\text{PO}_4^{3-}] = 1:1:1.7$ or more with regard to the sodium hydrogen phosphate content. Under these conditions, the pH of the mother solution, following isolation of phosphates, was within 6.0–6.5. With the value of 4.0–5.2 the complete deposition was not reached.

The technique applied for the deposition of mixtures of silver and magnesium phosphates and silver and copper(II) phosphates was as follows. The weighed portions of the two specified nitrates were dissolved in 50 mL water in the first vial; pH of the resulting solution was 4. The weighed portion of sodium hydrogen phosphate was dissolved in 50 mL water in the second vial; pH of the resulting solution was 8.5. Both vials with the solutions were heated to boiling. The solution of the nitrate mixture was added by pouring to the solution of sodium hydrogen phosphate with vigorous mixing. The formation of a yellow precipitate of a silver and magnesium phosphate mixture was observed. The precipitate and the mother solution were allowed to stand for 2 weeks with regular mixing; then filtered using a blue ribbon paper filter. The first portions of the filtrate penetrated the filter along with the precipitate. The resulting filtration residue was washed out with a 1% sodium nitrate solution and distilled water till negative identification tests for PO_4^{3-} ion with silver nitrate in wash water; the final washing out was performed using acetone. The pH-level of the resulting mother solution was 6.5.

To achieve concomitant production of the phosphates, the calculated quantities of silver nitrates (in some cases magnesium carbonate was used, which interacted with nitric acid) and bivalent metal were dissolved in 50 mL water in a separate vial with subsequent pH-level verification for the obtained solution (determined values are $(3.5-4.0)\pm 0.2$). The weighed portion of sodium hydrogen phosphate without surplus and with 20 % or 70 % surplus with regard to its stoichiometric ratio of $[\text{Ag}^+]:[\text{Me}^{2+}]:[\text{PO}_4^{3-}] = 1:1:1$ was dissolved in the other vial with 50 mL of water (pH of obtained solution about 8.5 ± 0.2). When pouring the first solution into the second one at 22°C, a high-volume precipitate was formed, which partially clogged the blue ribbon paper filter; it was difficult to filter it off and long time was required to be washed out. The use of hot reacting solutions of 80–95°C simplified the process. The precipitates and their mother solutions were periodically mixed and allowed to stand for 2 weeks with subsequent filtering. The resulting filtration residues were washed out, first with a 1 % sodium nitrate solution and then with distilled water till negative identification tests for the contents of Ag^+ , Mg^{2+} , Cu^{2+} , and PO_4^{3-} ions, with subsequent washing out with acetone and air drying at 22°C for two weeks. Dry depositions of phosphates were analyzed for the content of phosphorus by dissolution of a weighed portion ($0.1500\cdot 10^{-3}$ kg) in 5 mL diluted 1:3 nitric acid with subsequent deposition of a $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]\cdot 2\text{H}_2\text{O}$ precipitate, which was filtered, dried and heated at 400°C. The ash mass of the paper filter after following heating to 400°C was $0.0007\cdot 10^{-3}$ kg. The weight form had the following composition: $\text{P}_2\text{O}_5\cdot 24\text{MoO}_3$, the conversion factor for the content of phosphorous was 0.017232 [16]. The measure of inaccuracy was within ± 0.20 %. The content of silver in the isolated phosphates has been determined by rhodanide method [16] using the weighed portion of $0.400\cdot 10^{-3}$ kg (following separation of silver as silver oxide). The measure of inaccuracy was below 0.5 %.

The thermogravimetric analysis of the air-dried samples of phosphates was performed using a derivatograph constructed by F.Paulik, J.Paulik, and L.Erdey, in platinum crucible with weighed portion of $0.20\cdot 10^{-3}$ kg and at a heating rate of $0.33^\circ\text{C}/\text{s}$; DTA = 50, DTG = 1000, TG scale — 20 %.

X-ray diffraction analysis was carried out using diffractometer DRON 3M with Cu-K α radiation and computer processing of data; the inaccuracy in calculations of reflection angles 2Θ was $\pm 0.04^\circ$.

3. Results and discussion

The co-deposition of silver and magnesium and silver and copper(II) phosphates was performed using the above described technique; the results are illustrated in Examples 1 and 2.

Example 1. Co-depositon of silver and magnesium phosphates:

Silver nitrate (anhydrous) — $1.6988 \cdot 10^{-3}$ kg; magnesium nitrate (crystalhydrate containing 15.50 % of MgO) — $2.6050 \cdot 10^{-3}$ kg; sodium hydrogenphosphate (crystalhydrate containing 20.20 % of water) — $3.00 \cdot 10^{-3}$ kg.

