CHAPTER - IV

CETYLTRIMETHYLAMMONIUM BROMIDE AS AN ANALYTICAL REAGENT

Quaternary ammonium salts are very popular analytical reagents for the spectrophotometric determination and detection of a good number of metals. Quarternary ammonium salts with long carbon chain have an affinity to form ion-pairs with large anions and these ion-pairs are soluble in organic solvents. This property has been applied to the separation of number of metal ions. Cetyltrimethyl ammonium bromide (CTAB) belongs to this category.

A.I. Kirlov et al[1] determined uranium (VI) by using bromopyrogallol red and CTAB at pH 6-7. The complex absorbs maximum at 635 nm. Niobium (V) was determined[2] spectrophotometrically by using various organic dyes in presence of CTAB. A sensitive method was suggested by Jadav and Venkateswarlu[3] for the determination of niobium. The molar absorptivity of the niobium-Bromopyrogallol red-IDTA system with CTAB was 1.55×10^5 at 620 nm. This method was applied to the analysis of steel.

The 1:2 ion-association complex of rare earth metal -m-cresolphthalexon complex with CTAB has been investigated by Shanlina and Kirilov[4]. Chrome Azural and CTAB[5] were used for the photometric determination of Ruthenium at pH 4.6-5.6. The complex absorbed maximum at 610 nm. Tellurium (IV) was determined[6] spectrophotometrically with the help of iodide and CTAB. The complex, extractable in to $CHCl_3$ absorbed at 630 nm with molar absorptivity 5.9×10^4 1 $mol^{-1}cm^{-1}$. A spectrophotometric method was devised by Gordeva et al[7] for vanadium (V). The reagents used were pyrocatechol

violet and CTAB. The complex showed maximum absorbance at 670 nm with pH at 5.0.

Shen. Hanxi[8] determined zirconium spectrophotometrically with salicylfluorone and CTAB. The complex absorbed at 512 nm with molar absorptivity 1.38×10^5 (in 0.3 M HCl).

Guanghui et al[9] determined tin spectrophotometrically with salicylfluorone and CTAB in metallic materials. The complex exhibits maximum absorbance at 510 nm (in 0.5-7.5 N H_2SO_4).

Hanxi[10] determined tungsten by dibromo alizarin violet and CTAB. In 1M HCl medium the W:DBA:CTAB ratio was found to be 2:3:6. The blue complex absorbed maximum at 620 nm. The molar absorptivity was 8.2×10^4.

Cr(VI)-bromopyrogallol red-CTAB system has been investigated by Huaigang and Guoquan[11]. Cr(VI) forms a 1:3 complex with Bromopyrogallol red in presence of CTAB. The absorbance was measured at 635 nm with molar absorptivity 3.64×10^4 l $mol^{-1}cm^{-1}$.

Weiwa et al[12] proposed a photometric method for the determination of titanium using O-nitrophenyl fluorone and CTAB. The absorbance of the complex was measured at 535 nm (pH 1.5-2.0) with molar absorptivity 1.3×10^5 l $mol^{-1}cm^{-1}$.

Daopei[13] determined Vanadium with Erichrome cyanine R and CTAB, at pH 5-6. Absorbance was measured at 585 nm with molar absorptivity 6.63×10^4 l $mol^{-1}cm^{-1}$. Oiheng[14] determined Hf spectrophotometrically with bromopyrogallol red and CTAB or cetylpyridinium bromide in 0.2 M HCl medium. The absorbance of the complex was found at 670 nm with molar absorptivity 6.3×10^4 l mol^{-1} cm^{-1}.

Xue Guang[15] studied the colour reaction of thorium with semixylenol orange in presence of CTAB. At pH 1.5-4.0 the complex thorium-semixylenol orange ratio was found to be 1:2 with molar absorptivity 5.5×10^4 l mol^{-1} cm^{-1} at 550 nm.

Bismuth in tin was determined spectrophotometrically by A.T. Pilipenko et al[16] using polysulphide ion and CTAB. The complex absorbed maximum at 440 nm. The solvent used was $CHCl_3$.

Aluminium was determined spectrophotometrically by Zhe and Shuisheng[17] using salicyl fluorone and CTAB. The complex exhibits maximum absorbance at 559 nm with molar absorptivity 1.4×10^5 l $mol^{-1}cm^{-1}$ at pH 5.7-6.5.

The reaction of Al(III)[18] with sodium 2-bromo-4, 5 dihydroxy benzene-4'-sulphonate in the presence of CTAB has been studied spectrophotometrically. Maximum absorbance was found at 527 nm in the pH range of 6.7-8.0.

