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Synthesis of Bismuth (III) Compounds for Technology and Medicine

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Abstract

Literature data and experimental results of research of chemistry and synthesis of different bismuth compounds for technology and medicine were systematized and generalized. The advisability of using processes of hydrolysis and heterogeneous solid-solution reactions to produce high-purity and reactivity bismuth compounds was demonstrated.

Keywords: bismuth compounds, carboxylates, oxide, nitrates, oxochloride, hydroxochromate, citrate, bismuth tripotassium dicitrate, solutions, high purity

INTRODUCTION

World bismuth consumption is 15–16 thousand tons per year, and its use in the production of compounds is 57.2 % of world consumption, metallurgical additives – 26.4 %, alloys – 8.8 %, and in other areas – 7.6 % [1]. Herewith, bismuth compounds are widely used in the preparation of catalysts, optical glasses, ceramics, luminophores, pigments, ferroelectric, acoustooptical, pharmaceutical, superconducting, magnetic, and other materials [2–4].

Currently, bismuth compounds are prepared from Bismuth Bi1 metal (no less than 98 % of Bi) produced resulting from the pyrometallurgical processing of bismuth-containing ores and concentrates. The main impurities therein are lead, silver, copper, zinc, antimony, arsenic, iron, and tellurium.

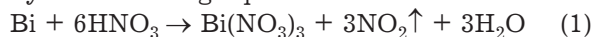
Disadvantages of existing schemes for the production of bismuth compounds are the release of toxic nitrogen oxides at the step of obtaining bismuth-containing nitric acid solutions, and also the complexity of producing bismuth compounds of the required purity in the hydrolytic processing of these solutions.

This paper presents authors results on the preparation of bismuth-containing nitric acid solutions followed by their processing with the preparation of high-purity bismuth compounds most widely used in technology and medicine.

PREPARATION OF SOLUTIONS OF BISMUTH SALTS

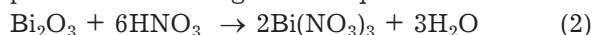
Dissolving Bi metal in nitric acid that is one of the best solvents for bismuth, its alloys and compounds is used in the production of Bi

compounds. Bismuth-containing nitric acid solutions are produced by dissolving bismuth metal granules in nitric acid with a concentration of 7–9 mol/L. Herewith, about 50 % of nitric acid is released into the gas phase as nitrogen oxides, and dissolution may be described by the following equation:



To decompose nitrogen oxides evolved during bismuth dissolution, it is proposed to use urea, hydrogen peroxide, and oxygen delivery to the dissolution zone [5]. Herewith, emission of nitrogen oxides into the gas phase can be eliminated, however, the rate of bismuth dissolution is significantly reduced.

In our view, in order to produce solutions of bismuth salts, it is desirable to use Vi_2O_3 as the initial compound, as its dissolution reaction proceeds according to the equation:



It is suggested to produce bismuth (III) oxide from metal bismuth by heating its melt to 800–1200 °C in the oxygen flow followed by rapid cooling vapours [2]. It is worth noting that bismuth vapours and its oxide melt have high reactivities, whereupon the oxide may be contaminated with the material of the crucible and the reactor.

An opportunity to oxidize bismuth metal was demonstrated by the introduction of 10–30 % bismuth oxide or sodium carbonate into a melt at 350±50 °C and stirring followed by increasing temperature to 600±50 °C [5]. Paper [6] explored the effect of pre-mechanochemical treatment of mixtures of bismuth metal and different compounds on the process of bismuth oxidation with air oxygen. It was determined that oxidation of bismuth metal took place at the dispersing stage. Herewith, it was demonstrated that mechanochemical treatment of a mixture of bismuth metal with 10–30 % of its oxide resulted in reducing bismuth oxidation temperature beginning from 350 to 200 °C. Furthermore, during calcination of the mechanochemically treated mixture of bismuth metal and its oxide (20 %) the complete transfer of bismuth to the oxide can be carried out at 300 °C with a time of ignition of 12 h, and an ignition temperature of 400 °C for 1 h.

