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THE DETERMINATION OF BISMUTH IN BISMUTH CONCENTRATES BY CHELATOMETRIC TITRATION

A. HITCHEN AND G. ZECHANOWITSCH

EXTRACTION METALLURGY DIVISION

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THE DETERMINATION OF BISMUTH IN BISMUTH CONCENTRATES BY CHELATOMETRIC TITRATION

by

A. Hitchen* and G. Zechanowitsch**

ABSTRACT

Two methods for the determination of bismuth in bismuth concentrates are described, both based on titration of the bismuth with sodium ethylenediamine-tetraacetate (EDTA). In one method, the end-point is detected visually by means of xylenol orange indicator, whereas in the other, the end-point is detected amperometrically using a rotating platimum electrode maintained at + 1.2 volts vs the s.c.e. The advantages and disadvantages of each method are discussed.

The effects of a number of elements peculiar to the particular sample material analyzed here and of others commonly found in other bismuth concentrates were investigated. Procedures for the elimination of those that interfered were investigated and their effectiveness has been established. In particular, a rapid acid attack-volatilization procedure for the simultaneous dissolution of the sample and volatilization of arsenic, antimony, and tin (without significant loss of bismuth) has been developed and is presented here. A hitherto undescribed interference due to aluminum, when xylenol orange is used, has been observed and causes and remedies for it are discussed. It is also shown that aluminum, which interferes when xylenol orange is used, does not interfere when amperometric end-point indication is used, whereas iron and ascorbic acid, which interfere with the amperometric end-point method, do not interfere with the xylenol orange end-point.

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LA DÉTERMINATION DU BISMUTH DANS LES CONCENTRÉS DE BISMUTH PAR LE TITRAGE CHELATOMÉTRIQUE

par

A. Hitchen* et G. Zechanowitsch**

RÉSUMÉ

Les auteurs décrivent deux méthodes de détermination du bismuth dans les concentrés de bismuth; les deux méthodes sont fondées sur le titrage du bismuth à l'aide de tétraacétate-éthylènediamine de sodium. Dans une méthode le virage, au titrage, est observé visuellement au moyen d'un indicateur orangé au xylénol, tandis que dans l'autre, on le détecte à l'aide d'un ampèremètre muni d'une électrode tournante de platine maintenue à 1.2 volt contre une électrode au calomel ordinaire. Il est question des avantages et désavantages de chaque méthode.

Les auteurs ont étudié les effets de certains éléments particuliers à l'échantillon analysé ainsi que les effets d'autres éléments habituellement présents dans d'autres concentrés de bismuth. Les méthodes d'élimination des effets nuisibles ont été étudiées et leur efficacité a été prouvée. Plus particulièrement, on a mis au point, et on décrit ici, une méthode rapide d'attaqué par l'acide et de volatilisation qui permet simultanément de dissoudre l'échantillon et de volatiliser l'arsenic, l'antimoine et l'étain (sans qu'il y ait une perte considérable de bismuth). On a observé une interférence, jusqu'à présent non décrite, par l'aluminium losqu'il y avait utilisation de l'indicateur orangé au xylénol; on traite également des causes de cette interférence et des remèdes à apporter. Il est également démontré que l'aluminium qui est une source d'interférence lorsque l'indicateur orangé au xylénol est utilisé, ne cause aucune interférence lorsqu'on se sert de l'ampèremètre comme indicateur du virage, tandis que le fer et l'acide ascorbique qui sont des sources d'interférence lorsqu'on se sert de l'ampèremètre, ne causent aucune interférence lorsqu'on utilise l'indicateur orangé au xylénol.

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INTRODUCTION

A rapid, accurate method for the determination of bismuth in concentrates was required as part of a research project to recover bismuth as a bismuth concentrate from a complex tin-copper-lead-zinc ore. The gravimetric methods, in which bismuth is isolated and weighed as bismuth oxychloride or bismuth phosphate[1,2], are subject to many interferences which necessitate their removal, making the methods too time-consuming. Colorimetric or polarographic methods are suitable for small amounts of bismuth but lack sufficient accuracy to be applied to high-grade concentrates. Previous experience here[3] indicated that a volumetric EDTA method would be suitable. The previous work, however, was primarily concerned with the simultaneous determination of lead and bismuth in lead-zirconate-titanate ceramic material and a separation of these elements from large amounts of zirconium and titanium by means of a solvent extraction step was necessary prior to their titration with EDTA. Because significant amounts of titanium and zirconium were not present in the bismuth concentrates, the solvent extraction step was considered unnecessary, moreover, its omission would also shorten the analysis time.

The determination of bismuth by titration with EDTA has been the subject of many reports[4,5,6,7] in which the end-point of the titration has either been detected visually by innumerable indicators or instrumentally by amperometric, photometric, or potentiometric methods. Because of the very high stability constant of the Bi-EDTA complex ($\log K_{BiY} \cong 28$), the titration can be done at low pH values and is

relatively selective. This is fortuitous because at higher pH values the EDTA reacts with many other elements that are commonly associated with bismuth and in addition, the bismuth readily hydrolyzes at higher pH levels.

