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Spectrophotometric Determination of Impurities such as Iron and Copper in High Purity of Antimony with 8-Hydroxy-quinoline

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高純度안티몬 中의 不純物(鐵 및 銅)의 8-Hydroxy-quinoline에 依한 吸光光度定量法

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要 約

8-Hydroxy-Quinoline (Oxine)에 依한 高純度 Antimony 中 不純物(鐵 및 銅)의 吸光光度 定量法을 檢討하였다. 試料의 黃酸溶液에 안티몬을 Masking 하기 위하여 必要한 酒石酸의 影響을 調査한 結果, 0.5M—酒石酸溶液 10ml로서 600mg 까지의 안티몬을 Masking 할 수 있었다.

pH 範圍는 鐵은 5.0—5.7, 銅은 3.5—4.0 이었다. 鐵은 580mμ에서 吸光度를 測定하면 되나, 銅은 15% 苛性소오다溶液으로 逆抽出하고, 남은 鐵을 580mμ, 410mμ에서 測定하여 補正할 必要가 있다.

500mg 안티몬에 對하여 鐵은 150μg(0.005~0.03%)까지, 銅은 100μg(0.006~0.016%)까지 定量이 可能했다.

Abstract

A spectrophotometric method for the determination of major impurities, such as iron and copper, in high purity of antimony with 8-hydroxyquinoline (oxine)has been studied. The iron-oxinate is stable at the pH range 5.0 to 5.7, and the copper-oxinate at the pH range 3.5 to 4.0. To mask antimony in sulfuric acid solution of sample, author has investigated the effect of tartaric acid on antimony, and found that 10mL of 0.5M tartaric acidsolution could mask up to 600mg of antimony. The absorbance of iron-oxinate was measured at 580mμ and iron could be determined, but it is necessary for copper-oxinate to measure at 410 and 580mμ respectively after removing heavy metals other than copper by back extraction with 15% solution of sodium hydroxide, and copper could be determined by making a correction for the amounts of iron present. Up to 150μg of iron (0.005—0.03%), and 100μg of copper (0.005—0.016%), in 500mg of antimony could be determined.

Introduction

Recently, there is a demand for high purity of antimony as foils and thermoelectric materials[1], but few reports for the methods of determination of trace amounts of impurities in high purity of antimony are known. According to JIS K8080, hydrogen sulfide is passed in the solution of sample and precipitated sulfides are dissolved in hydrochloric acid solution. The solution is oxidized with ammonium peroxydisulfate, the ammonium thiocyanate solution is added as chromogenic reagent, and iron is determined by colorimetric method. For copper, the solution is neutralized with ammonium hydroxide solution and then solution is made alkaline, the solution of ammonium thiocyanate and of pyridine in acetic acid-ammonium hydroxide buffer solution is added, the copper is extracted with chloroform, and it is determined by the colori-

metric method. However, this method was limited to minimum concentrations of 0.02% iron and 0.001% copper in analytical reagent grade antimony, and was tedious and time consuming one.

The present paper describes a relatively rapid and simple spectrophotometric method for the determination of micro amounts of impurities such as iron and copper in high purity of antimony.

Experimentals

Apparatus: Absorbances were measured with a Shimazu spectrophotometer, type QR-50 using 1.0cm. glass cells. All apparatus, pH-meter, separatory funnel, and automatic measuring pipetter for chloroform were used following to the direction of K. Motojima[3].

Reagents: Iron and copper standard solutions. Stock solutions containing 100μg of iron and 100μg of copper per ml respectively, were prepared by dissolving pure iron and copper in concentrated nitric acid. The standardization was made by titration with a standard potassium permanganate solution for iron, and with a standard EDTA solution and PAN as an indicator at pH 8.0 for copper. Dilutions of these solutions were made as required. Antimony was purchased from Kanto Chemical Co., of Japan.

(a) 2% Oxine solution——A 2% solution was prepared by dissolving 2g of oxine in 4ml of glacial acetic acid and then bringing up to final volume 100ml with water.

