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Spectrophotometric Determination of Copper and Bismuth After Coprecipitation of Their *n*-Butylxanthates on Microcrystalline Naphthalene

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Conditions have been developed for the adsorption of copper and bismuth as their *n*-butylxanthates over microcrystalline naphthalene. The mixture of the metal complex and naphthalene is separated by filtration and dissolved in choloroform. The absorbance is measured at 423 nm for copper and 362 nm for bismuth. Beer's law is obeyed in the concentration ranges 2.5—65.0 μg of copper and 5.0—130.0 μg of bismuth in 10 ml of the final chloroform solution. The molar adsorptivities and sensitivies are calculated to be Cu: 8.260×10^3 dm^3 mol^{-1} cm^{-1}, 0.0076 μg/cm^2 and Bi: 1.231×10^4 dm^3 mol^{-1} cm^{-1}, 0.016 μg/cm^2. Aliquots containing 20 μg of copper and 50 μg of bismuth give mean absorbances of 0.260 and 0.295 with standard deviations of 0.0023 and 0.0028 and relative standard deviations of 0.88% and 0.95 % respectively. The optimum pH range for the adsorption is 1.5—4.4 for copper and 2.2—6.6 for bismuth. The interferences of various ions have been studied in detail and the method has been applied successfully for the determination of copper in certain alloys and bismuth in an ore.

INTRODUCTION

Xanthates have been widely used as analytical reagents in the determination of a number of metal ions.[1] They react with metal ions at room temperature to form chelates of the type $M(RCOS_2)_n$. Various solvents[2-4] have been tried for the extraction of these metal chelates but the results are not very encouraging. The present communication describes the conditions for the microdetermination of copper and bismuth after adsorption of their *n*-butylxanthates on microcrystalline naphthalene and dissolution in chloroform. The method is an improvement over the extraction into molten naphthalene[5-7] described by Satake *et al.*[8] since the adsorption is very rapid. Only a small amount of naphthalene (0.4 g) is required, and this can be dissolved in 2—3 ml of chloroform, the whole of which can be used for absorbance measurement, making the technique highly sensitive. This method has been applied successfully for the determination of copper in certain alloys and bismuth in an ore.

EXPERIMENTAL

Reagents

Solutions of copper nitrate and bismuth nitrate were prepared in distilled water from analytical grade chemicals and standardized by known methods.[9] Potassium *n*-butylxanthate was prepared according to the method given in the literature[1] and used as a 0.2% solutions in distilled water. Aqueous solutions of perchloric acid (1 mol dm^{-3}) and ammonia (1 mol dm^{-3}) were used for adjustment of pH. Naphthalene and chloroform of reagent grade were checked spectrophotometrically before use. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations respectively.

Equipments

An Elico pH meter, a Pye Unicam SP 500/700 spectrophotometers and a Pye Unicam 191 atomic absorption spectrophotometer were used.

General Procedure

To aliquots of the metal ions solution (Cu: 2.5—65 μg and Bi: 5—130 μg) taken in stoppered Erlenmeyer flasks, were added 2.0 ml of reagent and adjusted pH 1.5—4.4 for copper and 2.2—6.6 for bismuth with perchloric acid and ammonia solutions. Mixed well, digestion of this solution for 5 min resulted in a precipitation of the complex. After digestion, 2.0 ml of a 20% solution of naphthalene in acetone were added in a fast stream and the solution was shaken for 1—2 min. The solid mass formed was filtered off on a Whatman filter paper (No. 1042), washed 2 or 3 times with distilled water, drained dry, dissolved in chloroform and made up to volume in a 10.0 ml standard flask. The chloroform solutions were dried with anhydrous sodium sulphate (2 g) and their absorbances were measured in a 1 cm cell at 423 nm for copper and 362 nm for bismuth against reagent blanks prepared similarly.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of potassium *n*-butylxanthate and the copper *n*-butylxanthate and bismuth *n*-butylxanthate complexes in naphthalene chloroform solution were measured against water and a reagent blank (Figure 1). The copper and bismuth complexes show absorption maxima at 420—425 and 360—365 nm, respectively. The reagent absorbs negligibly over the ranges. All measurement were therefore made at 423 nm for copper and 362 nm for bismuth.