Gattow and Schott[8] made a thorough and critical investigation of the titration of bismuth with EDTA in which the indicator pyrocatechol violet as the standard was compared with many others, including xylenol orange, PAR, PAN, thiourea, methylthymol blue, Thoron, haematoxylin, and bromopyrogallo red. In their study PAR was found to be the best indicator because it gave correct results with the lowest standard deviation over a wide range of concentrations. Methylthymol blue gave equally accurate results but the scatter was somewhat greater. Xylenol orange gave a smaller standard deviation but slightly high results compared to the pyrocatechol violet. According to Schwarzenbach and Flaschka[5] pyrocatechol violet is the indicator most to be recommended because there is a transitional blue to red colour change warning of the approach to the end-point which is pure yellow and exceptionally sharp. Fritz[9] used thiourea as the indicator and found it was subject to fewer interferences. The bleaching of the bi-thiourea complex, however, is not as sharp as the transition of the dyestuff indicators.

The titration of bismuth is very selective and interferences can occur only with elements that form very stable complexes, e.g. Fe, In, Hg, Sn, Zr, Hf, etc. Addition of ascorbic acid eliminates the interference of iron, and mercury can be masked by thiocyanate. Shteiman, Dobrynina and Mordovskaya[10] masked tin and small amounts of iron by means of fluoride in order to determine Bi and Pb in Sn-Bi-Pb alloys. The titration of bismuth was performed at pH 1.5 to 2.0 by means of xylenol orange as the indicator. The error

of the determination did not exceed 1% relative in the range of 20 to 50% Bi.

The amperometric titration of bismuth with EDTA, by means of either a dropping mercury electrode (DME) or a rotating wire electrode for end-point detection, has been proposed. These two techniques differ in their means of detecting the end-point. For example, Pribil and Matyska[11] used a DME and titrated the bismuth in a nitric acid solution at pH 2, using the disappearance of the limiting current due to bismuth (at -0.4 volts vs the s.c.e.) to follow the progress of the titration. The resulting graph is thus L shaped. Zhdanov, Kapitsa and Akent'eva [12], on the other hand, made use of the well-defined polarographic wave given by EDTA [13] to titrate synthetic mixtures of bismuth, copper, mercury, zinc, and lead in 0.25 N nitric acid with EDTA. They employed a rotating tantalum electrode, maintained at + 1.2 volts vs the s.c.e. The bismuth is not reduced at this potential so does not give rise to a limiting current. The residual current, therefore, remains small until an excess of EDTA is present when it increases in proportion to the amount of excess EDTA. The resulting graph has a reversed-L shape. These workers did not report any study of possible interfering elements and confined their work to three component synthetic mixtures.

Vorlicek, Petak and Sulcek [14] also followed the EDTA concentration with biamperometric indication of the end-point. However, they titrated the nitric acid solution (pH 0.8 to 1.2) with EDTA, using two stationary platinum plate electrodes and an applied voltage of 1.4 volts. As before, the current remained constant until the end-point was reached then increased with an excess of EDTA; the graph of the titration had a reversed-L shape. These authors applied the method to the determination of bismuth in ores and concentrates. If Zr, Tl, In, Mo, Cu, and Fe were present, they extracted the bismuth from an ammoniacal tartrate-cyanide solution with sodium diethyldithiocarbamate and chloroform, a procedure previously described by us [3]. Vorlicek et al imply that indium is not extracted by this procedure, but we have found that it is quantitatively removed along with bismuth and lead [15].

An investigation was therefore undertaken of the titration of bismuth with EDTA to compare the use of xylenol orange as a visual end-point indicator with that of an amperometric method using a rotating metal electrode. These two methods were chosen in order to provide alternative procedures in the event interferences were encountered in one method which could be overcome by the other method.

Xylenol orange was chosen as the visual end-point indicator in this investigation because in preliminary tests it was found to be superior to pyrocatechol violet and methylthymol blue. For example, out of three brands of pyrocatechol violet tested, two were useless because the solid indicator had deteriorated and the third, though better than the others, showed signs of

deterioration in that its end-point was not snarp. Methylthymol blue was more satisfactory that the pyrocatechol violet but the initial colour of the bismuth complex was indistinct rather than clear and brilliant blue. The transitional colour change from blue to yellow was drawn out and not very sharp, although correct recoveries of bismuth were obtained.

In this respect, xylenol orange had behaved similarly on the determination of lead [3] and the difficulties were traced to the differences between different brands of xylenol orange. The difficulties were eliminated by subjecting a solution of the xylenol orange to a cation exchange separation. In our recent work, however, the particular brand of indicator used did not exhibit the former behaviour and it could be used for the determination of bismuth without undergoing the ion exchange treatment. One can emphasize only that it is necessary to thoroughly check the behaviour of each brand or lot of indicator before it is used for a particular determination.

