theory is fairly correct.

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Differential Titrimetric Determination of Bismuth[1]

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A precise EDTA titrimetric method involving a weight titration of major portion with solid reagent followed by titration of the remainder with a very dilute standard solution has been developed for the determination of bismuth. When the end point is determined by means of amperometry with a rotating mercury electrode, the error in bismuth analysis is less than 0.01 % even when Pb^{2+}, Zn^{2+}, or Cd^{2+} is present. However, copper interferes appreciably and masking with thiourea gives too low results.

It is well know fact that analog measurements by reading a single scale produce results of limited precision. As in differential thermal analysis, weighing with chemical balance, or bridge circuit measurement, if an analog measurement is applied to the difference of an unknown quantity and an accurate quantity close to the quantity to be measured, the precision of the result can be improved darstically. Although similar but not exactly the same principle has been applied in differential spectrophotometry.

In the determination of Te or Se, Barabas and Bennett[2] reduced the major portion of the analyzing constituent first with a measured amount of reducing agent then titrated the remainder with a dilute solution of the same reducing agent, in order to improve the precision of titrimetric procedure. Determination of Co (II) employing weight titration followed by back titration with dilute standard solution of EDTA has been applied in indirect determination of beryllium in order to improve precision.[3] Oxidation of U (IV) with potassium dichromate has been carried out with a precision better than ±0.01 % by adding almost stoichiometric amount of the solid reagent and titrating the remainder with a dilute solution.[4]

In the present work, a procedure for differential titration of bismuth with EDTA has been developed. Since high purity bismuth is readily available and the atomic weights involved in the stoichiometric calculations are known to the highest precision, development of a high precision titrimetric procedure appears to be feasible not only for the determination of bismuth but also for standardization of the EDTA solution. Furthermore, the atomic weight of bismuth and the formula weight of EDTA are both large, facilitating precision analytical procedure. Extremely large stability of EDTA complex of bismuth enables the precise determination of the end point. In the present work, a procedure for the differential titration of bismuth with EDTA is desribed.

Experimental

Apparatus. The apparatus has been described previously.[5]

Reagents. High purity (9N) bismuth (Nippon Mining Co. Ltd., Lot No. 014–13–785) and disodium salt of EDTA (Fisher, GR grade) are used without further treatment.

Procedure. A weighed amount of bismuth metal is dis-

TABLE 1: Stoichiometric Ratio EDTA/Bi (Theoretical 1.78123)

Bi taken	EDTA added	EDTA in	EDTA/Bi	Deviation	
g	g	titrant, g		g	%
2.10637	3.71610	0.03653	1.78156	−0.00006	−0.003
2.11927	3.74071	0.03495	1.78159	−0.00003	−0.002
2.11844	3.73588	0.03849	1.78167	+0.00005	+0.003
2.11746	3.73894	0.03392	1.78179	+0.00017	+0.010
2.11488	3.73500	0.03339	1.78185	+0.00023	+0.013
2.11784	3.73875	0.03779	1.78152	−0.00010	−0.006
2.11263	3.72564	0.03786	1.78143	−0.00019	−0.011
2.12187	3.74816	0.03187	1.78146	−0.00016	−0.009
2.09890	3.70342	0.03630	1.78175	+0.00013	+0.007

Relative standard deviation: 0.009 %.

solved in 5–10 m*l* nitric acid. When solution is complete 50 m*l* water is added. While stirring add 5 m*l* of urea solution (40%). About 99% of the stoichiometric quantity of EDTA is weighed out and dissolved in minimum amount of water. Add thus prepared EDTA solution to the bismuth solution while stirring vigorously to prevent local precipitation; once the precipitate forms, it is rather tedious to redissolve it. Adjust the pH of the solution with nitric acid or ammonium hydroxide to 1.2~1.5 After passing nitrogen for about 10 minutes to remove the oxygen in the solution, titrate the unreacted bismuth with 0.002M EDTA solution amperometrically using a rotating mercury electrode (600 rpm) at −0.16~−0.20 V vs. SCE.

Results and Discussion

When pH is greater than 1. 3, the end point can be accurately determined as shown in Figure 1. However, bismuth begins to preciptitate when pH approaches 1. 7. Therefore,

the optimum pH is in the range of 1.3–1.5.