In the case of mechanochemical activation of a mixture of bismuth metal and sodium carbonate followed by washing the resulting product with water, it is mainly bismuth oxide and oxo/hy-

droxo-carbonate and can be used at the stage of preparation of solutions of bismuth salts. It was demonstrated that resulted from mechanochemical activation of a mixture of bismuth metal in sodium chloride followed by washing with water the resulting product, the latter was a mixture of bismuth oxide and oxo chloride that could be used at the stage of preparation of bismuth-containing hydrochloric acid solutions. In order to prepare bismuth oxide, pre-mechanochemical activation of bismuth metal with sodium nitrate or ammonium nitrate could also be used. Herewith, the specific surface area of bismuth oxide derived resulted from mechanochemical activation of bismuth metal with various compounds varies within 0.29–5.87 m²/g. As it follows from the data of paper [5], pre-oxidation of bismuth allows obtaining concentrated solutions of bismuth perchlorate (1200 g/L Bi), nitrate (500 g/L Bi), and chloride (400 g/L Bi).

PURIFICATION OF BISMUTH FROM IMPURITY METALS BY PRECIPITATION FROM NITRIC ACID SOLUTIONS AS OXOHYDROXONITRATE

As bismuth compounds are produced from Bi1 metal, then in order to prepare high purity species, pre-treatment of bismuth from impurity metals is required. In order to purify bismuth from impurity metals, hydrolysis of bismuth is used when alkaline reagents (usually, aqueous ammonia) are added to bismuth-containing nitric acid solutions [7]. An opportunity to efficiently purify bismuth from impurity metals was demonstrated by the addition of water or a solution of ammonia carbonate to a bismuth-containing nitric acid solution [8]. In order to prepare high purity bismuth oxohydroxonitrate, hydrolytic treatment of bismuth from impurities was carried out by the addition of a nitric acid solution of bismuth and water heated as high as 65±5 °C with a volume ratio of H₂O and a Bi-containing solution of 8 : 1 followed by bringing the pH of the mixture by aqueous ammonia to pH 1.0. The residue was washed with water at 25±5 °C and dried at 105±5 °C.

Resulting from the processing of 1.0 kg of Bi1 bismuth metal (Kazsvetmet LLP, Ust-Kamenogorsk), containing (%): 99.1 bismuth; 0.71 lead; $1.0 \cdot 10^{-3}$ zinc; $1.0 \cdot 10^{-3}$ antimony; $3.3 \cdot 10^{-3}$ copper; $1.0 \cdot 10^{-1}$ silver; $2.0 \cdot 10^{-4}$ arsenic; $1.0 \cdot 10^{-3}$ iron, and $1.0 \cdot 10^{-4}$ tellurium, there was prepared 1.32 kg basic bismuth nitrate

containing (%): bismuth oxide 79.93; lead $1 \cdot 10^{-3}$; zinc $<4 \cdot 10^{-5}$; antimony $<5 \cdot 10^{-6}$; copper $<1 \cdot 10^{-5}$; silver $1 \cdot 10^{-4}$; arsenic $<5 \cdot 10^{-5}$; iron $7 \cdot 10^{-5}$; and tellurium $<1 \cdot 10^{-4}$. The direct extraction of bismuth into bismuth oxohydroxonitrate from bismuth metal was 96.5 %, and its specific surface area was $1.08 \text{ m}^2/\text{g}$. Extra pure oxohydroxonitrate may be used in the synthesis of bismuth compounds by the solid solution reaction.

SYNTHESIS OF BISMUTH (III) COMPOUNDS FOR TECHNOLOGY

Out of Bi compounds used in technology, bismuth oxide, bismuth nitrate, and bismuth basic nitrate, bismuth sulphate, bismuth hydroxochromate, bismuth carboxylates, and also complex bismuth-containing metal oxides occupy the largest production volume. Bismuth oxide may be prepared by thermal decomposition of bismuth oxohydroxonitrate, bismuth nitrate, and bismuth oxocarbonate, and also organobismuth species, such as bismuth acetate, bismuth citrate, and bismuth salicylate [8].