For the amperometric titrations the use of a rotating metal electrode was preferred to a dropping mercury electrode (DME) because the technique is simpler and because of the presence of copper and other elements that would be reduced at the potential used for performing the titration with a DME. Copper does not interfere in the usual sense because it is not titrated with EDTA at pH 2 but, with a DME, it would give rise to a residual limiting current so that the current resulting from the excess EDTA would actually be the difference between two relatively large current readings if the copper content were higher than the bismuth content. Moreover, in using a DME, it is necessary to de-aerate the sample solution before titrating and after each addition of titrant to

eliminate oxygen interference. The removal of oxygen is unnecessary if a rotating metal electrode is used because oxygen is not reduced at the positive potential used for the titration. A tantalum electrode was not available, so a platinum electrode was used. Details of the behaviour of various elements in the proposed method for the determination of bismuth while using a platinum electrode were lacking or not readily available, so several elements were studied; these included Cu, Fe, Zn, Pb, Al, Sn, Sb, As, and W, expected in significant amounts, as well as In, Ag, Co, Ni, Mn, and Cd, associated with bismuth concentrates as minor or trace constituents. The behaviour of fluoride and ascorbic acid was examined to see if they could be used to mask certain interferants.

Procedures for the elimination of certain interferences were investigated and established. A rapid acid attack-volatilization procedure for the simultaneous dissolution of the samples and volatilization of arsenic, antimony, and tin (without significant loss of bismuth) has been developed and is described. A hitherto undescribed interference due to aluminum, when xylenol orange is used, has been observed and causes and remedies for it are discussed. It is also shown that aluminum, which interferes when xylenol orange is used, does not interfere if amperometric end-point detection is used; whereas iron and ascorbic acid, which interfere with the amperometric end-point method, do not interfere with the xylenol orange end-point.

The methods finally developed were successfully applied to determining bismuth in various bismuth concentrates containing between 60 and 80 % Bi.

APPARATUS AND REAGENTS

Apparatus

Polarographic instrumentation, suitable for amperometric titrations;

pH meter; and

magnetic stirrer.

Reagents

0.01 M EDTA solution:
dissolve 3.722 g of the disodium dihydrate salt in water and dilute to 1 litre; standardize the solution against pure bismuth or lead;

ascorbic acid crystals;

xylenol orange indicator(0.1 % solution in water);

1 M sodium acetate solution; and

Other reagents of A. R. quality.

ANALYTICAL PROCEDURES

A. Visual End-point Detection Method

Transfer an accurately weighed sample containing 50 to 100 mg of bismuth to a 250 or 400-mg beaker. Add 5 ml each of 12 M hydrochloric acid, 48 % hydrobromic acid, and 72 % perchloric acid and evaporate to light fumes of perchloric acid to remove any tin. antimony, or arsenic. Repeat the treatment several times, if necessary, to volatilize the tin etc. completely. If silica is present in significant quantities, remove it at this point by adding hydrofluoric acid and evaporating to fumes of perchloric acid.

Neither evaporate to dryness nor prolong the fuming lest excessive amounts of bismuth be volatilized.

Add 3 ml of 16 M nitric acid and dilute to 100 ml with water to dissolve the sample. Filter out insoluble residue (largely WO_3) on either a Whatman No. 40 paper or a Millipore filter and wash with hot 0.25 M nitric acid (3 ml 16 M nitric acid per 100 ml of water).

Cool the filtrate to room temperature and adjust the pH to 2.0 ± 0.2 with 1 M sodium acetate. Add about 100 mg of ascorbic acid and a few drops of xylenol orange indicator, then titrate the bismuth with standard 0.01 M EDTA solution. If aluminum is known to be present, titrate the solution slowly near the end-point in order to avoid the formation of an irreversible pink coloured aluminum-xylenol orange complex which interferes with the true end-point.

B. Amperometric End-point Detection Method

Treat the sample in the same manner, as described above in Method A, up to and including the filtration step. Cool the filtrate to room temperature and adjust the solution, if necessary, to make it 0.25 M in nitric acid. Immerse the rotating platinum and saturate calomel electrodes in the solution using a 20 % w/v ammonium nitrate solution bridge to isolate the s.c.e. from the sample solution. Apply a potential of + 1.2 volts vs the s.c.e. to the rotating platinum electrode and titrate the bismuth with standard 0.01 M EDTA solution.

Plot graphically the current readings versus the volume of EDTA solution used and extrapolate to determine the end-point. Ignore the readings in the vicinity of the end-point while determining the end-point in this manner.