The relative standard deviation of 0.009 % calculated from the results of Table 1 shows that the method is highly precise if no interfering impurity is present. The presence of an impurity that forms much less stable complexes with EDTA than with bismuth, such as lead ($pK_{MY}=18$), zinc ($pK_{MY}=16.5$), and Cd ($pK_{MY}=16.5$), does not interfere, as can be seen from Table 2. However, the presence of copper which has about the same pK_{MY} value results in a rounded titration curve causing difficulty in end–point determination
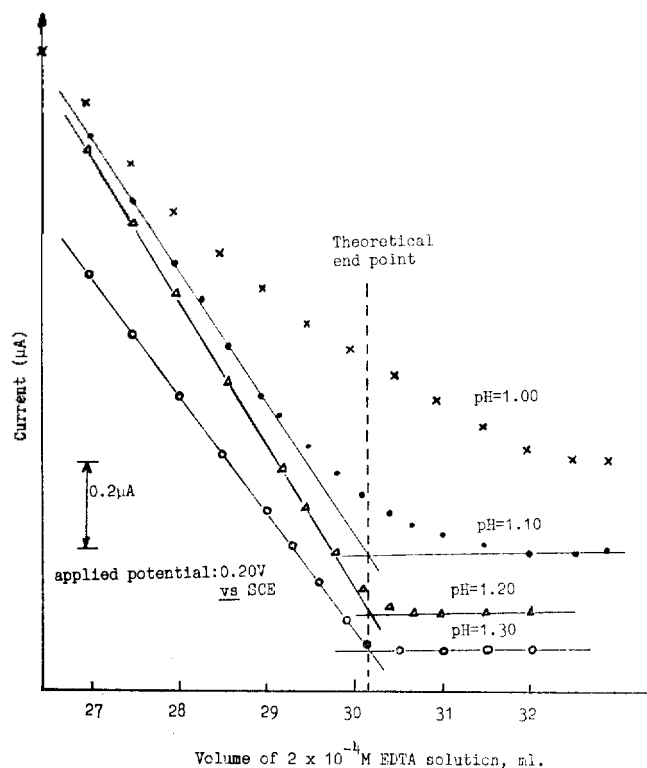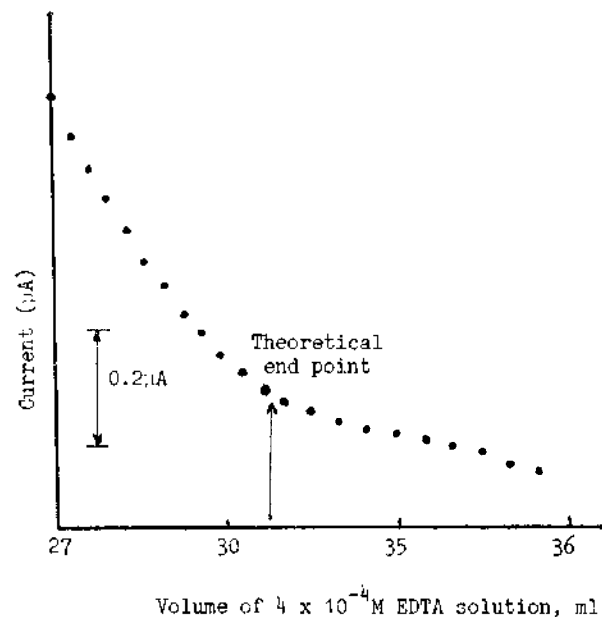

Figure 2. Amperometric titration curve of bismuth solution in the presence of copper (2 mg per gram of bismuth) without thiourea.

TABLE 2: Effect of the Presence of Impurities

Bi taken	Impurity added	Bi found	Deviation
g	mg	%	%
2.18914	0	100.016	+0.016
2.17644	0	99.992	−0.008
2.06266	Pb, 20	100.007	+0.007
2.10690	Pb, 40	100.007	+0.007
2.09137	Pb, 100	100.011	+0.011
2.10356	Cd, 40	100.006	+0.006
2.09327	Zn, 40	99.998	−0.002