The industrial production of bismuth oxides is mainly related to thermal decomposition of nitric acid salts at $670 \pm 20 \text{ }^\circ\text{C}$. Nevertheless, there is atmospheric evolution of toxic nitrogen oxides, when bismuth nitric acid salts are thermally decomposed. From this standpoint, it is more desirable to produce bismuth oxide by thermal decomposition of bismuth oxocarbonate at $400 \pm 20 \text{ }^\circ\text{C}$.

Bismuth(III) oxide may be obtained, when bismuth salts are treated with NaOH solutions. Herewith, one manages to eliminate the atmospheric evolution of nitrogen oxides in case of using nitric acid salts and significantly reduce energy consumption, as it is possible to carry out the alkaline dehydration process at $23 \pm 3 \text{ }^\circ\text{C}$. This being said, the specific surface area of the resulting oxide is $8.8 \text{ m}^2/\text{g}$, while that of the oxide derived by thermal decomposition of bismuth nitrates is $0.6 \text{ m}^2/\text{g}$ [8].

Alongside with bismuth (III) oxide, bismuth (III) nitrate pentahydrate that is used in the synthesis of bismuth-molybdenum and bismuth-antimony catalysts in medicine upon preparation of pharmacopeial drugs and in the paint industry is widely used in the chemicals sector. Synthesis of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is carried out by dissolution of bismuth metal in nitric acid followed by solution evaporation to a den-

sity of $1.9 \text{ g}/\text{cm}^3$ and cooling. The drawbacks of this process are atmospheric emission of nitrogen oxides and high energy consumption when a bismuth-containing nitric acid solution is evaporated. From the environmental standpoint, it is advisable, in our opinion, to produce bismuth nitrate by the reaction of bismuth oxohydroxonitrate with a composition of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with aqueous solutions of nitric acid with free acid concentration of 2.8–10.6 mol/L in a solution and a final temperature of the process of 15–20 °C. Herewith, the bismuth extraction degree into the final product reaches 90 % [9].

Papers [10, 11] demonstrate an opportunity to produce bismuth oxychloride (BiOCl) and bismuth (III) hydroxochromate (BiOHCrO_4) from nitric acid process solutions. As demonstrated by the research undertaken on the hydrolytic processing of bismuth-containing hydrochloric acid solutions, the bismuth extraction degree into Bi(III) oxochloride is 95% at $65 \pm 5 \text{ }^\circ\text{C}$, when they are diluted with distilled water (1 : 10). However, there is no purification of bismuth from such main impurity metals, as lead and silver. In order to produce high-purity bismuth oxochloride, bismuth was pre-purified from impurity metals by precipitation from nitric acid solutions as oxohydroxonitrate; the latter was dissolved in nitric acid and HCl was added to the resulting solution at a process temperature of 60 °C and a 1.0 molar ratio of chloride ions to bismuth [10].

As testified by the undertaken research on bismuth(III) hydroxochromate precipitation from nitric acid process solutions, the bismuth extraction degree into the precipitate is significantly dependent on the introduced amount of dichromate ions and almost does not depend on reagent addition order and solution temperature. Nevertheless, process temperature, reagent addition order, and rate have an effect on product morphology and structure.

A monoclinic modification of BiOHCrO_4 may be acquired regardless of reagent addition rate and order at a process temperature of $23 \pm 3 \text{ }^\circ\text{C}$, and also in case of elevated temperatures of about 60 °C when adding a solution of potassium dichromate to that of bismuth nitrate. In order to precipitate bismuth(III) hydroxochromate as an orthorhombic modification, slow addition of bismuth nitrate solution to that of potassium dichromate and carrying

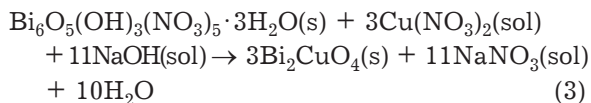
out the process at a temperature not less than 60 °C are required. The specific surface area of the monoclinic modification of bismuth hydroxochromate varies within 0.2–8.8 m²/g, and orthorhombic 0.8–1.9 m²/g depending on synthesis conditions [11].