The yield of the air-dried mixture on the filter was $1.838 \cdot 10^{-3}$ kg (with heating to 250°C , its weight loss was 8.7 %, and at 850°C — 11.6 %). For the samples of this mixture obtained under different conditions the weight loss with heating to 850°C reached 15.6 %. The color of the mixture was light-yellow and changed to brown with heating to 500°C .

Analysis of the data for the mixtures of silver and magnesium phosphates identified: Ag — 40.3 %, P — 10.00 % calculated for the mixtures of $\text{Ag}_3\text{PO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$, $x + y = 3.33$ mole: Ag — 43.65 %, P — 12.53 %.

Example 2. Co-deposition of silver and copper(II) phosphates:

Silver nitrate (anhydrous) — $1.6988 \cdot 10^{-3}$ kg; copper(II) nitrate (crystalhydrate containing 28.40 % of CuO) — $2.7971 \cdot 10^{-3}$ kg; sodium hydrogen phosphate (crystalhydrate containing 20.20 % of water) — $3.00 \cdot 10^{-3}$ kg.

The procedures described in Example 1 were applied. The pH-level for the silver and copper(II) nitrates solution was 3.5 and for the mother solution, following isolation of phosphates from filtration residue — 6.

The yield of the air-dried mixture on the filter was $2.68 \cdot 10^{-3}$ kg (with heating to 250°C its weight loss was 4.0 %, and at 850°C — 8.5 %). For the samples of silver and copper(II) phosphates mixture obtained under different conditions, the weight loss with heating to 850°C reached 12.7 %. The color of the mixture was light-green, and with heating to 720°C it showed the formation of dark-green small polycrystals with sparkling edges, which, when heated to

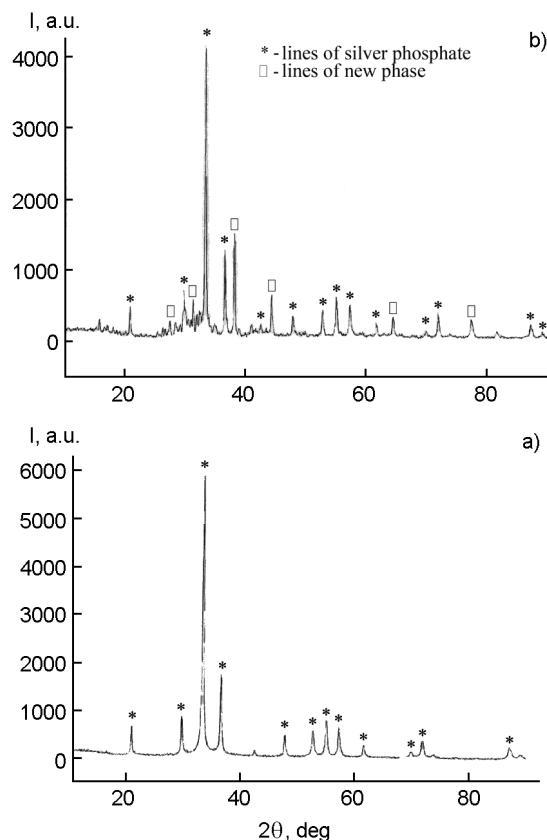


Fig. 1. Diffraction patterns of air-dried mixture of co-deposited silver and magnesium phosphates (a); the same mixture heated at 500°C for 1 h (b).

850°C , produced porous mass that turned into light-blue powder following grinding.

Analysis of the data for the mixtures of co-deposited silver and copper(II) phosphates identified: Ag — 37.4 %, P — 11.50 % calculated for the mixtures of $\text{Ag}_3\text{PO}_4 \cdot x\text{H}_2\text{O} + \text{Cu}_3(\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$, $x + y = 0.617$ mole: Ag — 38.88 %, P — 11.16 %.

Fig. 1 demonstrates the diffraction patterns for the air-dried mixture of silver and magnesium phosphates and for the same mixture heated at 500°C . The first pattern demonstrates lines of a single Ag_3PO_4 phase of a cubic system only; no lines for magnesium phosphate are visible indicating its X-ray amorphous state. This is possible only when the size of particles of this substance is below 100 nm [18]. The diffraction pattern for the sample of this phosphate mixture heated at 500°C for 1 h shows the same lines of the major phase — Ag_3PO_4 , and the lines of a new phase, which may belong both to the reaction product of the said two phosphates and to magnesium phosphate. The lines of the new phase fall

to match to the average magnesium phosphate or magnesium diphosphate, however they are indicative of the presence of X-ray amorphous magnesium phosphate in the air-dried precipitate.

