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## Synthesis of Bismuth (III) Oxocarbonate for Medicine

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### Abstract

The formation of bismuth (III) oxocarbonate ( $\text{BiO})_2\text{CO}_3$  was studied by means of X-ray phase analysis, electron microscopy and chemical analysis. Comparative analysis of different methods of obtaining bismuth oxocarbonate was carried out: bismuth precipitation from nitric solutions with the addition of ammonium carbonate and with the inverse order of reagent addition, as well as the interaction of solid bismuth oxohydroxonitrate with the aqueous solution of ammonium carbonate. The reasonability of the synthesis of fine crystalline highly pure bismuth (III) oxocarbonate through the interaction of oxohydroxobismuth (III) nitrate monohydrate with the solutions of ammonium carbonate.

**Key words:** bismuth oxocarbonate, high-purity compounds, chemical synthesis, nitric solutions

### INTRODUCTION

Bismuth (III) oxocarbonate ( $\text{BiO})_2\text{CO}_3$  is widely used as a pharmacopoeic preparation and exhibits antibacterial properties against *Helicobacter pylori*, gastro pathogenic bacteria [1–3]. According to the data reported in [4], bismuth oxocarbonate forms layered crystal structure with orthorhombic symmetry, space group  $I\ mm2$ .

The industrial method of the production of bismuth (III) compounds is based on processing bismuth-containing nitric solutions because nitric acid is the best solvent for the granules of metal bismuth and its oxide, which are usually as initial compounds. The basic requirements to the compounds obtained for medicine and technology are high purity and reactivity.

It is known [5] that potassium, sodium and ammonium carbonates at  $\text{pH} \geq 7$  cause the formation of white precipitates from the solutions of bismuth salts; these precipitates are bismuth oxocarbonate. The interaction of bismuth oxohydroxonitrate with the solutions of ammonium carbonate resulting in the formation of bis-

muth oxocarbonate, and its subsequent thermal decomposition at  $400\text{ }^\circ\text{C}$  are used in industry to obtain monoclinic (a) modification of bismuth oxide [6]. This method is successfully used to obtain bismuth oxide with high specific surface and allows eliminating the evolution of toxic nitrogen oxides into the atmosphere.

The goal of the present work was to carry out comparative analysis of different methods of obtaining high-purity bismuth (III) oxocarbonate through precipitation from nitrate solutions by adding ammonium carbonate solution and using the reverse order of adding the reagents, as well as through the interaction of solid bismuth oxohydroxonitrate with the solution of ammonium carbonate.

### EXPERIMENTAL

Mineral acids, salts and alkalis of kh. ch. or os. ch. reagent grade were used in the work. Initial bismuth nitrate solution (420 g/L) was prepared by dissolving bismuth oxide of Os. Ch.

13-3 reagent grade in nitric acid with the concentration of 6 mol/L or metal of Vi grade (not less than 98 % Bi) in 8 mol/L HNO<sub>3</sub>; the resulting solutions were diluted with distilled water in the 1 : 1 proportion.

Bismuth precipitation from solutions was carried out in fluoroplastic or glass vessels equipped with mixers. Thermostating was carried out with WB-2 water baths. Precipitation of basic bismuth carbonate from nitric solutions was carried out by adding ammonium carbonate solution to the bismuth-containing solution or using the reverse order of reagent addition. The ratio of the volumes of initial and final solutions was 1 : 5, it was corrected by adding distilled water. The mixture was stirred for 1 h. The precipitate was separated by filtering, washed with distilled water and dried in the air.

Determination of the macro amounts of Bi(III) in solutions was carried out by titrating with the solution of complexon III with xylene orange as indicator; micro amounts were determined by means of photocolormetry with sodium iodide [7]. The concentrations of impurity metals in the products were determined by means of atomic absorption using a 280FS AA spectrophotometer (Varian, Australia). Reaction products were dissolved preliminarily in diluted HNO<sub>3</sub> (1 : 1). Determination of nitrate ions in the solid reaction products was carried out by means of photometry with sodium salicylate [8] after their transfer into solution by treating with 2 M NaOH for 1 h at (80±10) °C.

X-ray phase analysis (XPA) of precipitated products was carried out with a Bruker D8 Advance diffractometer using CuK<sub>α</sub> radiation; the speed of counter rotation was 0.5 deg/min. Phase identification was carried out using the powder diffraction database PDF-2 (2008) [9]. To measure specific surface of the samples, we used the chromatographic method of thermal desorption of argon.