Li Shaoqing et al[19] have made an investigation on the spectrophotometric determination of Vanadium (IV) with diphenyl-carbazide and CTAB. The met : DPC:CTAB ratio was found to be 1:2:2.

The molar absorptivity of the complex was calculated to be 5×10^4 l mol^{-1} cm^{-1}. The method was applied in the determination of V(IV) in minerals, rocks and coal.

Rhodium was determined spectrophotometrically by the Hu Shokum et al[20] using salicylfluorone and CTAB. The complex has maximum absorbance at 595 nm.

Jiang Shufa et al[21] determined scandium using 7-iodo-8-hydroxyquinoline-5-sulphonic acid and CTAB. The complex exhibits its maximum absorbance at 505 nm in the pH range 4.5-6.0.

Clun Ziruo[22] described a spectrophotometric method for the determination of tin with o-chlorophenylfluorone and CTAB. The complex has an absorption peak at 520 nm with molar absorption coefficient 0.97×10^5.

Zinc was determined[23] with chrome zyral-s-semi-xylenol orange-CTAB spectrophotometrically. The absorbance was measured at 525 nm. The molar absorptivity was 1.18×10^2 l $mol^{-1}cm^{-1}$.

Yang Suqing et al[24] determined micro amounts of Cu with 4,5-dibromophenyl fluorone in presence of CTAB. The complex absorbed maximum at 590 nm (pH 5.0). The molar absorptivity was 1.5×10^5 l $mol^{-1}cm^{-1}$.

Hu Shoukun et al[25] carried out the spectrophotometric determination of Pd(II) with p-aminophenyl fluorone and CTAB. The Pd(II):PAPF was found to be 1:3. The absorbance was measured at 583 nm (pH 6.9-7.8) with molar absorptivity 8.56×10^4 l $mol^{-1}cm^{-1}$.

Cao-Shitl et al[26] used 5-nitrosalicyl fluorone in presence of CTAB to determine spectrophotometrically Ga. The complex showed maximum absorbance at 555 nm with molar absorptivity 1.91×10^5 l $mol^{-1}cm^{-1}$.

Ren Xing et al[27] have suggested a method for photometric determination of Zr with chlorophosphonazo-DBC and CTAB. The complex absorbed well at 650 nm with molar absorptivity 6.3×10^4 l $mol^{-1}cm^{-1}$.

9-(p-fluorophenyl) fluorone[28] and CTAB were used as reagents for the determination of Ge at 505 nm. The molar absorptivity was calculated to be 1.5×10^5 l $mol^{-1}cm^{-1}$.

Mo. Weiming et al[29] spectrophotometrically determined molybdenum using C-hydroxynaphthylfluorone and CTAB. The complex absorbs at 514 nm and has molar absorptivity of 1.17×10^5. Beer's law is obeyed in the range 0 to 10 μg Mo/25 ml.

Tang. Yangqiang[30] devised a method for determination of Ge with vanillyl fluorone and CTAB in 0.48-1.92 mol HCl/L. The complex showed maximum absorbance at 510 nm. The molar absorptivity was found to be 1.24×10^5 l $mol^{-1}cm^{-1}$.

Here CTAB finds applications in the extraction and spectrophotometric determination of bismuth and copper in optimum conditions.

Extraction and Spectrophotometric Determination of Bismuth with Cetyltrimethylammonium bromide (CTAB)

Introduction

From the literature survey it has been observed that Bismuth has an affinity to form complexes with different organic reagents like dithizone, dithiocarbamates, 8-quinolinol, bromopyrogallol red etc. In most of the cases, the after-extraction organic phases have been used for the colourimetric determination of the metal. Some of the methods are mentioned here.

Dithizone[31] has been used as a reagent for the spectrophotometric determination of bismuth. The bismuth-dithizone complex was extractable into chloroform showing its absorbance at 500 nm.

8-quinolinol[32] is another reagent that was utilised for the determination of bismuth at a pH of 4.0. The complex was extracted into chloroform and absorbed well at 395 nm.

Diethyldithiocarbamate[33] forms a complex with bismuth which is extractable into carbontetrachloride. The complex showed strong absorbance at 370 nm and 400 nm.

2-mercapto-4,4,6-trimethyl-1H, 4H-pyrimidine has been chosen as a spectrophotometric reagent for Bi(III) by Singh Ajai K. et al[34]. The orange red complex was extractable into chloroform from 1.5-3.0N perchloric acid. The complex absorbed well at 500 nm.

Kotelyanskaya L. I. et al[35] carried out the solvent extraction of Bismuth using lumogallion and diphenylguanidine. The metal: ligand:ligand ratio was found to be 1:1:1. The pH was adjusted between 1.8 and 2.0. The complex absorbed well at 490 nm.