PRELIMINARY INVESTIGATIONS

1. Titration of Bismuth with EDTA Using Xylenol Orange as a Visual Indicator

Gattow and Schott[16] in their investigations of the titration of bismuth with EDTA observed that low results or long-drawn-out colour transitions at the end-point occurred if the pH of the solution was adjusted with sodium hydroxide, ammonium hydroxide,or pyridine. They concluded that these difficulties were due to the formation, by a local excess of the alkali, of hydrolytic or polynuclear cautions which react with EDTA either very slowly or not at all. These authors recommended the use of sodium bicarbonate or sodium acetate to adjust the pH prior to titration with EDTA. Initial tests with solutions of pure bismuth confirmed the difficulties observed by Gattow and Schott when ammonium hydroxide was used to adjust the pH of the solutions. For example, solutions containing 50 to 100 mg of bismuth and 3 to 5 ml of 16 M nitric acid in 200 ml of water were adjusted to pH 2, 100 mg of ascorbic acid was added to reduce any traces of iron, the bismuth then being titrated with a standard 0.01 M EDTA solution using xylenol orange as the indicator. When ammonium hydroxide was used for the pH adjustment, it was observed that, although the end-point colour change from red to yellow was usually extremely sharp, the red colour often rapidly returned after the end-point was first observed and that, if the solution was stirred briskly and/or heated,the red colour reappeared more rapidly this suggested that not all the bismuth had been titrated. Moreover, the reproducibility of the end-point was only fair for duplicate amounts of bismuth. If, on the other hand, sodium acetate was used, sharp stable end-points were obtained and no anomalous

behaviou was observed. The recovery of bismuth in these titrations was satisfactory; see Table 1.

2. Study of Elements that May Interfere in the Visual End-point Method

A study was made to the effect of Cu, Fe, Zn, W, Pb, Al, Su, Sb, and As, expected to be present in significant amounts, and of In and Ag, expected to be present in small or trace amounts. The effect of Zr, Hf, and Hg (known interferants) was not studied because they were not present in amounts sufficient to warrant concern.

Of the elements mentioned above, only iron, tin, arsenic, antinomy, and indium interfered seriously. Tungsten, in a Bi:W ratio of 2.1, caused the results for bismuth to be about 0.3 to 0.4 mg low when 45 mg of bismuth was present, apparently because WO_3 precipitate adsorbed or entrapped bismuth. The interference of iron was eliminated by adding ascorbic acid. Shteiman et al [10] used fluoride to mask tin and iron, but we found that fluoride interfered to some extent with the detection of the end-point with xylenol orange and caused results to be low by 0.3 to 0.4 mg even in the absence of tin or iron.

Arsenic (III) did not interfere in the titration of bismuth but arsenic (V) seriously interfered because it precipitated the bismuth as bismuth arsenate at the pH required for the titration. Antimony interfered because it hydrolyzed and the recoveries of bismuth were low because significant amounts of bismuth were apparently adsorbed on the precipitate. Indium interfered because it was partly titrated with EDTA at pH 2 and the recoveries of bismuth were erroneously high. This pH was less than the optimum for the

titration of indium but, at pH 3.5, it was found to be stoichiometrically titrated with EDTA and the sum of bismuth and indium was obtained.

Silica, although not investigated, also may be expected to interfere if it is present in significant amounts due to entrapment of some bismuth on the precipitate. It can however, be removed by adding hydrofluoric acid and evaporating the solution to fumes with perchloric acid.

In the analysis of samples we prefer to remove tin, antimony, and arsenic by volatilizing them with a mixture of hydrochloric, hydrobromic, and perchloric acids. In testing synthetic bismuth plus tin, antimony, or arsenic solutions, we found that small amounts of bismuth were lost by volatilization; see later section on the volatilization of bismuth. However, the losses are small and acceptable for control purposes.

The behaviour of aluminum was unusual because although it was not titrated with EDTA at pH 2, it reacted slowly but irreversibly, with the xylenol orange indicator after the bismuth end-point had been reached, to form a pink-coloured complex. This complex was not formed immediately on addition of the xylenol orange to the solution because the bismuth forms a more stable red complex with the indicator instead and the aluminum complex can appear only after the bismuth has been titrated. If the EDTA is added slowly as the end-point is approached, the colour change due to an excess to EDTA is clearly visible before the aluminum-xylenol orange complex is produced and the titration can be completed successfully. In these tests about 6 mg of aluminum and 45 mg of bismuth were present. However, more aluminum will cause some difficulty.

3. Amperometric Titration of Bismuth with EDTA

In preliminary tests, the method proposed by Zhdanov et al [12] was investigated. Solutions containing 25 to 100 mg Bi in 200 ml of 0.25 N nitric acid were titrated with a standard 0.01 M EDTA solution using a rotating platinum electrode maintained at + 1.2 volts vs the s.c.e. The results are shown in Table 2A.

The results were consistently low because, it was believed, traces of potassium chloride leaked through the s.c.e. bridge into the sample solution, to precipitate some bismuth oxychloride. Subsequent titrations, in which an ammonium nitrate solution bridge was used to isolate the s.c.e. from the sample solution gave quantitative results (Table 2B) showing that use of this bridge had effectively prevented any chloride leaking into the sample solution.

A typical titration graph is presented in Figure 1 and shows considerable curvature in the vicinity of the end-point. This effect is believed to be due to dissociation of the Bi-EDTA complex at very low pH values, i.e., pH 1 existing under the conditions of the titration. Thus a small amount of the EDTA exists in the free state and causes a small current before the end-point. A similar behaviour was observed by Pribil and Matyska [11] when they titrated bismuth with EDTA at pH values less than 1 using a DME. Theoretically, this behaviour should

not affect the end-point, which is obtained by extrapolation of the current measurements at points distant from the end-point, but a sharper indication of the end-point is nevertheless desirable. Accordingly, tests were made to establish whether buffering the solutions at pH 2 (under conditions that are employed for the titration using xylenol orange as the indicator) would eliminate the curvature. However, the curvature in the vicinity of the end-point remained. Further investigations to overcome this effect were not attempted.