## RESULTS AND DISCUSSION

The studies on bismuth precipitation from nitric solutions by adding ammonium carbonate solution showed that the degree of bismuth precipitation (*R*) and the composition of the precipitated compound are substantially depen-

dent on pH and process temperature. With an increase in pH, the degree of bismuth isolation into precipitate increases and reaches 93–97 % at pH 0.8–1 and process temperature (22±2) °C (residual concentration of bismuth in solution is 5–10 g/L). With an increase in process temperature, the quantitative precipitation of bismuth is achieved at lower pH values, so that at 60 °C within pH 0.8–1.0 *R* = 97–99 % (residual concentration of bismuth in solution is 2–5 g/L). An increase in pH to 3–9 allows almost complete (*R* = 99.99 %) precipitation of bismuth (residual concentration of bismuth does not exceed 0.05 g/L).

Bismuth is precipitated from nitric solutions after the addition of ammonium carbonate at pH 7 and higher. However, major impurity metals (such as lead and silver) are precipitated together with bismuth. because of this, to obtain high-purity bismuth oxocarbonate, it is necessary to purify it preliminarily from im-

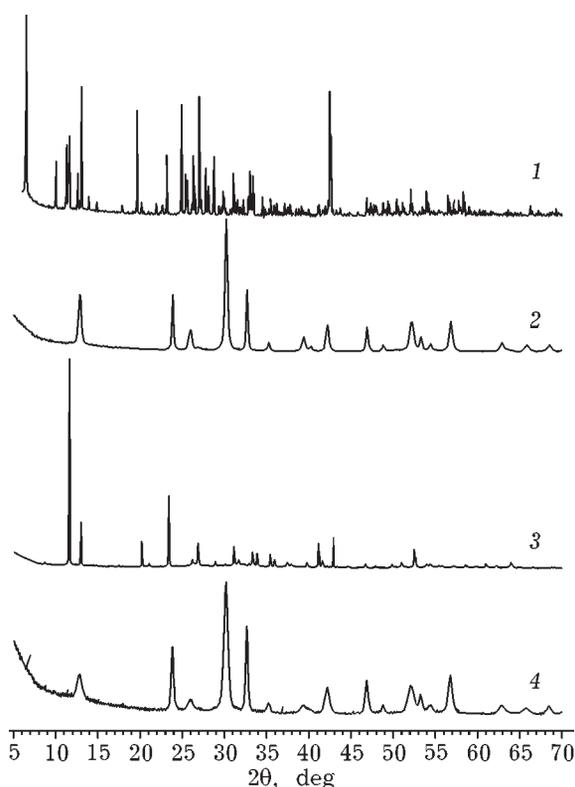


Fig. 1. Diffraction patterns of the samples: 1, 2 – oxohydroxobismuth nitrate trihydrate and bismuth oxocarbonate obtained as a result of its treatment with ammonium carbonate solution, respectively; 3, 4 – oxohydroxobismuth nitrate hydrate and bismuth oxocarbonate obtained as a result of its treatment with the solution of ammonium carbonate, respectively.

purity metals. It was demonstrated in [10] that for bismuth precipitation from nitric solutions the procedure meeting the requirements of the purity of final product is precipitation at a temperature not lower than 50 °C up to pH ~ 0.9, single washing with nitric solution (pH ~ 1) and

double washing with water. The studies provide evidence that according to XPA data (Fig. 1, curve 1) bismuth oxohydroxonitrate obtained at a temperature of (22±2) °C has the composition  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and is represented by elongated flat-prismatic crys-