(b) Chloroform——Chloroform was purified by washing several times, with 6N-sulfuric acid, aqueous solution of 2N· in ammonium hydroxide and then water respectively, drying over anhydrous calcium chloride and distilling. The recovery of chloroform was also made by this procedure.

(c) 15% Sodium hydroxide washing solution ——10ml of chloroform was added to about 500ml of water and shaken vigorously for I min. After it has settled, the organic layer was discarded, the aqueous layer was run through filter paper and 75g of sodium hydroxide was dissolved in the above filtrate.

The other reagents were of ananalytical reagent grade or were used with further purification.

Regular laboratory distilled water was used and stored in polyethylene carboys.

Standard procedure

(a) Iron——Dissolve a 500mg of sample containing up to 5μg of iron in a beaker with concernt-rated sulfuric acid, keeping the solution heated on plate and evaporate excess of the acid. Add 10ml of 0.5M tartaric acid solution and 3ml of 2% oxine solution, and adjust pH of the resulting solution between 5.0 to 5.7 with 2N ammonium hydroxide. Transfer the solution to 150ml separatory funnel and bring the volume to 100ml with water. Extract with 10ml of chloroform added from automatic measuring pipetter, by vigorous shaking for about one min. Draw off organic layer into erlenmeyer flask with glass stopper, containing 1g of anhydrous sodium sulfate. Measure the absorbance at 580mμ against a blank solution.

(b) Copper——— Dissolve a 500mg of the sample containing up to 5μg of copper in a beaker with concentrated sulfuric acid following above (a) procedure. Add 10ml of 0.5M tartaric acid solution and 3ml of 2% oxine solution. Adjust pH between 3.5 and 4.0 with 2N ammonium hydroxide solution, and transfer the solution to 150ml separatory funnel, and bring the volume to 100ml with water. Extract with 10ml of chloroform added from automatic measuring pipetter, by vigorous shaking for about one min.. Draw off organic layer into another 150ml separatiory funnel and add 100ml of 15% sodum hydroxide washing solution. Shake vigorously for one min. After it has settled, draw off the second organic layer into erlenmeyer flask with glass stopper containing 1g of anhydrous sodium sulfate. Measure the absorbances at 410 and 580mμ against a blank solution respectively. Copper can be determined by making a correction for the amounts of iron present.

The following formula[3] holds:

$$C_{Cu} = \frac{A_{410} - A_{580} \cdot \frac{a^{Fe}_{410}}{a^{Fe}_{580}}}{a^{Cu}_{410}}$$

Where, C_{Cu}: copper present, A_{410} and A_{580}: absorbances measured at 410 and 580mμ. respectively. a^{Cu}_{410}, a^{Fe}_{410} and a^{Fe}_{580}: absorbance indexes of copper and

iron at each wavelength. The values of a^{Cu}_{410}, a^{Fe}_{410} and a^{Fe}_{580} are found from the calibration curves for copper and iron at 410 and 580mμ, respectively.

Therefore a^{Cu}_{410} : 0.00946, $\frac{a^{Fe}_{410}}{a^{Fe}_{580}}$: 0.94.

Results and Discussion

(A) Masking effect of Tartaric Acid on Antimony

The masking effect of trataric acid on antimony was studied. Approximately 100ml of solutions containing 5 and 10ml of tartaric acid solution respectively, 3ml of oxine solution each, and with varying amounts of antimony, were extracted with each 10ml of chloroform at a pH 5.0 to 5.4, by vigorous shaking for about one min. The extracts were dried in the erlenmeyer flask with glass stopper, containing 1g of anhydrous sodium sulfate. The measurements of the absorbances at 410mμ versus a blank solution, were made on these dried extracts. As is shown in Fig 1, 5ml. of tartaric acid is sufficient for up to 250mg of antimony as masking agent which is useful at the same time to prevent the precipitation while 10ml of tartaric acid is sufficient for up to 600mg of antimony. It is effective to add oxidation agent on dissolving the antimony sample in sulfuric acid solution since antimony (V) is not extracted at all[4] while antimony (Ⅲ) is extracted partly.

