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Obtaining Hydrated Antimony Pentoxide for the Sorption of Cesium and Strontium Ions

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Abstract

Potentialities were studied concerning the obtaining of hydrated antimony pentoxide (HAP) *via* much simpler methods than the method of SbCl_5 hydrolysis described in the literature. A sorption capacity was tested for the HAP obtained with respect to Cs^+ and Sr^{2+} , whose radionuclides are of environmental hazard when released into water basins. The oxides obtained were studied by means of powder X-ray diffraction method. It is established that the treatment of Sb powder by 16 M HNO_3 solution and the subsequent drying at 150 °C results in obtaining antimony tetroxide rather than pentoxide. Evaporation of antimony solution in nitrohydrochloric acid (aqua regia) and drying at the same temperature results in the formation of HAP, whose composition is close to $\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. Adding HNO_3 to the solutions in the course of evaporation results in decreasing the hydration level. It was revealed that when HNO_3/HCl molar ratio in aqua regia is equal to 5 : 1 the HAP composition approaches to $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ (H_3SbO_4), whereas with $\text{HNO}_3/\text{HCl} = 9 : 1$ therein the hydrate composition approaches to $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ($\text{H}_4\text{Sb}_2\text{O}_7$).

Key words: hydrated antimony pentoxide, sorption of cesium, strontium, antimony tetroxide

INTRODUCTION

The interest with respect the hydrated antimony pentoxide (HAP) is caused by its high, as compared to other sorbents, ability of absorbing Na^+ . Under certain conditions, as it was determined in [1], the absorption proceeds in a very selective manner, which helped solving the problem of neutron-activation analysis for many objects. Thus, radionuclide ^{24}Na was selectively removed in an exclusive manner. Afterwards, different studies were performed concerning the properties of HAP [2–6], but from the preparative standpoint, mainly hydrolysis SbCl_5 was considered. It was found that the HAP could be obtained either in an amorphous (or glassy) form, or in a crystalline form; the latter can be peptized to a less extent. In the review [7] the authors listed a number of ways to transfer the substance from the amorphous state to the crystalline one, the most rapid and convenient among those consists in the

HAP drying within the temperature range of 110–180 °C. The authors of [5] indicate that at the temperature approximately equal to 150 °C, the samples immediately become crystalline. To improve the sorption properties of HAP the authors of [6] recommended carrying out the hydrolysis of SbCl_5 at 70 °C, whereas the drying should be performed at 110 °C. There researchers noted also a very high sorption capacity of HAP for Na^+ (about 1 mg-eq/g of the sorbent).

In order to synthesize SbCl_5 , researchers use the process of metallic antimony chlorination. Further, the hydrolysis is carried out, wherein the molar ratio between the amount of water used and SbCl_5 is higher than 500 [5]. To avoid the conversion of Sb(V) into Sb(III) it is recommended to preliminary saturate the water with chlorine. In this connection, it seemed appropriate to study the possibility of HAP obtaining *via* easier methods, to investigate its sorption capacity with respect to Cs and Sr, whose radionuclides are of environmental hazard.

The authors of [7] mentioned the possibility of obtaining HAP *via* dissolving antimony in aqua regia, evaporating the solution with adding HNO_3 in the course of and the subsequent drying at the temperature of 110–120 °C. A number of authors [8–11] mentioned the reaction of antimony treatment by HNO_3 as a possible method for obtaining HAP without indicating the conditions of the reaction. Data concerning the conditions of the reaction, as well as data concerning the sorption and other properties of antimony oxides obtained by these methods are not available from the literature.

EXPERIMENTAL

Weighed Sb samples grinded into powder (300 mg) was poured with 10 mL of 16 M HNO_3 solution, the suspension was evaporated at the temperature of 155 °C. Oxide glasses were kept until the termination of evolving the vapour, as judged by the absence of colouring the indicator paper, and then oxides were dried during 0.5 h. The oxides cooled were used in the experiments.

The identical weighed samples of antimony were dissolved in 4 mL of aqua regia (1 mL of 16 M HNO_3 solution and 3 mL of 11 M HCl solution); the solutions were evaporated. In the course of evaporation, as recommended by the authors of [7], periodically were added 2, 4, 8.5 and 17 mL of 16 M HNO_3 solution, by 0.5 mL aliquots. Further processing the samples was carried out using the above mentioned method.

The oxides obtained *via* the evaporation of the Sb solution in aqua regia with the addition of HNO_3 (and without), represented white coarse-grained sediments. As against, the oxides obtained *via* Sb treatment by 16 M HNO_3 , represented fine loose powders with a weakly pronounced light-cream shade.