4. Study of Elements that May Interfere in the Amperometric End-point Method

A study was made of the effect of several potential interferants on the titration of bismuth by the amperometric method. A solution containing a known amount of bismuth, together with the element to be studied in 200 ml of 0.25 N nitric acid, was titrated with standard 0.01 M EDTA solution using a rotating platinum wire electrode maintained at + 1.2 volts vs the s.c.e. The amount of potential interferant taken in these tests greatly exceeded the amount expected to be present in the samples of bismuth concentrate to be analyzed. The results of these tests are shown in Tables 3 and 4.

The results in Table 3 show that bismuth can be determined accurately and with good precision, without interference, in the presence of significant amounts of Ag, Al, Cd, Co, Cu, Mn, Ni, Pb,and Zn.

The results in Table 4 show the extent of interference by iron, tin, arsenic, antimony, indium, fluoride, and tungsten. Ferric iron contributes to a large residual current but, up to 0.5 mg of Fe(III), can be tolerated. With amounts of ferric iron in excess of 0.5 mg, the end-point cannot be detected because the residual current decreases very rapidly throughout the titration and stable readings cannot be obtained. The interference of iron cannot be eliminated by the addition of ascorbic acid, as is done in the visual end-point method, because the ascorbic acid itself interferes both by producing an extremely large residual current and by preventing attainment of the required potential of + 1.2 volts at the platinum electrode. Fluoride seriously interferes with the detection of the end-point and the recoveries of bismuth are low. Therefore, fluoride cannot be used to complex iron, tin, etc., if bismuth is determined amperometrically by direct titration.

Indium is a serious interference because it is titrated with EDTA under the conditions of the method. In 0.25 N nitric acid, the indium is titrated just partly because the pH of this medium is not at the optimum for the titration of indium and the end-point is reached prematurely. At pH 3.5, however, the indium and bismuth are both stoichiometrically titrated with EDTA. The presence of tungsten leads to low recoveries of bismuth, apparently due to entrapment of the bismuth on the WO_3 precipitate. Dehydration of the tungsten oxide by evaporation to dryness with nitric acid improves the recovery of bismuth but the results are still 0.3 to 0.4 mg low.

The extent of interference by arsenic not only depends on how much of it is present but on its valence state. For example, a small amount of arsenic (III) is not a serious interference because it is neither titrated with EDTA nor precipitated in the titrating medium. The interference by arsenic (III) is related to the fact that it gives a large residual current and because, in its presence, the bismuth end-point is not very sharply defined. Amounts of arsenic (III) smaller than that listed in Table 4 will therefore interfere less but larger amounts will interfere more. Arsenic (V) interferes because it precipitates the bismuth as bismuth arsenate in 0.25 N nitric acid and it must therefore be removed or reduced before the bismuth can be determined. Antimony is a serious interference if present in significant amounts because it is hydrolyzed and causes the bismuth recovery to be low due to adsorption of bismuth on the precipitate. Tin is a known interference because it forms a strong EDTA complex even at low pH levels. Removal of tin by dehydration with nitric acid, on the other hand, leads to lower results because of adsorption of the bismuth on the tin oxide precipitate.

Losses of Bismuth as a Result of Fuming Either Perchloric or Sulphuric Acids Containing Hydrochloric and Hydrobromic Acids to Remove Tin, Arsenic and Antimony

Because small amounts of tin, arsenic and antimony were expected in the bismuth concentrates, it was necessary to provide for their removal in the analysis scheme. They can be removed either by solvent extraction[3] or by volatilizing them after treatment with hydrochloric, hydrobromic, perchloric, or sulphuric acids.

Volatization would have the advantage that the dissolution and removal of several interferences are combined in one step. However, significant amounts of bismuth are also known to be volatilized due to the relatively low boiling point of bismuth bromide or chloride. For example, Hoffman and Lundell[17,18], investigating the loss of bismuth and various other elements by volatilization from either perchloric or sulphuric acid in admixture with hydrochloric, hydrobromic, or phosphoric acids, under controlled distillation conditions, found,with 20 to 100 mg of the element in an HCl + $HClO_4$ mixture, that approximately 0.1 % bismuth was lost and all the tin was volatilized but only small amounts of arsenic or antimony were removed. With mixtures of HBr + $HClO_4$, HBr + H_3PO_4 + $HClO_4$,or HBr + H_2SO_4 the loss of bismuth rose to 1 % and under the same conditions virtually all the arsenic, tin,and antimony were volatilized. On the other hand, no loss of bismuth occurred from HCl + H_3PO_4 mixtures, but,in these media,arsenic, tin,and antimony were removed incompletely or not at all. In fact, this volatility of bismuth halides has been used to effect its removal. Thus Milner and Barnett[19] volatilized up to 1 gram of bismuth and separated it from uranium in bismuth-base alloys by evaporating a HBr + Br_2 solution of the alloy to dryness, with further heating of the walls of the beaker to remove condensed bismuth compounds. Similar procedures have been used by Wild[20] and Edwards and Milner[21] prior to determining uranium in bismuth alloys. The loss of bismuth due to volatilization of its bromide or chloride has also been observed in other work in our laboratories[22].