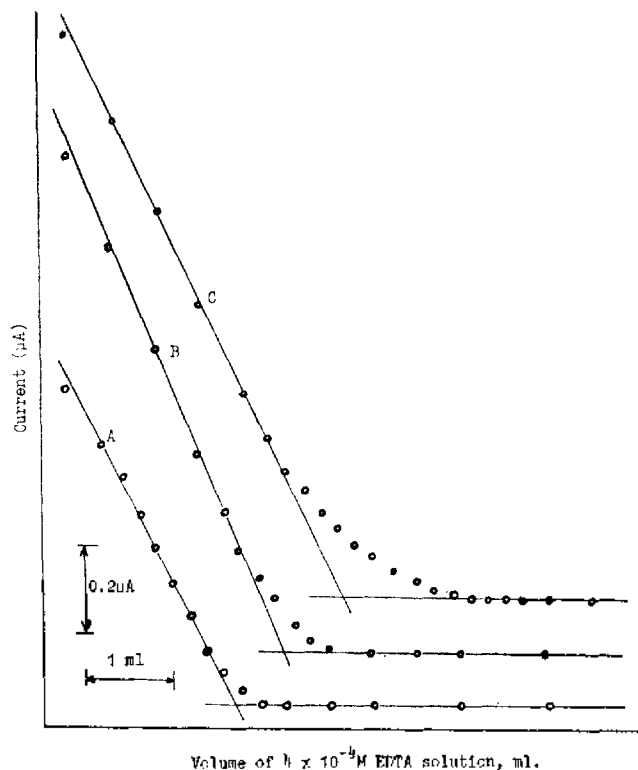Figure 1. Effect of pH on amperometric titration curve; 0.00102 g Bi in 150 m*l*.

Figure 3. Effect of thiourea on the titration of bismuth in the presence of copper; concentration of thiourea 0.02M, pH=1.2. Amount of copper: A 2mg, B 4mg, C 10mg, per gram of bismuth.

as shown in Figure 2. When thiourea is added to mask copper the end-point can be becomes sharper, but the results are

TABLE 3: Effect of Thiourea in the Presence of Copper

Bi taken g	Cu added mg	Bi found %	Deviation %	Remarks
1.12125	0	99.993	−0.007	Without thiourea
1.14255	0	100.000	0.000	Without thiourea
1.13584	0	100.001	+0.001	With thiourea
1.17175	0	99.997	−0.003	With thiourea
1.12212	2	99.993	−0.007	With thiourea
1.11930	4	99.989	−0.011	With thiourea
1.12214	6	99.936	−0.064	With thiourea
1.10240	10	99.929	−0.071	With thiourea

appreciably lower (Figure 3 and Table 3). From the data for pH = 1.10 plotted in Figure 1, the formation constant of bismuth-EDTA complex (assuming 1:1 stoichiometry) is estimated to be 1.5×10^{24} at room temperature. Thus, the interference caused by the presence of copper ($pK_{MY} = 18.8$) requires further study.

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Reaction of Thianthrene Cation Radical Perchlorate with N-Free and N-Alkylsulfonamides

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Thianthrene cation radical perchlorate (1) reacted with N-free sulfonamides to give directly N-sulfonylsulfilimines (5a–5c) but reaction with N-alkylsulfonamides afforded, inter alia, 5-(2-thianthreniumyl) thianthrene perchlorate (6).

Introduction

In the previous paper,[1] we have shown that thianthrene cation radical perchlorate (1) reacted with N-arylbenzene- and N-aryl-p-toluenesulfonamides to give 5-(p-N-arylbenzenesulfonamidophenyl)-and 5-(p-N-aryl-p-toluenesulfonamidophenyl) thianthrenium perchlorates (2) according to the following stoichiometry (Scheme 1).

This result indicates that a pair of nonbonding electrons on nitrogen atom of sulfonamides delocalizes into phenyl ring attached to nitrogen to cause the phenyl ring active although a sulfonyl group, i. e. a strong electron-withdrawing group is bonded to nitrogen.[2]

X	Me	H	H	Me	Me
y	H	H	Me	H	H
z	H	H	H		
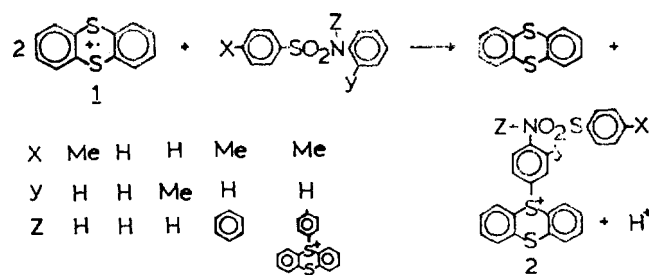
Scheme 1.

In order to understand further inherent electronic nature of nonbonding electrons on nitrogen, with the expectation