The sorption capacity of the obtained oxides was determined under static conditions with respect to extracting Cs^+ and Sr^{2+} in millimolar solutions of the nitrates of these elements (pH ~ 2). The volume of the solutions amounted to 50 mL, the weighed portion of the sorbent was equal to 0.5 g, the procedure was performed at a room temperature. We used the method of atomic absorption (Z-800 spectro-

photometer). The sorption level value was calculated from the difference between the content of the component in the initial solution and that in the solution at the end of the process after the phase separation. The total error does not exceed 10 %. According to the results of the experiments for the sorbent obtained by treating Sb by concentrated HNO_3 , the value of Cs^+ sorption level was equal to 2.4 and 2.7 mg/g of the sorbent (two experiments), the value of sorption level for Sr^{2+} amounted to 8.7 mg/g of sorbent. For the sorbent obtained from Sb solution in aqua regia, the value of sorption level for Cs^+ was equal to 17.1, 17.9, 17.2 mg/g of sorbent (three experiments), the value of sorption level for Sr^{2+} amounted to 5.1, 6.2 mg/g sorbent (two experiments).

It is obvious that the sorption of Cs^+ is almost an order of magnitude higher than when using the oxide derived from aqua regia solution. The phase separation after the sorption in this case was easier to perform, too: after the contact with the sorbent the solutions grow tur-

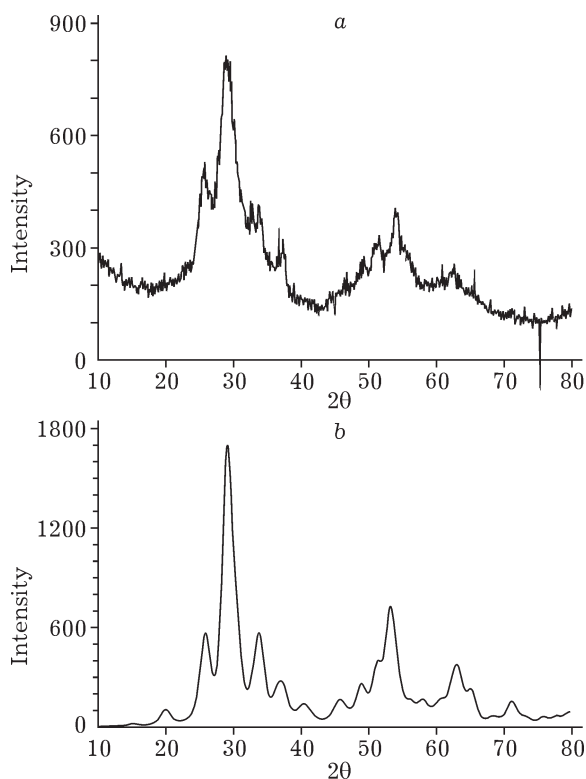


Fig. 1. Diffraction pattern for antimony oxide obtained by treating Sb powder by 16 M HNO_3 solution (a) and diffraction pattern for Sb_2O_4 according to [12] (b).

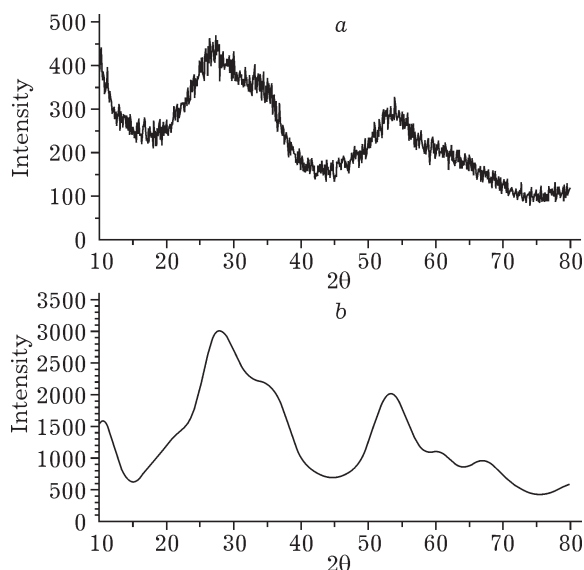


Fig. 2. Diffraction pattern for antimony oxide obtained *via* evaporation of Sb solution in aqua regia with a small amount of HNO_3 (a) and diffraction pattern for oxide obtained by the authors of [13] (hydroxonium pentaantimonate) (b).

bid to a lesser extent. The value of Sr^{2+} sorption level we took to be the same in both cases.

One should note the fact that with using the oxides of Sb, obtained *via* the treatment of Sb by 16 M HNO_3 solution, the value of sorption level for Cs^+ was low being less as compared to the sorption of Sr^{2+} .