Bismuth carboxylates are often used as initial compounds when bismuth-containing oxide materials are synthesized. These compounds are also promising to produce nanoscale bismuth particles during the thermal processing of carboxylates. Papers [12, 13] investigated high-purity bismuth ortho-hydroxo-laurate and bismuth oxohydroxostearate with a composition of Bi₆O₄(OH)₄R₆, where R is the lauric or stearic acid anion. These carboxylates were produced by the addition of a solution of sodium laurate or sodium stearate into bismuth nitrate solution at 60±10 °C with the molar ratio HR/Bi = 1.0–1.1 and free nitric acid solution concentration of 0.1 mol/L.

Paper [14] explored an opportunity to produce bismuth formates resulting from the interaction of bismuth oxohydroxynitrate with a composition of [Bi₆O₄(OH)₄](NO₃)₆ · H₂O with formic acid solutions. It was determined that solubility isotherms had two branches driven by producing bismuth formates (BiOCOOH and Bi(COOH)₃) in the system. It was demonstrated that thermal decomposition of basic formate in air allowed obtaining bismuth oxide of the trigonal modification, while thermal degradation of the bismuth oxonitrate – bismuth oxoformate mixture is a promising procedure for obtaining bismuth oxonitrate species with a composition of Bi₅O₆(NO₃)₂OH and Bi₅O₇NO₃.

Synthesis of complex oxides based on bismuth oxide is usually carried out by alloying oxides at temperatures above 850 °C and the repeated repulping of the resulting products that leads to contaminating the materials. It was demonstrated that reactions of bismuth oxohydroxynitrate with solutions of metal salts could be used for the synthesis of complex oxide materials. The performed research testifies the desirability of the synthesis of bismuth cuprate by the reaction of bismuth oxohydroxynitrate with copper salt solutions [15].

With a Cu/Bi molar ratio of 0.5, process temperature of ≥50 °C and solution NaOH concentration of 0.25 mol/L, a compound with a composition of Bi₂CuO₄ is generated by the reaction:



Comparison of this hydrolytic procedure of synthesis with known ones demonstrated that in order to completely transfer a stoichiometric mixture of bismuth and copper oxides to cuprate, its annealing for no less than 100 hrs with several intermediate millings at 720±20 °C is required.

In order to provide better mixture quality for growing bismuth germanate monocrystals, the interaction of bismuth oxohydroxynitrate with a solution of ammonium germanate was explored [16]. It was demonstrated that it was optimum to carry out the process of hydrolytic preparation of bismuth germanate at 50–70 °C, treating solid bismuth oxohydroxynitrate in aqueous ammonia in the pH range of 7–10. Products with a composition of Bi₄Ge₃O₁₂ with the eulytine structure or that of Bi₁₂GeO₂₀ with the sillenite composition were produced depending on stoichiometry. In order to produce bismuth orthogermanate (Bi₄Ge₃O₁₂) during the hydrolytic procedure of synthesis, interaction product calcination at 520 °C is sufficient. The solid-phase interaction of bismuth and germanium oxides occurs very slowly at *T* > 780 °C with the formation of a number of intermediate products.

SYNTHESIS OF BISMUTH (III) COMPOUNDS FOR MEDICINE

High-purity and reactivity bismuth compounds, such as bismuth basic nitrate and bismuth medium nitrate, bismuth basic carbonate, bismuth salicylate, bismuth tartrate, bismuth gallate, bismuth tribromophenolate, and bismuth citrate, currently find broad applications in medicine in Russia and abroad. These compounds are used as active ingredients in the synthesis of medicinal drugs, such as Vikalin, Vikair, Xeroform, Dermatol, Bismoverol, Biyohinol, De-Nol, Desmol, Pylorid *etc.* Requirements that are imposed on compounds used in medicine are high purity and therapeutic activity.

As noted above, bismuth purification from impurity metals may be reached during its precipitation from nitrate solutions as [Bi₆O₄(OH)₄](NO₃)₆ · H₂O by the addition of water or a solution of ammonium carbonate. Its

hydrolysis with generating bismuth oxohydroxynitrate ($[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$) that is used as a pharmacopoeial drug in medicine takes place at the washing stage of this compound.