Reaction Conditions

The copper(II) and bismuth(III) complexes were quantitatively formed and adsorbed on microcrystalline naphthalene in the pH ranges 1.5—4.4 and 2.2—6.6, respectively (Figure 2). The spectra measured for reactions at various pH values showed that only one type of complex was adsorbed on naphthalene in each case.

It was found that for 20 μg of copper and 50 μg of bismuth, a minimum of 0.6 ml of reagent was required for complete reactions. Hence, to provide a safety margin, 2.0 ml of reagent was used.

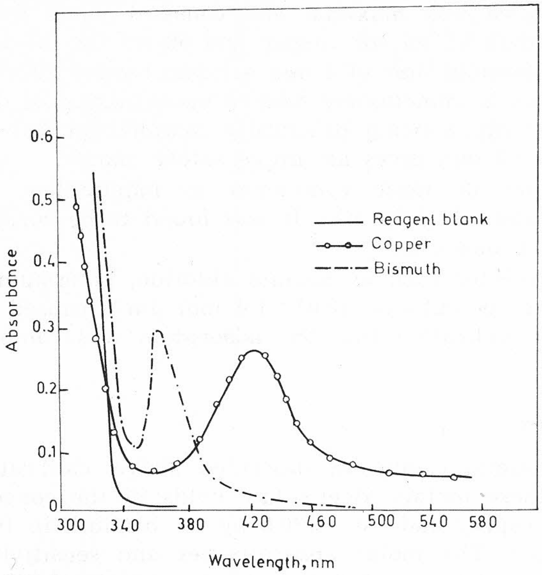

Figure 1. Absorption spectra of potassium *n*-butyl-xanthate and its copper and bismuth xanthates in naphthalene-chloroform solution. Cu: 20.0 μg, reagent: 2.0 ml (0.2%), pH 3.2; Bi: 50.0 μg, reagent: 2.0 ml (0.2%), pH; 5.1; naphthalene: 2.0 ml (20%), digestion time: 5 min; shaking time: 1 min; reference: reagent blank.

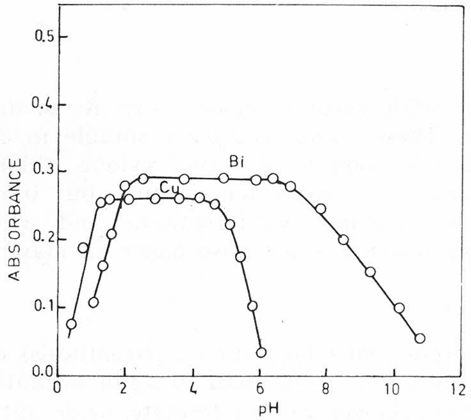

Figure 2. Effect of pH
Wavelength: 423 nm for copper and 362 nm for bismuth, remaining cnoditions were the same as for Figure 1.

Adsorptions were carried out according to the general procedure and the volume of naphthalene solution (20%) were varied from 0.2—5.0 ml. It was found that the absorbance remained constant from 0.5 to 5.0 ml for copper and from 0.9 to 5.0 ml for bismuth. Therefore, 2.0 ml of the naphthalene acetone solution were used in subsequent studies. Since only a small amount of the organic phase (0.4 g) was used, the volume of the aqueous phase was important. The absorbance was maximal and constant when the aqueous phase volume was less than 65 ml for copper and 50 ml for bismuth.

A minimum standing time of 5 min at room temperature is recommended, though the complex is immediately formed upon mixing of the solutions. The adsorption is very rapid, being practically complete in less than 10 s and a shaking time of 1—2 min gives an ample safety margin.

The absorbance of these complexes in naphthalene chloroform was measured at an interval of 30 min. It was found to be constant for 24 h for copper and 8 h for bismuth.