Little attention, however, has been paid to the application of the volatilization technique to accomplish removal of tin, arsenic,and antimony from bismuth prior to its determination.

Experiments were therefore undertaken to establish the extent of the loss of bismuth in the proposed acid attack-volatilization procedure for dissolution of sample with simultaneous removal of tin, antimony and arsenic. These experiments consisted of two series of tests. In one, known amounts of bismuth were treated with 10 ml of 12 M hydrochloric acid, 15 ml of concentrated hydrobromic acid,and 1 to 2 ml of either 72 % perchloric acid or 18 M sulphuric acid and evaporated to fumes of perchloric or sulphuric acid. The treatment was repeated once more and then the solutions were evaporated to dryness. The residue was taken up in 3 to 5 ml of 16 M nitric acid, diluted to 200 ml with water, the pH adjusted to 2 with sodium acetate,and the bismuth was finally titrated with standard 0.01 M EDTA solution using xylenol orange as the indicator.

In the second, solutions containing known amounts of pure bismuth and solutions containing bismuth plus arsenic, tin, or antimony were treated with 5 ml each of concentrated hydrochloric, hydrobromic, and perchloric or sulphuric acids and evaporated to light fumes of perchloric or sulphuric acid. This treatment was repeated once more but the solutions were <u>not</u> evaporated to dryness. The residual solution was treated with 3 ml of 16 M nitric acid, the walls of the beaker were rinsed down with a little water and the solution heated for a few minutes to remove any free bromine produced by the reaction of the nitric acid with the residual bromide in the solutions. The bismuth was then determined

by titration with EDTA as described above. The results of these tests are shown in Table 5.

The results in Table 5 show that considerable amounts of bismuth are lost by volatilization if the treatment with mixtures of hydrochloric, hydrobromic, and either perchloric or sulphuric acids is followed by evaporation to complete dryness, and that the losses are much greater with increasing amounts of bismuth. On the other hand, if the solutions are evaporated only to light fumes and not to dryness, the interferences due to arsenic, tin, and antimony are eliminated, but the losses of bismuth generally do not exceed 1 % relative, a value that is in agreement with the observations of Hoffman and Lundell[17] who distilled the solutions under controlled conditions. The actual amount of bismuth volatilized will depend on how hot the residual solution gets and thus, the fuming step should not be prolonged unduly.

For control purposes this slight loss of bismuth is acceptable. If, on the other hand, a higher degree of accuracy is required, it will be more satisfactory to extract the bismuth from a sodium hydroxide + cyanide + tartrate solution with sodium diethyldithiocarbamate and chloroform[3]. After removal of the chloroform and destruction of the organic residue, the bismuth may be titrated with EDTA using either one of the proposed methods. The extraction procedure will separate the bismuth from almost all other elements except lead and indium. Lead does not interfere in the titration step but indium, if present in significant amounts, will have to be removed in a further step if it is deemed necessary. The inclusion of the extraction step, however, adds to the complexity of the procedure, lengthens the analysis time, and is unwarranted unless high accuracy is necessary.

Analyses of Samples

Several samples of bismuth concentrates were analyzed by the recommended methods described in this report, using both visual and amperometric end-point detection. Individually weighed 0.1-gram samples were taken for each titration.

The results in Table 6 show that good agreement between the two methods was obtained. The results are considered satisfactory because no attempt was made to ensure the samples were homogeneous and they were analyzed on an "as is" basis. Because the samples were treated to remove tin, arsenic,and antimony by means of a mixture of hydrochloric, hydrobromic,and perchloric acids,the results may be about 0.5 % low but they are satisfactory for control purposes.

In the dissolution of the samples with nitric and perchloric acids it was observed that a significant amount of insoluble residue remained. Examination of the residues by an X-ray fluorescence technique revealed the presence of a significant amount of tungsten and trace amounts of copper, iron and bismuth. The amount of bismuth lost in the residue, however, was not sufficient to affect the results.

CONCLUSIONS

Two methods for the determination of bismuth in bismuth concentrates, by titration with EDTA using either xylenol orange as a visual end-poing indicator or amperometric end-point detection, are proposed, they are rapid, simple, relatively selective and, in general, free from interferences. Iron, tin, arsenic, antimony, fluoride,and indium constitute the most serious of the potential

interferences in the EDTA titrations. In the proposed procedures, the interference of iron can be eliminated with ascorbic acid if xylenol orange is used as the indicator but only about 0.5 mg of iron can be tolerated in the amperometric method and ascorbic acid cannot be used to mask it. Two methods can be employed for removal of tin, arsenic, antimony, and fluoride. One (solvent extraction) has been previously described but the other (volatilization with hydrochloric, hydrobromic and perchloric acids) was developed during this investigation. It is simple and rapid and, though some loss of bismuth may occur, it is generally less than 1 % relative. Aluminum may, in certain circumstances, interfere in the method using xylenol orange (by blocking this indicator) but relatively large amounts can be tolerated in the amperometric method.