The advisability of preparation of basic pharmacopoeial bismuth from bismuth metal by hydrolytic purification of bismuth nitrate added to the solution of water or of a solution of ammonium carbonate at a pH of 0.55–1.0 and a temperature of at least 50 °C, followed by washing the precipitate with water and drying the product at 80–120 °C was demonstrated [17].

Paper [18] considers the preparation of basic bismuth carbonate ($(\text{BiO})_2\text{CO}_3$) for medicine. The performed comparison of preparation methods of bismuth oxocarbonate by both precipitation of bismuth from nitric acid solutions during the addition of ammonium carbonate solutions thereto and by the reaction of solid bismuth oxohydroxynitrate with an aqueous solution of ammonium carbonate testifies the advisability of synthesis of finely high-purity finely crystalline oxohydroxobismuth (III) nitrate monohydrate and ammonium carbonate solutions.

Bismuth compounds with gallic and tartaric acids are widely used in medicine. Paper [19] explored the precipitation process of gallic acid bismuth basic salt by the addition of an aqueous solution of gallic acid thereto. The composition of the resulting compound, *i.e.* bismuth oxogallate trihydrate ($\text{C}_6\text{H}_2(\text{OH})_3\text{COOBiO} \cdot 3\text{H}_2\text{O}$), was determined. It was demonstrated that the specific surface area of the product depended on the concentration of free nitric acid in a solution and process temperature and had values from 29 to 2 m²/g. Relying on the performed research, a variant of synthesis of high-purity gallic acid bismuth basic salt by its precipitation from nitrate solutions in a 0.95–0.98 molar ratio of gallate ions to bismuth at 60 °C was suggested.

The advisability of preparation of high-purity basic bismuth gallate by the reaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of gallic acid [20]. Synthesis of high-purity basic bismuth gallate was carried out by the reaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of gallic acid in a 1.0–1.1 molar ratio of gallate ions to bismuth; nitric acid concentration in a solution of 0.5–1.0 mol/L, and process temperature of 20–70 °C.

In order to synthesize high-purity bismuth tartrate, the reaction of oxohydroxobismuth

(III) nitrate trihydrate with aqueous solutions of tartaric acid was investigated [21].

It was determined that high-purity bismuth ditartrate trihydrate might be obtained resulting from the reaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of tartaric acid to bismuth with a 2.1 ratio, 0.2–0.6 M concentration of hydrogen ions in a solution, and process temperature of 20±3 °C. As demonstrated in [22], the basic bismuth tartrate obtained by precipitation from lacto-acetic acid solutions is not an individual compounds but a mixture of bismuth(III) tartrate ($\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$) and bismuth(III) oxoacetate ($\text{BiOC}_2\text{H}_3\text{O}_2$).

Bismuth salts with succinic acid are widely used for medicinal purposes. The basic salt of succinic acid is a medicinal substance of the drugs Ubiquinol (Merck, Germany) and Pholcones (Cooper, France), used to treat angina, laryngitis, and pharyngitis. Paper [23] explored precipitation of bismuth from nitric acid solutions depending on the concentration of malate ions, process temperature, pH values of the solution during the addition of an optically active L(-)-isomer and racemic form of DL-malic acid thereto. It was demonstrated that in the addition of L(-)-malic acid in nitric acid solutions monohydrate bismuth malate ($\text{BiC}_4\text{H}_3\text{O}_5 \cdot \text{H}_2\text{O}$) is precipitated, while in case of DL-malic acid, a compound with a composition of $\text{BiC}_4\text{H}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ was formed. The advisability of preparation of bismuth malates for medical use by the deposition of bismuth malate was demonstrated, when a bismuth-containing solution is added to that of sodium malate in a 1.1–1.2 molar ratio of malate ions to bismuth and process temperature of 60±10 °C.

Bismuth citrate is widely used in microbiology to prepare nutrient media, and it is also a precursor for preparation of bismuth tripotassium dicitrate, *i.e.* the main active component highly effective anti-ulcer drugs of the type De-Nol (Netherlands). Paper [24] determines conditions for the formation of bismuth nitrates with compositions of $\text{BiC}_6\text{H}_5\text{O}_7$, $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$ and $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$.