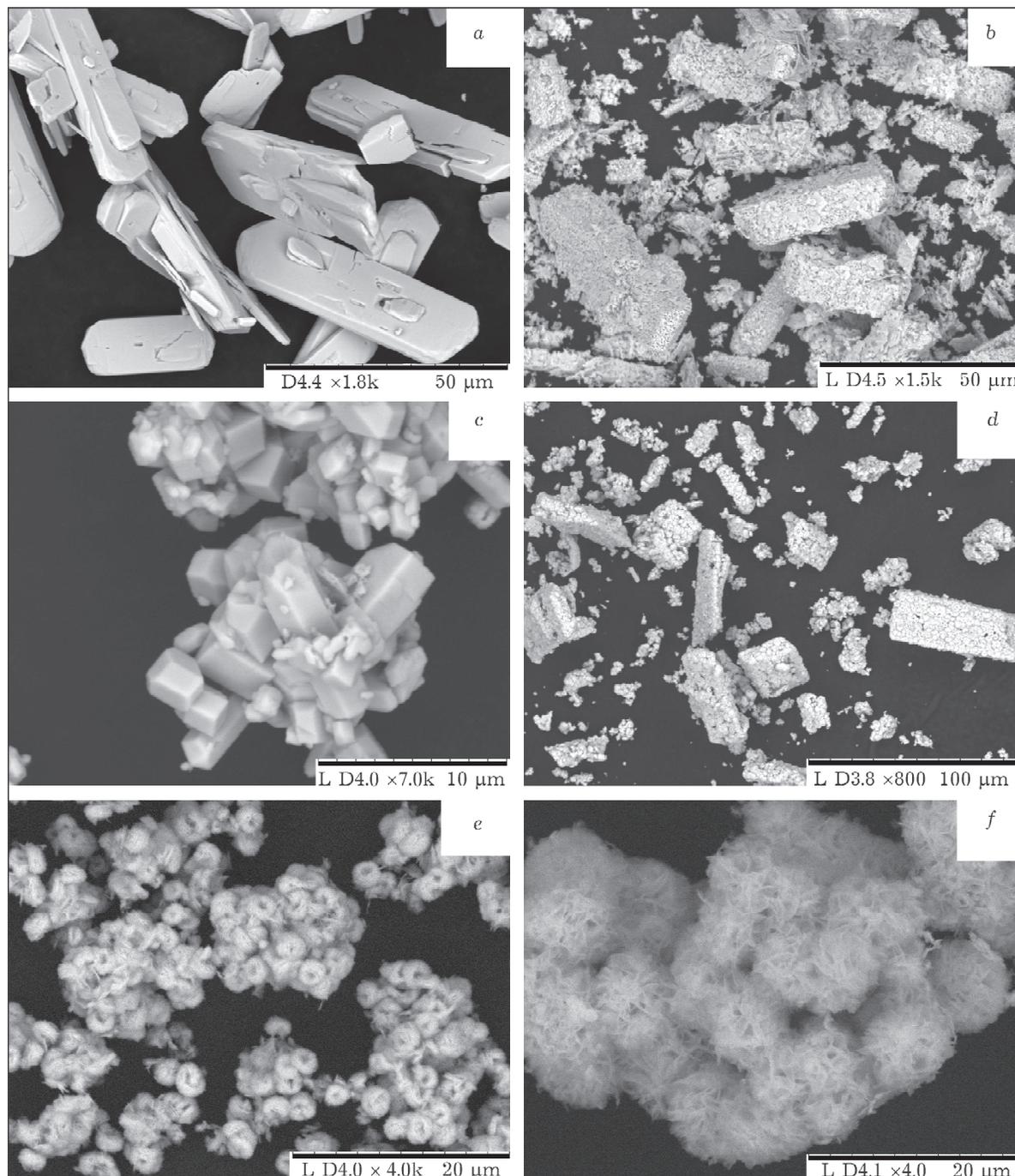


Fig. 2. Microphotographs of samples: *a*, *b* – oxohydroxobismuth (III) nitrate trihydrate (*a*) and bismuth oxocarbonate obtained by its treatment with ammonium carbonate solution (*b*); *c*, *e* – oxohydroxobismuth nitrate monohydrate (*c*) and bismuth oxocarbonate obtained by its treatment with ammonium carbonate solution (*e*); *d*, *f* – bismuth oxocarbonate obtained after the double treatment of oxohydroxobismuth nitrate monohydrate with water and the solution of ammonium carbonate (*d*) and after the addition of bismuth nitrate into the solution of ammonium carbonate (*f*).

tals with the size in the basal plane 10–30  $\mu\text{m}$  and thickness about 1–3  $\mu\text{m}$  (Fig. 2, *a*). The treatment of bismuth oxohydroxonitrate with the solution of ammonium carbonate at  $\text{pH} \geq 8$  involves the substitution of nitrate ions by carbonate ions with the formation of oxocarbonate having the composition  $(\text{BiO})_2\text{CO}_3$  (see Fig. 1, curve 2). The coarse crystals of the product have the same prismatic appearance as the crystals of initial bismuth oxohydroxonitrate. However, now these are not oriented joints of flat-prismatic blocks but a voluminous arrangement of the joints of plate-like crystals (see Fig. 2, *b*). Specific surface of the product is 3.1  $\text{m}^2/\text{g}$ .