The diffraction patterns of the samples of silver and copper(II) phosphates mixture, air-dried, kept at 500°C for 1 h and kept at 720°C for 1 h (see Fig. 2), provide reasons enough to confirm the deposition of polycrystalline cubical silver phosphate [19] and X-ray amorphous copper(II) phosphate from the specified solutions. The latter shows low-intensity diffuse lines with reflection angles $\Theta_1 = 5.15^\circ$ and $\Theta_2 = 14.45^\circ$, which is indicative of the nano-sizes of its particles. In the sample of the mixture heated to 720°C, the lines of silver phosphate, copper(II) phosphate [19] or copper(II) diphosphate have not been observed. There are, however, lines of a new phase, which has an X-ray pattern similar to that for rhomboidal $\alpha\text{-KMgPO}_4 \cdot 2.5\text{H}_2\text{O}$ in terms of location of lines, and differing in terms of lines intensity. Considering the splitting of lines of the new phase, it can be assumed that the phase has a triclinic distorted structure of rhomboidal $\alpha\text{-KMgPO}_4 \cdot 2.5\text{H}_2\text{O}$ [15] and belongs to the AgCuPO_4 compound. In order to finally prove this, it is necessary to study at least two sections of the triple system of $\text{Ag}_2\text{O}-\text{CuO}-\text{P}_2\text{O}_5$, namely: $\text{Ag}_3\text{PO}_4-\text{Cu}_3(\text{PO}_4)_2$ and $\text{Ag}_2\text{O}(50 \text{ mol.}\%)-\text{CuO}(50 \text{ mol.}\%)-\text{P}_2\text{O}_5$ by long-term samples' heating under isothermal conditions at 500, 600 and 700°C with their subsequent X-ray analysis.

The thermogram of the mixture of silver and magnesium phosphates (DTA-curve) shows (Fig. 3) that adsorbed water is lost at 30–110°C, crystallization water — at 150–250°C, and constitutional water — at 250–360°C; this is due to the endoeffects. This fact is also confirmed by the weight loss curve. The exo-effect observed at 440°C corresponds to the transition of magnesium phosphate from an X-ray amorphous into a crystalline state.

The adsorbed water is excreted from the mixture of silver and copper(II) phosphates at 70–120°C, and crystallization water — at 162–375°C (Fig. 3). The exo-effect, which starts at 320°C, has been triggered by the transition of copper(II) phosphate from an X-ray amorphous into a crystalline state. Here, in the DTA-curve, two superimposed effects have been observed at 320–375°C — crystallization of the X-ray amorphous substance (exo-effect) and weigh loss (TG-