It was demonstrated that bismuth citrate ($\text{BiC}_6\text{H}_5\text{O}_7$) used in medicine in synthesis of pharmaceuticals and in microbiology during the production of bacterial drugs was advisable to prepare by precipitation from nitric acid solutions from the production of bismuth compounds during the addition of solutions of

citric acid thereto in a 1.1–1.2 molar ratio of citrate ions to bismuth in a solution and process temperature of 60 ± 5 °C.

High-purity bismuth citrate with $\text{BiC}_6\text{H}_5\text{O}_7$ composition could be obtained using a solid-solution reaction [25, 26]. Reference [26] demonstrates an opportunity to produce bismuth citrate resulting from treatment of bismuth oxohydroxonitrate ($\text{Bi}_6\text{O}_4(\text{OH})_4(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$) with an aqueous solution of citric acid in a 10.4 mass ratio of L/S in a range of pH values of 0.1–0.3 with process temperatures of 22 ± 2 °C or with that of 2.3 at 70 ± 2 °C. Bismuth citrate was also produced resulting from the treatment of bismuth oxohydroxonitrate monohydrate ($\text{Bi}_6\text{O}_4(\text{OH})_4(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$) with an aqueous solution of citric acid with L/S of 2.3 and process temperature of 22 ± 2 °C.

As bismuth tripotassium citrate is the main active component of highly effective anti-ulcer drugs, paper [27] explored the interaction of bismuth citrate ($\text{BiC}_6\text{H}_5\text{O}_7$) with aqueous solutions of potassium hydroxide of different concentrations. Conditions for the formation of the potassium salt of bismuth (III) citrate with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ were determined. The advisability to produce this compound was demonstrated resulting from the reaction of an aqueous solution of KOH with bismuth citrate with their molar and mass ratio of 1.0.

Bismuth tripotassium dicitrate is included in the List of vital and essential medicinal products for medical use for 2018 by Order of the government of the Russian Federation of October, 23, 2017 No 2323-p. Relying on the performed research, it was determined that bismuth tripotassium dicitrate (colloidal bismuth subcytrate) used as a medicinal substance in anti-ulcer drugs was bismuth-potassium-ammonium citrate. The advisability to produce it by the synthesis of high-purity bismuth citrate was demonstrated according to the reaction of oxohydroxobismuth (III) nitrate trihydrate with solutions of citric acid, dissolution of the resulting citrate in an aqueous solution of KOH in the presence of ammonium hydroxide followed by product crystallization by vaporization or spray drying.

Pre-clinical investigations on the exploration of general toxic and local irritant effects of the drug bismuth tripotassium dicitrate were carried out during course intragastric adminis-

tration; it was concluded that that the investigated preparation was safe [28].

The developed technologies of high-purity bismuth(III) oxide (ultra pure grade 13-3) for bismuth citrate and bismuth nitrate have been incorporated into the production in the Rare Metals Plant UK JSC (Novosibirsk region). The Institute of Solid State Chemistry and Mechanochemistry (Siberian Branch of Russian Academy of Sciences) that has the license of the Ministry of Industry and Trade of the Russian Federation of July 18, 2018 for the manufacture of drugs has adapted a technology in the pilot production of bismuth tripotassium dicitrate to produce the domestic anti-ulcer drug Vitridinol, *i.e.* an analogue of De-Nol medicine (Netherlands), in the pilot production.

CONCLUSION

It has been demonstrated, that it is advisable to prepare concentrated solutions of bismuth salts from bismuth metal as a result of its oxidation by air oxygen *via* mixing a melt at 600 °C or using the mechanical activation process at 300 °C. It has been found that bismuth precipitation from nitric acid solutions as bismuth oxohydroxonitrate using water and alkaline reagents makes it possible to efficiently purify bismuth from foreign-metal impurities at a process temperature of 60–70 °C and produce bismuth compounds with impurity metal content of less than $1 \cdot 10^{-3}$ %. It has been determined that high purity bismuth compounds for technology and medicine may be produced by the reaction of bismuth oxohydroxonitrate and a solution of acid, alkali, or metal salt.

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