Figure 1 demonstrates the XRD patterns for Sb_2O_4 [12] and the oxide powder obtained *via* treating Sb by 16 M HNO_3 solution. One can see that the X-ray diffraction patterns have much in common (the authors of [12] obtained Sb_2O_4 *via* heating Sb_2O_3 up to 460 °C). This fact was unexpected because, according to the literature, the temperature of 150 °C is insufficient for converting pentoxide into tetroxide.

Figure 2 demonstrates the diffraction patterns for the oxide obtained *via* evaporating the aqua regia solution of Sb and for the antimony oxide obtained by the authors of [13], those appeared similar, too.

The authors of [13] described the resulting oxide by formula $\text{H}_3\text{OSb}_5\text{O}_{13}$ and named it oxonium oxopenta antimonate. However, from the chemical point of view, it is improbable that the condensation of ions $[\text{Sb}(\text{OH})_6]^-$ could result in the formation of singly charged ions $[\text{Sb}_5\text{O}_{13}]^-$.

Such condensation, according to [14], results in the formation of $[\text{Sb}_3\text{O}_{10}]^{5-}$ and $[\text{Sb}_4\text{O}_{13}]^{6-}$.

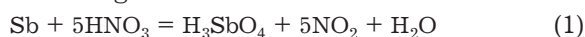
It should be emphasized that the evaporation of Sb solutions in aqua regia results in the formation of HAP, to all appearance, due to the generation of a strong oxidant according to the reaction



In this case, the causes are obvious for a much higher sorption level of these oxides with respect to Cs^+ compared to the sorption level of oxides obtained in the processing of Sb by 16 M HNO_3 solution. According to generally accepted estimates, antimony oxides with a lower valence are bad absorbents for alkali metal ions.

Due to the fact that the obtaining of tetroxide instead of HAP in the course of Sb processing by 16 M HNO_3 solution is not consistent with the data of [8–11], we performed an additional investigation.

The authors of [11] indicate that concentrated HNO_3 makes antimony to convert into antimonic acid (conditional formula H_3SbO_4) according to the reaction



where $2\text{H}_3\text{SbO}_4 = \text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$

or



with the assumption that the two water molecules are included into the structure of the HAP. Otherwise, the indication that there is the formation of the only ortho-acid observed made by the authors of [11] is not sufficiently justified, since there could be an entry through pyro- and meta-acids.

However, according to the authors of [15], the oxidation of antimony with nitric acid results in the formation of Sb_2O_4 instead of the HAP and "... it can be considered as antimony oxide antimonate". (However, Sb_2O_4 , in our opinion, corresponds to formula $\text{SbO} \cdot \text{SbO}_3$). As it was mentioned by the authors of [16], " Sb_2O_4 ... is formed *via* the oxidation of the metal, Sb_2O_3 or Sb_2S_3 by HNO_3 ". The author of monograph [17] noted that whereas "... Sb_2O_5 is formed *via* the oxidation of antimony with nitric acid; the substance in its pure form is very difficult to obtain, since in the course of drying the hydrate initially formed in the above mentioned reaction, a partial loss of oxygen occurs resulting in the formation of Sb_2O_4 ".

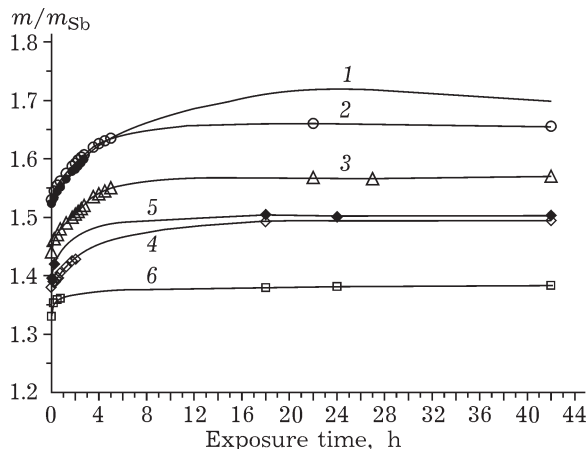


Fig. 3. Stabilizing the hydration level of antimony oxides depending on exposure time after cooling down to a room temperature: 1–5 – oxides obtained *via* evaporating the Sb solutions with HNO_3/HCl molar ratio equal to 0.5 (1), 1.5 (2), 2.5 (3), 4.5 (4) 9 (5); 6 – oxide powder obtained *via* Sb treatment by 16 M HNO_3 solution.

Against the background of these contradictory judgments, a question remains open whether H_2O removal occurs (with a partial loss of oxygen at the same time) resulting in the formation of Sb_2O_4 , even with such a low drying temperature value as 150°C . So, according to [4], the removal of water (and a partial loss of oxygen) starts at 230°C . To all appearance, the reaction between Sb and 16 M HNO_3 solution occurs in a somewhat different manner than it was indicated by the authors of [8–11].