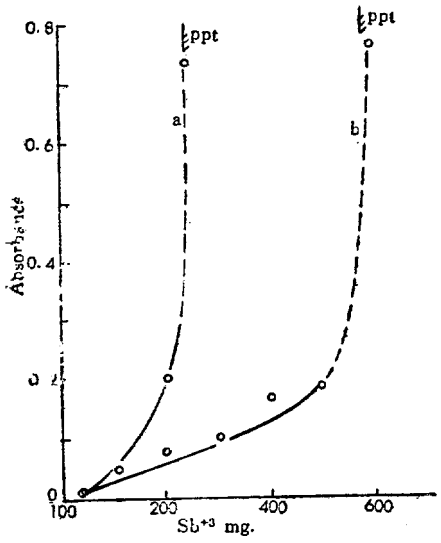

Figure 1. Effect of tartaric acid onSb oxinate.
pH 5—5.2, 2% oxine 3ml. at 410mμ, a: 0.5M—Tartaric acid 5ml., b: 0.5M—Tartaric acid 10ml.

(B) The Effect of Tartaric Acid on Iron and Copper Oxinate

In order to study the effect of tartaric acid on the extraction of iron, approximately 100ml of solutions containing 50μg of iron, 3ml of oxine solution each, and with varying amounts of tartaric acid, were extracted with each 10ml of chloroform at a pH 3.5 to 4.0. Then measurements of the absorbances at 580mμ versus chloroform, were made on these dried extracts. To study the effect of tartaric acid on the extraction of copper, similar sets but 48μg of copper present at a pH 5.0 to 5.4 were also run. Absorbances were measured at 410mμ on these dried extracts. As is shown in Table 1, 10ml of tartaric acid do not affect on the extraction. The addition of 10ml of 0.5M tartaric acid solution, therefore, was decided for the standard procedure.

Table 1. The Effect of Tartaric Acid on the Extraction of Fe-oxinate and Cu-oxinate.

Fe(μg)	pH	0.5M Tartaric acid	Absorbances 580mμ	Found (μg)
50	5.2	··· ml	0.373	50.5
50	5.3	2 〃	0.363	49.1
50	5.4	4 〃	0.370	50.1
50	5.2	6 〃	0.380	51.4
50	5.2	8 〃	0.367	49.7
50	5.3	10 〃	0.367	50.8

Cu(μg)	pH	0.5M-Tartaric acid	Absorbance 410mμ	Found (μg)
48	3.5	··· ml.	0.450	47.6
48	3.5	2 〃	0.439	46.4
48	3.6	4 〃	0.450	47.6
48	3.5	6 〃	0.450	47.6
48	3.5	8 〃	0.460	48.6
48	3.5	10 〃	0.450	47.6

(C) The Effect of pH on Iron and Copper Oxinate in Tartaric Acid

In order to study the effect of the pH on the extraction of iron and copper oxinate in tartaric acid, the following series of experiments were made. Approximately 100ml of solutions containing 50μg of iron and copper respectively, 3ml of oxine solution and 10ml of tartaric acid each and sufficient amounts of either hydrochloric acid, or ammonium hydroxide and

ammonium chloride to attain the desired pH, were extracted with each 10ml of chloroform. Measurements of pH were made on the aqueous layer after extraction. The extracts were dried with anhydrous sodium sulfate. The absorbances were measured at 580mμ for iron and at 410mμ for copper respectively against a blank solution on these dried extracts. As is shown in Fig. 2, there is a maximum and constant absorbance over the pH range above 4.0 for iron and above 3.5 for copper.

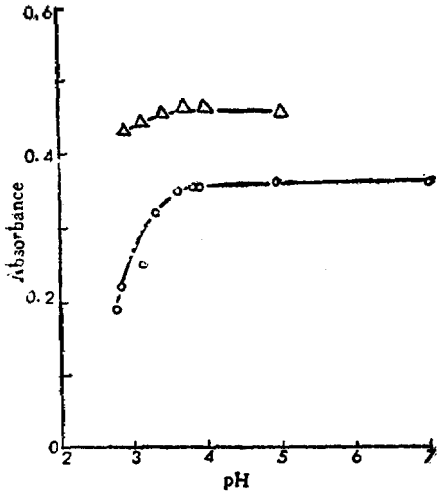

Figure 2. Effet cof pH on extraction of Fe-oxinate, Cu-oxinate in tartaric acid solution.