Gorene D. et al[36] prepared a method for the spectrophotometric determination of bismuth using ammonium tetramethylene dithiocarbamate in excess. The spectrophotometric determination of bismuth with diacetyl monoxime-4-phenyl-3-thiosemicarbazone was carried out by Cano Pavan J.M. et al[37]. The metal : ligand ratio was found to be 1:2 and the complex was extracted into amyl alcohol with an absorbance at 385 nm. The Beer's law was obeyed upto 1-10 ppm Bismuth.

Nenova P. et al[38] investigated the spectrophotometric determination of bismuth with diethylene triamine pentaacetic acid. The complex was stable in 1.6 M aqueous $HClO_4$. The complex absorbed well at 270 nm. Beer's law was obeyed over the range 1-40 μ g/ml.

Bismuth (III) was extracted by coprecipitation of its 2-mercaptobenzothiazole complex with naphthalene by Satake Mosatada et al[39]. The absorbance of the complex was measured at 394 nm at the pH 4.5. Beer's law was obeyed over the range from 10 to 100 μg Bi/10 ml.

Procedures based on the formation of Bismuth(III) complexes with chlorophosphonazo III and cetyl pyridinium chloride[40], bromopyrogallol red[41], dipyrazolonylhexyl methanol[42], diethyl

dithiocarbamate[43], 3-methyl-1, 2-cyclopentanedione dithiosemicarbazone[44], iodide and rhodamine B[45], pyrocatechol violet and tridodecyl ethyl ammonium bromide[46], N-benzoyl-N-phenyl hydroxyl amine[47], have been suggested by various workers.

Vakhsyshiva L.E. et al[48] photometrically determined bismuth in nonferrous metallury products. Serrol F. Bosch et al[49] determined bismuth by using 0.5M Sn(II), 0.1M Sn(IV), 1M HCl, 2 ml polyvinylalcohol and 2 ml Se(IV) solutions at pH 0.8-1.3. The absorbance was measured at 380 nm. Agrawal et al[50] used N-m-tolyl-p-chlorobenzohydroxamic acid and xylenol orange for Bi(III) determination at pH 4.5 with λ_{max} 530 nm for the spectrophotometric determination of bismuth in the pH range 2.2-6.6 with absorbance at 362 nm. Salim Rodi et al[51] carried out the photometric determination of Bi(III) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol with its absorbance at 583 nm. The spectrophotometric determination of Bi(III) with pyrocatechol derivatives was investigated by Guseinov J.K. et al[52] at pH 2, showing the absorbance at 540 nm. Bismuth was determined spectrophotometrically by Shchemeleva G.G. et al[53] with the phenyl hydrazones of 1,3,3-trimethyl-2-formylindolinium perchlorate. Zhang Rende et al[54] provided a method for determination of bismuth with alizarine violet in presence of N-cetylpyridinium chloride in the pH range 5-5.8. The absorbance was found at 620 nm. N-n-cetyl aniline was used for spectrophotometric determination of Bi(III) from HCl media in benzene solvent by Mulik G.N. et al[55].

Extraction photometric determination of Bismuth was worked out by Presnyak I.S. et al[56] with tetramethylene thiourea and iodide from 1 mol. H_2SO_4/L solution into chloroform at 485 nm. Beer's law was obeyed for 2-50 μg Bi.

Burns D. Thorburn et al[57] determined bismuth spectrophotometrically using hexadryl tributyl phosphonium tetraiodide and microcrystalline benzophenone. The complex extractable into carbontetrachloride. The absorbance of the complex was measured at 495 nm.

Rakhamatullaev K. et al[58] used 2-(2-pyridylazo)-5-diethyl-m-aminophenol, Singh Ishwar et al[59] used 2,4,6-tris (2-hydroxy-4-sulpho-1 naphthylazo)-1,3,5-triazine trisodium salt and Honova Dagmar et al[60] utilised pyrocatechol violet and septonex for the spectrophotometric determination of Bi(III). The absorbances of the complexes were measured at 580 nm, 530 nm and 612 nm respectively.

Spectrophotometric determination of bismuth with O-nitrophenylfluorone was investigated by Zuoshiyu et al[61]. The pH range was chosen between 1.84-2.34 and the absorbance was found at 532 nm.

Zhang Guang et al[62] devised a method for spectrophotometric determination of Bi(III) with 2-(3,5-dichloro-2-pyridylazo)-5-(diethyl amino)-phenol, in the pH range of 8.5 to 9.5 and showing the absorbance at 580 nm. The metal : ligand ratio was found to be 1:4 and the molar absorptivity was calculated to be 1.32×10^5.