The visual end-point method employing xylenol orange is the simplest and is recommended if the samples contain relatively large amounts of iron because the interference of iron is easily eliminated by adding ascorbic acid. On the other hand, the amperometric method, though requiring more complex instrumentation, is recommended for samples that contain relatively large amounts of aluminum and small amounts of iron. In the event that large amounts of aluminum and iron are present, solvent extraction of the bismuth may be necessary.

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Table 1

Titration of Bismuth with EDTA after pH Adjustment with Sodium Acetate*

Bi Taken mg	Bi Found mg	Difference mg
51.12	51.11	- 0.01
73.51	73.58	+ 0.07
130.68	130.55	- 0.13

*Xylenol orange used as indicator

Table 2

Amperometric Titration of Bismuth with EDTA

A. Without Ammonium Nitrate Bridge

Bi Taken mg	Bi Found mg	Difference mg
25.33	25.22	- 0.11
25.35	25.23	- 0.12
29.17	28.54	- 0.43
38.17	38.11	- 0.06
52.33	52.06	- 0.27
70.43	69.99	- 0.44
107.47	106.45	- 1.02
109.65	109.34	- 0.31

B. With Ammonium Nitrate Bridge

5.38	5.20	- 0.18
20.47	20.51	+ 0.04
44.87	44.95	+ 0.08
44.87	44.97	+ 0.10
44.87	44.95	+ 0.08
83.96	83.86	- 0.10