Various electrolytes such as sodium chloride, potassium nitrate, sodium acetate and sodium perchlorate (0.01—1.0 mol dm^{-3}) caused no improvement in the adsorption, indicating that the adsorption was complete under these conditions.

Calibration Curves

Under the optimal conditions described above, calibration curves were constructed for these metals. Beer's law holds in the concentration ranges, 2.0 —65.0 μg for copper and 5.0 —130.0 μg for bismuth in 10 ml of the final chloroform solution. The molar absorptivities and sensitivities in terms of Sandell's definition were calculated to be, for copper: 8.260×10^3 dm^3 mol^{-1} cm^{-1}, 0.0076 $\mu g/cm^2$ (423 nm) and for bismuth: 1.231×10^4 dm^3 mol^{-1} cm^{-1}, 0.016 $\mu g/cm^2$ (362 nm), respectively. Aliquots containing 20 μg of copper and 50 μg of bismuth gave mean absorbances of 0.260 and 0.295 with standard deviations of 0.0023 and 0.0020 and relative standard deviations of 0.88% and 0.95%, respectively.

Choice of Solvent

Tests were made with various organic solvents to dissolve the collected naphthalene mixture. These complexes were soluble in chloroform, benzene, toluene, N-N'-dimethyl-formamide, dioxane, xylene, chlorobenzene, dichlorobenzene and nitrobenzene at room temperature but insoluble in propylene carbonate, acetonitrile, acetone, dichloroethane and methylisobutylbenzene. Chloroform has been selected since absorbance is maximal in this solvent.

Effect of Diverse Ions

The following foreign ions (amount in parenthesis) did not interfere in the determination of 20 μg of copper and 50 μg of bismuth: fluoride, chloride, bromide, iodide, acetate, thiosulfate, thiocyanate, azide, nitrate, nitrite, sulfate, carbonate (100 mg each), tartrate, orthophosphate, oxalate, citrate (50 mg each), V(V), Cr(III), Mn(II), Ni(II), Zn(II), Cd(II), Pb(II), Mo(VI), Al(III), Pt(IV), Rh(III), Ru(III), Ag(I), As(III), Sb(III), Au(III), W(VI), Th(IV), Zr(IV), Be(II), U(VI) (500 μg each), Co (125 μg) and Os(VIII) (250 μg). EDTA interfered seriously in the determination of these metal ions. The adsorption was not possible in the presence of EDTA in both cases probably because of the higher formation constants of these metal EDTA complexes when compared to their xanthates. In the determination of copper, 250 μg of bismuth and 500 μg of palladium could be tolerated whereas in the determination of bismuth, 250 μg of copper could be tolerated provided adsorption was carried out at

TABLE I

Determination of Copper in Some Alloys

Alloy	Composition of the alloy (%)	Copper in the sample (µg)	Copper found by AAS (µg)	Copper found by the present method (µg)	Average (µg)	Error (%)
Aluminium alloy	Cu: 1.2, Si: 12.5 Ni: 0.95, Mg: 1.1 Fe: 0.52, Al: 83.73	24.0	24.2	24.30 24.10 24.40 24.10 24.35	24.27	1.12
Brass No. 41.2	Cu: 58.78, Pb: 2.56 Zn: 38.99, Fe: 0.09 Sn: 0.12	34.9	35.1	35.50 35.10 34.80 35.70 35.20	35.26	1.03
N.B.S.SRM-85B Aluminium alloy	Cu: 3.99, Mg: 1.49 Mn: 0.61, Fe: 0.24 Cr: 0.21, Si: 0.18 Ni: 0.084, Zn: 0.03 Ti: 0.022, Pb: 0.021 Ga: 0.019, V: 0.006	39.9	40.3	40.60 40.40 39.70 40.30 40.80	40.36	1.16
N.B.S. SRN-94C Zinc-base alloy	Cu: 1.01, Al: 4.13 Hg: 0.042, Fe: 0.018 Mn: 0.014, Pb: 0.006 Ni: 0.006, Sn: 0.006 Cd: 0.002	20.2	20.3	20.30 20.70 20.10 20.60 20.40	20.42	1.08