2% Oxine 3ml., 0.5M-Tartaric acid 10ml., extracted with 10ml. of $CHCl_3$. ○ Fe: 50μg at 580mμ. △ Cu: 50μg at 410mμ.

(D) The Effect of pH on Iron Oxinate in Tartaric Acid and Antimony Solution

The optimum pH on the extraction of iron in antimony and tartaric acid was investigated in the extractions obtained from the solutions containing 25μg of iron and 500mg of antimony, and in those obtained from the solutions containing 500mg of antimony only. The desired series of pH is attained as described above, the absorbances were measured against chloroform. Other factors were kept as described in the foregoing section. As is shown in Fig. 3, the optimum pH range for the extraction is from 5.0 to 5.7. The pH range for the standard procedure, therefore, was adjusted from 5.0 to 5.7 on the extraction of iron in antimony.

(E) The Effect of pH on Copper Oxinate in Tartaric Acid and Antimony Solution

The optimum pH on the extraction of copper in tartaric acid and antimony was investigated in the extracts obtained from the solutions containing 25μg of copper and 500mg of antimony, and in those obtained from the solutions containing 500mg of antimony only. Other factors were kept as described in the foregoing section.

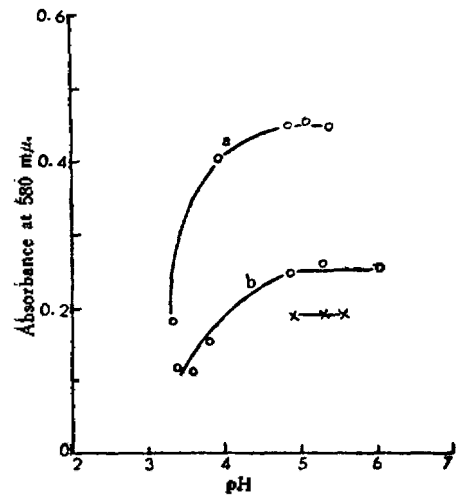

Figure 3. Effect of pH on extraction of Fe-oxinate in Tartaic acid and Sb solution.

2% Oxine 3ml. $CHCl_3$ 10ml. 0.5M Tartaric acid 10ml. a: Fe 25μg, Sb 500mg. b: Sb 500mg. only x: net value

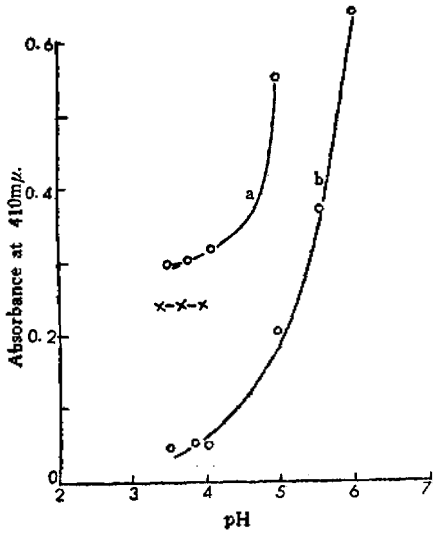

Figure 4. Effect of pH on extraction of Cu-oxinate in Tartaric acid andSb solution.