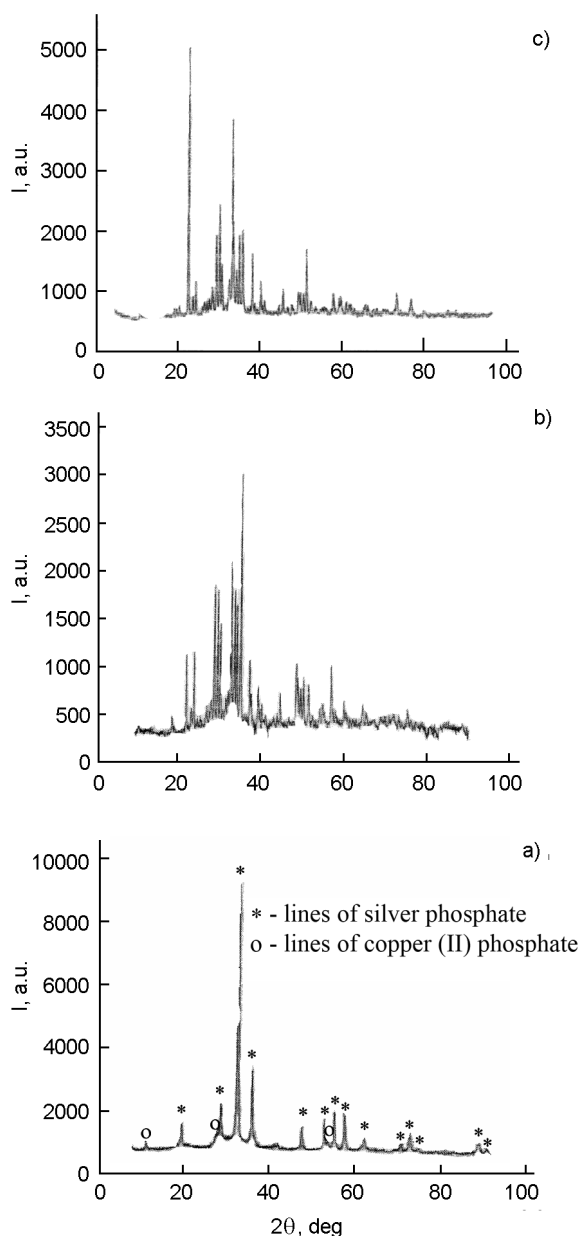


Fig. 2. Diffraction patterns of air-dried mixture of co-deposited silver and copper(II) phosphates (a); the same mixture heated at 500°C for 1 h (b); the same mixture heated at 720°C for 1 hour (c).

curve) (endoeffect). In addition, since the heat of the first effect obviously exceeds that of the second effect, the DTA-curve demonstrates the first effect only. The second exo-effect occurring at 417°C is associated with the interaction between silver and copper(II) phosphates with the formation of a double phosphate AgCuPO_4 , which is confirmed by X-ray diffraction analysis data.

Therefore, the cumulative results demonstrate that the mixtures of co-precipitated

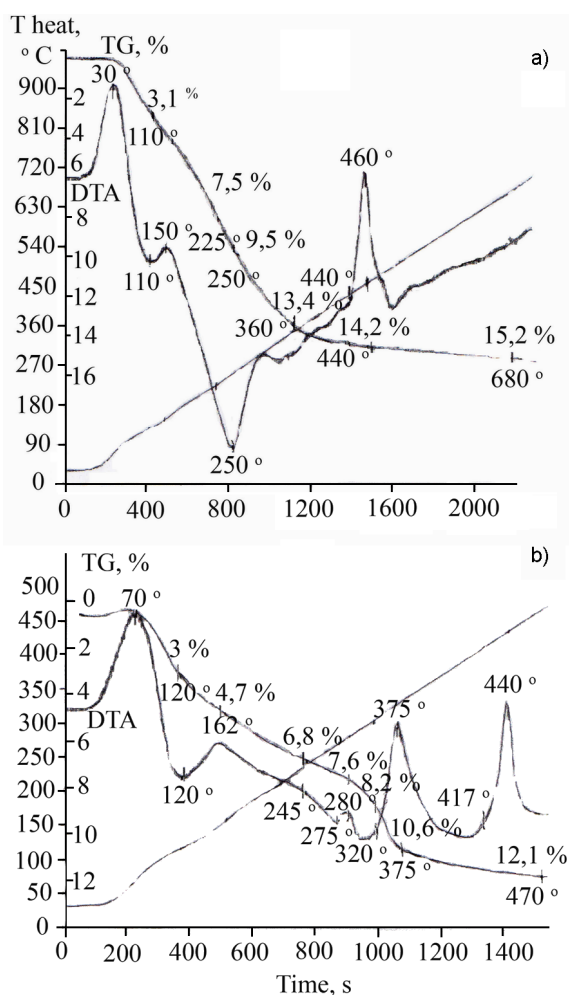


Fig. 3. Thermogram of air-dried mixtures of co-deposited argentum and magnesium phosphates (a) and argentum and copper(II) phosphates (b).

silver and magnesium or silver and copper(II) phosphates are deposited from the aqueous solutions. Under the conditions of this study, double phosphates have been only formed from the co-deposited mixtures of silver and copper(II) phosphates heated above 417–440°C (optimally, to 720°C).

The deposition of the mixtures of silver and magnesium or silver and copper(II) phosphates from solutions can be explained by different compositions of metallic ions hydrated in the aqueous solution. Their compositions differ by the coordination number of water molecules, size, motion rate of these hydrated metallic ions in the solutions, and by their physicochemical nature. In particular, Ag^+ ion, in the nearest coordination sphere, has two molecules, Cu^{2+} ion — four molecules, and Mg^{2+} ion — six molecules of water bound to it. Due to the different sizes of hydrated ions of silver

and magnesium or copper(II), the double phosphates containing these metals were not formed in the aqueous solutions under the conditions of the study. This, however, does not eliminate the possibility of production of double silver and magnesium or silver and copper(II) phosphates under different conditions, e.g. in free of water ionic fluxes.