pH 6.5. Palladium interfered in the determination of bismuth only. The interference of palladium (250 μg) and copper (500 μg) was eliminated by masking, with the addition of 10 ml of 5% sodium cyanide solution[10] during adsorption. Fe(III) and Hg(II) interfered in the determination of copper and bismuth but were masked by adding 10 ml of 5% solution of hydroxylamine hydrochloride in the case of Fe(III) and 10 ml of 5% potassium iodide solution in the case of Hg(II). Thus, the method is fairly selective and has been applied for the determination of copper in various alloys and bismuth in an ore sample.

Determination of Copper in Alloys

A 0.1 g sample of the alloy was dissolved in 15—20 ml of concentrated hydrochloric acid and 1—3 ml of concentrated nitric acid, with heating. The solution was evaporated somewhat, another 10 ml of concentrated hydrochloric acid were added and the solution was diluted, filtered and made up to volume in a 500 ml standard flask. An aliquot was taken and 10 ml of 5% hydroxylamine hydrochloride solution were added to it. The solution was shaken thoroughly and allowed to stand for 5 min. 2.0 ml of 2% of the reagent were added to it and the adsorption of this complex was carried out at appropriate pH range (1.5—4.4) according to the general procedure. The results are given in Table I.

Determination of Bismuth in JSS, 800-3 Rompin Iron Ore

The sample was finely powdered,[11] and a 2 g sample was boiled with 30—40 ml of aquua regia for about 1 h. The solution was diluted, filtered and made up to a volume in 250 ml standard flask. An aliquot of this solution was taken and 10 ml of 10% hydroxylamine hydrochloride were added to it. This solution was shaken thoroughly and allowed to stand for about 5 min. The pH of this solution was adjusted to about 5 and then 10 ml of 5% sodium cyanide solution were added to it. This solution was mixed thoroughly and bismuth was determined by the general procedure. The results are given in Table II.

TABLE II

Determination of Bismuth in Iron Ore

Ore	Composition of the ore (%)	Bismuth in the sample (μg)	Bismuth found (μg)	Average (μg)	Error (μg)
JSS, 800-3	CW: 4.48, T. Fe: 62.85	18.4	18.9	18.60	1.08
Rompin	FeO: 2.96, SiO_2: 2.60 Mn: 0.22, P: 0.042		18.5 18.8		
Iron Ore	S: 0.074, Cu: 0.065 TiO_2: 0.08, CaO: 0.2 MgO: 0.22, Al_2O_3: 2.01 As: 0.033, Si: 0.012 Zn: 0.103, Bi: 0.023 V: 0.006, Pb: 0.022		18.2 18.6		

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SAŽETAK

Spektrofotometrijsko određivanje bakra i bizmuta nakon taloženja njihovih *n*-butilksantata na mikrokristalnom naftalenu

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Određeni su uvjeti za adsorpciju bakra i bizmuta u obliku njihovih *n*-butilksantata na mikrokristalnom naftalenu. Smjesa metalnog kompleksa i naftalena se nakon odjeljivanja filtriranjem otopi u kloroformu i mjeri absorbancija organske faze pri 423 nm za bakar, odnosno 362 nm za bizmut. Molarni apsorpcijski koeficijent i osjetljivost metode iznosi $8{,}260 \times 10^3$ dm^3 mol^{-1} cm^{-1}, odnosno 0,0076 $\mu g/cm^2$ za bakar i $1{,}231 \times 10^4$ dm^3 mol^{-1} cm^{-1}, odnosno 0,016 $\mu g/cm^2$ za bizmut. Ispitan je utjecaj različitih iona na određivanje, i metoda je uspješno primijenjena za određivanje bakra u nekim legurama i bizmuta u rudama.