2% Oxine 3ml., $CHCl_3$ 10ml. 0.5 M-Tartaric acid 10ml. a: Cu 25μg, Sb 500mg. b: Sb 500mg, only x: net value

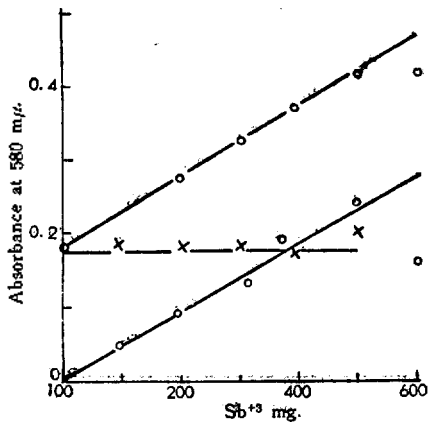

Figure 5. Influence of Sb^{+3} on extraction of Fe-oxinate.
Fe 25 μg., 2%Oxine 3ml.
0.5M-Tartaric acid 10ml.

As is shown in Fig. 4, the optimum pH range for the extraction of copper is from 3.5 to 4.0. The pH range for the standard procedure, therefore, was adjusted from 3.5 to 4.0 on the extraction of copper in antimony.

(F) The Effect of Antimony on Iron and Copper Oxinate

(a) Iron——The effect of antimony on the extraction of iron oxinate was studied in the extracts obtained from the solutions containing 25μg of iron with varying amounts of antimony, and in those obtained from the solutions with varying amounts of antimony only. Other factors were kept as described in the forgoing section. Absorbances were measured at 580mμ against chloroform on these dried extracts. The results are shown in Fig. 5.

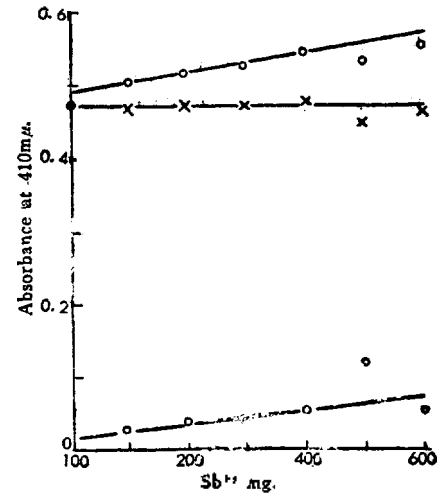

Figure 6. Influence of Sb^{+3} on extraction of Cu-oxinate.
Cu 50μg., 2% Oxine 3ml.
0.5*M*-Tartaric acid 10ml.

(b) Copper——The effect of antimony on the extraction of copper was studied in the extracts obtained from the solutions containing 50μg of copper with varying amounts of antimony, and in those obtained from the solutions with varying amounts of antimony only. Other factors were kept as described in the above section. Absorbances were measured at 410mμ on these dried extraxts and Fig. 6 shows the results.

As is shown in Fig. 5 and 6, up to 500mg of antimony for iron and up to 600mg of antimony for copper are independent on the extraction.

(G) Analysis of Iron and Copper in Antimony

Solutions of 250mg and 500mg of antimony containing various concentrations of iron and copper were analyzed following the standard procedures and obtained the results shown in Table 2. Up to 150μg of iron (0.005%—0.03%) and up to 100μg of copper (0.005—0.016%) in 500mg of antimony could be determined by this method.

Table 2. Analysis of Iron and Copper in Antimony

Sb (mg.)	Fe added (μg.)	Fe found (μg.)	Cu added (μg.)	Cu found (μg.)
250	—	—	—	—
250	25	23.6	24	26.3
250	50	49.2	48	47.6
250	100	97.6	96	97.1
250	150	148.6	144	140.0
250	200	185.6	182	178.0
500	—	—	—	—
500	25	23.9	24	26.0
500	50	50.7	48	47.0
500	100	102.0	96	96.0
500	150	150.0	144	130.0

(H) Diverse Ions

When large amounts of a foreign ion, e.g., vanadium are present in the sample solution, it is better to wash the extract with an ammonium hydroxide-ammonium chloride buffer solution of pH 5.0 to 5.7

containing 3ml of 10% hydrogen peroxide in order to reduce the interference.

Up to 40μg of Al^{3+}, 50μg of Ni^{2+}, 100μg of V^{5+}, Ti^{4+} and W^{4+} 120μg of Mo^{6+}, 200μg of Sn^{4+} did not interfere on the extraction of iron and copper in antimony.

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