The dissolution of antimony in aqua regia, according to [18], is described as

$$2\text{Sb} + 5\text{HNO}_3 + 5\text{HCl} = \text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O} + 5\text{NOCl} \quad (3)$$

We wrote the formula for ortho acid in the form of pentahydrate, by the analogy with reaction (1).

Figure 3 demonstrates the results of additional experiments performed in order to clarify the influence of HNO_3 upon the composition of oxides obtained *via* the evaporation of Sb solutions in aqua regia and processing Sb only by 16 M HNO_3 solution. It is seen that the mass of the dried oxide samples after cooling down to a room temperature still increases during several hours. There is no doubt that the amount of HNO_3 added in the process of evaporation affects the final result. With no HNO_3 added (curve 1), there is a good correlation with the reaction (3). The ratio between the mass of the obtained oxide and the mass of antimony initially taken into experiment is close to 1.7 (as it

is for $\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$). Increasing the amount of HNO_3 results in the fact that this ratio decreases down to 1.55, which corresponds to the composition such as H_3SbO_4 ($\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$) (curve 3). Curve 4 corresponds to the stabilization of the oxide cooled down to a room temperature, whose composition is $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ($\text{H}_4\text{Sb}_2\text{O}_7$). The successive dehydration of the oxides obtained in the course of increasing the amount of added HNO_3 should result in the formation of $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (HSbO_3).

However, curve 5, corresponding to the sample wherein the molar ratio between HNO_3 and HCl is twice comparing to that for the sample corresponding to curve 4, still indicates that the composition is close to $\text{H}_4\text{Sb}_2\text{O}_7$, *i. e.*, no further dehydration occurred. However, an “infinite” excess of HNO_3 with respect to HCl , *i. e.*, processing the Sb with HNO_3 only (curve 6) results in oxide with the ratio equal to 1.39 (for HSbO_3 this value is equal to 1.4). At the same time, the diffraction pattern for this oxide is similar to the diffraction pattern for Sb tetroxide presented in the literature (see Fig. 1). Thus, there is a significant deviation from the reactions (1) and (2) taking place; the fact requires for explanation.

To all appearance, the occurrence of the tetroxide structure (see Fig. 1) proceeds in the course of the reaction between Sb and HNO_3 (tetroxide, by an analogy to [15], could be understood as $\text{SbO} \cdot \text{SbO}_3$, *i. e.*, the antimony exists therein in both oxidation states (III) and (V)). This could be possible in the case when the reaction (1) is competed by reaction

$$2\text{NO}_2 + 2\text{H}_3\text{SbO}_4 = 2\text{H}_2\text{SbO}_3 + \text{N}_2\text{O}_5 + \text{H}_2\text{O} \\ = \text{SbO} \cdot \text{SbO}_3 \cdot 2\text{H}_2\text{O} + 2\text{HNO}_3 \quad (4)$$

This assumption is valid, since it is known that Sb(V) plays the role of a strong oxidant in the acidic environment. For the reaction (4) the mass ratio between the resulting oxide and antimony taken into reaction is equal to 1.41, which indicates that there is correlation observed with respect to the position of curve 6 (see Fig. 3).

CONCLUSION

1. Using the method of powder XRD, studies were performed concerning Sb oxides, obtained *via* treating Sb powder by 16 M HNO_3

solution with the further evaporation and drying at 150 °C. The same method was used for investigating the oxides derived from the Sb solution in aqua regia under similar conditions.

2. As it follows from the diffraction data, the oxides obtained via processing the Sb with 16 M HNO₃ solution only, exhibit a certain crystallinity level. Oxides obtained from the aqua regia solution of Sb exhibit almost no crystallinity. With processing Sb only by 16 M HNO₃ solution using the method described resulted in obtaining not HAP, but Sb₂O₄ which could be presented as SbO · SbO₃. However, the evaporation of the same Sb solutions in aqua regia results in the formation of HAP. Adding HNO₃ results in reducing the hydration level for the oxides obtained, whereas a great excess of HNO₃ promotes the transformation of HAP into antimony antimonate. Experiments concerning the sorption of Cs⁺ and Sr²⁺ were conducted for the obtained oxides. The efficiency they obtained oxides as sorbents appeared low.

3. The parameters for oxides obtained via evaporating the Sb solution in aqua regia as Cs⁺ sorbents as the sorbent are almost an order of magnitude better than those for oxides obtained via processing the Sb by 16 M HNO₃ solution only. However, the oxides obtained are prone to peptization: an initially clear solution after the sorption experiments grows turbid to a considerable extent within several days. This means

that using the HAP would result in the contamination of initial solutions with antimony.

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