In this regard, an attempt has been made to use the eutectic solution $\text{KNO}_3\text{--NaNO}_3$ (55 wt.% KNO_3) as a solvent for the synthesis of double silver and magnesium or silver and copper(II) phosphates. It has been found that even careful heating of the $\text{KNO}_3\text{--NaNO}_3\text{--AgNO}_3\text{--Mg}(\text{NO}_3)_2$ mixture with prior drying, or of the similar mixture with $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, does not lead to the production of nitrate flux containing anhydrous silver nitrates and bivalent metals. At temperature as low as $\sim 170^\circ\text{C}$, nitrates of bivalent metals start to turn into their oxonitrates and, with further heating — into oxides. This prevents the production of double phosphates at 240–300°C in these nitrate fluxes. However, this process becomes possible in anhydrous eutectic fluxes at 110–120°C [18].

The mixtures of $\text{KNO}_3\text{--NaNO}_3\text{--Ag}_2\text{O--AgNO}_3\text{--MgO}$ and $\text{KNO}_3\text{--NaNO}_3\text{--Ag}_2\text{O--AgNO}_3\text{--CuO}$ were treated with ~ 120 mL of water and a sodium hydroxide solution to reach pH ~ 11 . This resulted in magnesium and silver oxides in the precipitate of the first mixture, and copper(II) and argentum oxides — of the second mixture. Then, the precipitates in both mixtures were dissolved in the diluted (1:3) nitric acid and adjusted to pH 4.0 with the sodium hydroxide solution for the solution of silver and magnesium nitrates and pH 3.5 — for the solution of silver and copper(II) nitrates. Each solution had a volume of 150 mL. In each of two other vials, 3.1 g of sodium hydrogenphosphate were dissolved in 150 mL with pH-level 8.5. The solutions in all vials were heated to boiling. Then, respective solutions of nitrates were added to the solutions of sodium hydrogen phosphate with mixing. The formation of a yellow precipitate of co-deposited silver and magnesium phosphates and a green precipitate of silver and copper(II) phosphates was observed. The mother solutions had pH below 6, therefore, the solutions of the precipitates and mother solutions were supplemented with the sodium hydroxide solution until pH 6.5. The precipitates and their mother solutions were kept for 10 days with regular mixing. Then

the solutions were filtered, washed out and dried. The resulting filtration residues were the mixtures with a previously determined composition.

One of the obstacles to the isolation of individual double phosphates may be the size factor. In particular, in the $\text{Mg}_3(\text{PO}_4)_2$ compound, one PO_4^{3-} anion corresponds to one and a half ions of Mg^{2+} , which is equivalent in size to $1.5 \times 0.072 \text{ nm} = 0.108 \text{ nm}$ ($r_{\text{Mg}^{2+}} = 0.072 \text{ nm}$ at the coordination number six as per oxygen (according to Previt and Shannon)). The sum of ionic radii for Ag^+ and Mg^{2+} ions (0.115 nm and 0.072 nm, respectively) is 0.187 nm [20]. However, the key factor in the formation of the double phosphates, as well as other compounds with tetrahedral ions, is the size of voids caused by tetrahedra of PO_4^{3-} anions joined by their edges, vertices or faces. Therefore, the formation of the double phosphates becomes real under certain conditions of their synthesis.

The resulting mixtures of silver and magnesium phosphates and silver and copper(II) phosphates have antimicrobial properties. In particular, 1.5 L of deep-well water treated with a 0.5 g mixture of silver and magnesium phosphates may be used in the treatment of inflammations of urinary tract (tested over 20 days).

Electrolytic splitting of city water using a graphite electrode showed a catalytic effect of the silver and copper(II) phosphate mixture on the rate of hydrogen (at the cathode) and oxygen (at the anode) deposition. In this case, 150 mL of city water has been supplemented with 0.15 g of the specified mixture. A zinc-chloride 9 V battery of a DIGITAL type has been used as *dc* power supply. The studied mixture caused 1.6-fold increase in the rate of gases' deposition. Electrolytic water splitting under similar conditions but with silver electrodes would result in significantly increased rate of silver dissolution at the anode and in the rate of its deposition at the cathode (in the presence of the same mixture); this may find application in anodic refinement of silver.

4. Conclusions

The co-deposited silver and magnesium phosphates and silver and copper(II) phosphates have been studied using chemical, thermogravimetric and X-ray diffraction analyses. It has been shown that the particles of magnesium and copper(II) phosphates are nano-sized, in particular up to

100 nm. In parallel, the deposition of polycrystalline cubical silver phosphate from aqueous solutions has been observed under the same conditions. Heating of the mixture of co-deposited silver and copper(II) phosphates to more than 417°C (and up to 720°C) resulted in the formation of a double phosphate. The resulting mixtures have antimicrobial properties, thus, may be applied for the treatment of water. In addition, they act as catalysts of electrochemical processes (electrolytic waters plitting, anodic refinement of silver).

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