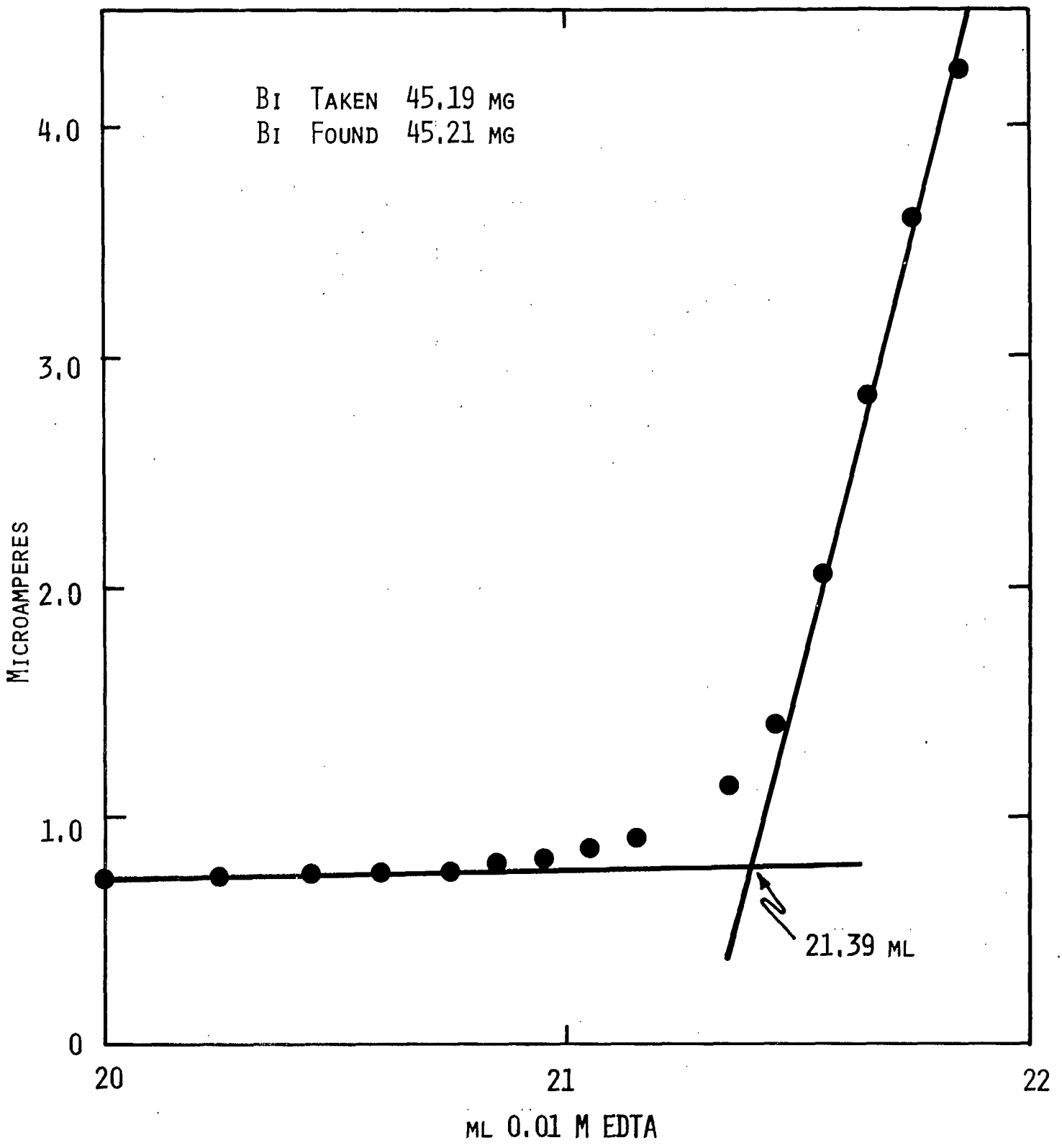

Fig. 1. Typical Titration Curve For Titration of Bismuth With EDTA

Table 3

Amperometric Titration of Bismuth with EDTA in the Presence of Non-Interfering Elements

Element Present	Bi Taken mg	Bi Found mg
None	45.19	45.13, 45.19, 45.21, 45.23
5 mg Ag	"	45.19, 45.19
20 mg Al	"	45.11, 45.11
20 mg Cd	"	45.11, 45.11
20 mg Co	"	45.25, 45.19
20 mg Cu	"	45.06, 45.11
30 mg Mn	"	45.08, 45.08
20 mg Ni	"	45.19, 45.17
20 mg Pb	"	45.21, 45.13
20 mg Zn	"	45.06, 45.06

Table 4

Amperometric Titration of Bismuth with EDTA in the Presence of Interfering Elements

Element Present	Bi Taken	Bi Found mg
20 mg As^{+3}	45.19	45.04, 44.81
20 mg As^{+5}	"	interferes; $BiAsO_4$ ppt'd
1 ml 48% HF	"	42.3
0.5 mg Fe^{+3}	"	45.08
2.5 mg Fe^{+3}	"	e.p. not detectable because of rapidly changing residual current.
4.8 mg In	"	52.00*
4.8 mg In	"	54.00**; stoichiometric recovery of Bi and In
10 mg Sb(a)	"	40.56, 41.05
10 mg Sn(b)	"	43.92, 44.03
20 mg W(c)	"	43.33, 43.96
20 mg W(d)	"	44.83, 44.96

* titrated at pH 1
** titrated at pH 3.5

(a) Sb not volatilized;
(b) Sn dehydrated with HNO_3 and filtered off;
(c) W precipitated in HNO_3 but not evaporated to dryness; filtered off;
(d) W precipitated in HNO_3, evaporated to dryness; filtered off.

Table 5

Loss of Bismuth by Volatilization after a Fuming Treatment with a Mixture of Hydrochloric, Hydrobromic, and Either Perchloric or Sulphuric Acids

Procedure	Element Added	Bi Taken mg	Bi Found mg	Difference mg	% Loss
$HCl + HBr + HClO_4$ evaporated to dryness		22.68	21.82	- 0.86	- 3.79
		22.68	21.78	- 0.90	- 3.97
		45.19	40.96	- 4.23	- 9.36
		45.19	43.43	- 1.76	- 3.89
		112.84	94.71	-18.13	-16.07
		112.84	86.11	-26.73	-23.69
	10 mg Sb	45.19	44.20	- 0.99	- 2.19
	"	45.19	43.75	- 1.44	- 3.19
	6 mg Sn	45.19	43.96	- 1.23	- 2.72
	"	45.19	44.83	- 0.36	- 0.80
$HCl + HBr + H_2SO_4$ evaporated to dryness		45.19	44.06	- 1.13	- 2.50
		45.19	44.06	- 1.13	- 2.50
		112.84	108.94	- 3.90	- 3.46
		112.84	109.94	- 2.90	- 2.57
$HCl + HBr + HClO_4$ fumed lightly, but not evaporated to dryness		45.19	44.90	- 0.29	- 0.66
		45.19	44.84	- 0.35	- 0.77
		45.19	45.28	+ 0.09	+ 0.20
		90.38	89.72	- 0.66	- 0.73
		90.38	89.89	- 0.49	- 0.54
	20 mg As(V)	45.19	44.73	- 0.46	- 1.02
	"	45.19	44.86	- 0.33	- 0.73
	10 mg Sb	45.19	44.90	- 0.29	- 0.64
	"	45.19	44.86	- 0.33	- 0.73
	10 mg Sn	45.19	44.86	- 0.33	- 0.73
	"	45.19	44.86	- 0.33	- 0.73
$HCl + HBr + H_2SO_4$ fumed lightly, but not evaporated to dryness		45.19	44.56	- 0.63	- 1.39
		45.19	44.65	- 0.54	- 1.19
		45.19	44.90	- 0.29	- 0.64

Table 6

Analysis of Bismuth Concentrates: A Comparison of Results Obtained by Visual End-point and Amperometric End-point Detection

Sample No.	% Bi Found	
	Visual E.P. Detection	Amperometric E.P. Detection
1253	61.82, 61.65	61.80
1456	74.55, 74.52, 74.64	75.06
1457	74.86, 75.16	75.19
1458	66.23, 66.41, 66.51	66.20
1459	64.88, 64.83, 64.80	64.85