The data of XPA (see Fig. 1, curve 3) provide evidence that bismuth precipitates from nitric solutions at the process temperature of  $(60 \pm 10)^\circ\text{C}$  and  $\text{pH} \sim 0.9$  in the form of well crystallized oxohydroxonitrate with the composition  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ , which is represented, according to the data of electron microscopy, by the joints of short prismatic crystals with the largest size of separate crystal in the basal plane 2–10  $\mu\text{m}$  and thickness 2–5  $\mu\text{m}$ . The volume of the precipitate in this case is 2–3 times smaller than in the case when the process is carried out at  $(22 \pm 2)^\circ\text{C}$ , while settling and filtration proceed 5–6 times more rapidly. However, at the stage of precipitate washing with the nitric solution with  $\text{pH} \sim 1$  and double washing with water at a temperature of  $60^\circ\text{C}$ , followed by the treatment of the precipitate with ammonium carbonate solution at the same temperature, the product is recrystallized into bismuth oxocarbonate (see Fig. 1, curve 4). Similarly to the first case, the product is shaped as coarse crystals (see Fig. 2, *d*), and its specific surface is equal to 4.2  $\text{m}^2/\text{g}$ .

For the purpose of obtaining bismuth oxocarbonate with high specific surface, we studied the treatment of bismuth oxohydroxonitrate, having the composition  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$  and obtained by bismuth precipitation at a temperature of  $60^\circ\text{C}$  and  $\text{pH} 9$  with subsequent single washing with nitric solution with  $\text{pH} 1$ , by ammonium carbonate solution. One can see in Fig. 2, *e* that bismuth oxocarbonate is represented by the aggregates up to 10  $\mu\text{m}$  in size, composed of spherical particles about 1–3  $\mu\text{m}$  in size; in turn, these particles are composed of thin plate-like

crystals. In this case, specific surface of bismuth oxocarbonate is equal to 8.6  $\text{m}^2/\text{g}$ . It should be noted that bismuth oxocarbonate with the specific surface equal to 12–16  $\text{m}^2/\text{g}$  can be obtained by adding the nitric solution of bismuth to ammonium carbonate solution at the acidity  $\text{pH} 8$ –9 and process temperature  $(22 \pm 2)^\circ\text{C}$ . Similarly to the previous case, bismuth oxocarbonate is represented by spherical particles 5–10  $\mu\text{m}$  in size, composed of thin plate-like crystals (see Fig. 2, *f*). However, in this case it is necessary to use bismuth nitrate solutions purified preliminarily from impurity metals. Investigations allowed us to propose the following scheme to obtain high-purity bismuth oxocarbonate with high specific surface from the metal of Vi 1 grade, which is usually used as the initial raw material. Metal bismuth (10 kg) of the composition (%): Bi 98.6, Pb 1.22, Cu  $1.5 \cdot 10^{-4}$ , Ag  $6.8 \cdot 10^{-2}$ , Fe  $4.2 \cdot 10^{-3}$ , Zn  $5.2 \cdot 10^{-4}$ , Cd  $2.0 \cdot 10^{-4}$  was fused at a temperature of  $350^\circ\text{C}$ , 20 % of technical-grade bismuth oxide was added, temperature was increased to  $600^\circ\text{C}$ , then the powder was mixed for 4 h. Thus obtained technical bismuth oxide was dissolved in nitric acid with the concentration of 7 mol/L. The bismuth-containing solution (410 g/L bismuth, 140 g/L free nitric acid) was diluted with distilled water (1 : 1), and the solution of ammonium carbonate with the concentration of 2.5 mol/L was added under mixing at the process temperature of  $60^\circ\text{C}$ . Still under mixing, the precipitate was washed once with the nitric solution ( $\text{pH} 1$ ) at a temperature of  $60^\circ\text{C}$ , then the treatment with ammonium carbonate solution was carried out at  $\text{pH} 8$  and temperature  $22^\circ\text{C}$  for 2 h. Bismuth oxocarbonate was washed twice with water and dried at  $70^\circ\text{C}$ . Bismuth oxocarbonate obtained in large-scale test had the following composition (%): bismuth 81.7, lead  $9 \cdot 10^{-5}$ , silver  $2 \cdot 10^{-5}$ , copper  $2 \cdot 10^{-5}$ , iron  $3 \cdot 10^{-5}$ , arsenic  $< 5 \cdot 10^{-5}$ , cadmium  $< 3 \cdot 10^{-5}$ , zinc  $4 \cdot 10^{-5}$ , nitrate ions 0.036. This corresponds to the requirements of USP 30 NF 25 for pharmacopoeic bismuth oxocarbonate. The specific surface of the product was 8.4  $\text{m}^2/\text{g}$ .

## CONCLUSION

Thus, it is reasonable to obtain high-purity bismuth (III) oxocarbonate with high specific

surface using the following route: metal bismuth is preliminarily oxidized with atmospheric oxygen, bismuth is purified from impurity metals by bismuth precipitation in the form of oxohydroxobismuth (III) nitrate monohydrate, the latter compound is transformed into bismuth oxocarbonate  $(\text{BiO})_2\text{CO}_3$  by treating with the aqueous solution of ammonium carbonate.

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