Zhou Nan et al[63] investigated a study on the spectrophotometric determination of bismuth by using semixylenol orange. It formed a 1:2 complex at 1.8 M $HClO_4$ with absorbance at 540 nm. The molar absorptivity was calculated to be 4.2×10^4 l $mol^{-1}cm^{-1}$.

Nonova D. et al[64] suggested a spectrophotometric procedure for the determination of bismuth with phenyl fluorescene and quaternary ammonium salts. It was a red coloured 1:1:2 complex (Bi:PF: GAS) with absorbance in the region 550-560 nm. The molar absorptivity value was 4.67×10^4 $dm^3mol^{-1}cm^{-1}$.

In the present investigation bismuth has been extracted and determined spectrophotometrically with CTAB.

EXPERIMENTAL

Apparatus and Reagents:

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer equipped with stoppered quartz cells of 10 mm. optical path length.

A stock solution of bismuth was prepared from bismuth trichloride and standardised. A working solution of Bi(III) (123.24 ppm) was prepared by appropriate dilution. Aqueous solutions of cetyl trimethyl ammonium bromide (CTAB) (0.1%) and potassium iodide (2%) were used.

Chloroform and other solvents were distilled before use. Buffer solution (pH 5), prepared by the standard method, was used to adjust the acidity of the aqueous phase. To study the inteferences, standard solutions of diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of bismuth:

To an aliquot containing 160.2 μg of bismuth(III) were added 2.5 ml of potassium iodide, 0.2 ml of cetyl trimethyl ammonium bromide followed by adequate amount of buffer to make the volume of the aqueous phase up to 10 ml and left for 1 min to ensure

complete complexation. Finally it was equilibrated with chloroform (10 ml) for 30 sec. The orange organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was read at 490 nm. against a blank. Amount of bismuth was deduced from a previously prepared calibration curve. To study the effects of diverse ions the desired foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

When potassium iodide in excess is added to an acid solution of bismuth(III), a yellow to orange colouration due to the formation of tetraiodobismuthate(III), $[BiI_4]^-$ is produced. This complex is not extractable into chloroform. On adding to it an aqueous solution of cetyl trimethyl ammonium bromide (CTAB), an orange precipitate completely soluble in chloroform is obtained. The precipitate is an ion-association complex of the type $[CTA]^+ [BiI_4]^-$.

Absorption spectra:

The absorption spectrum of the bismuth(III) complex in chloroform against a blank was taken. Maximum absorption of the complex, as seen from the spectrum, takes place at 490 nm Fig. 1.

The reagent blank prepared under similar condition does not have any absorption at this wave length.

Extraction as a function of pH :

The extraction of bismuth in terms of absorbance was investigated in the pH range 0-12. Although extraction starts from pH 1, the organic extracts showed maximum absorption when the extractions were carried out from aqueous solution and adjusted to pH 4-5. The aqueous phases, after extraction, were free from bismuth. This indicated a complete and quantitative recovery of bismuth in this condition. Extraction of the metal however decreases beyond pH 5.5. This has been shown in Table 1, Fig. 2.

Effects of solvents:

Apart from chloroform, some other organic solvents like carbon tetrachloride, benzene and ethylacetate were tested as extracting solvents. The bismuth(III) complex when extracted into chloroform showed maximum absorbance. The complex was not extractable into carbon tetrachloride. Hence chloroform was used for the purpose.

Reagent concentration and Beer's law:

The effect of reagent concentration on the extraction behaviour of bismuth was studied by using different concentrations

of cetyl trimethyl ammonium bromide (CTAB) or potassium iodide. One variable was varied, while keeping others constant. It was noted that 1.5 ml of cetyl trimethyl ammonium bromide (0.1%) along with 2 ml of potassium iodide (2%) was sufficient to extract 160 μg of bismuth in a single operation. Use of less than 1 ml of cetyl trimethyl ammonium bromide showed low absorbance of the complex, although increased concentration of cetyl trimethyl ammonium bromide (upto 5 ml) produced no significant effect on maximum colour development. Results are shown in Table 2 and 3. The absorbance of the chloroform extract showed a linear response over a concentration of 25 ppm of bismuth. The molar absorptivity of the complex (on the basis of metal content) was calculated to be 0.822×10^4 l $mol^{-1} cm^{-1}$ with Sandell's sensitivity 0.025 $\mu g/cm^2$. Beer's law data are tabulated in Table 4, Fig. 3.

Stability of colour:

The absorbance of Bi(III)-CTAB complex in chloroform was measured at elapsed intervals of time and the colour intensity was found to be stable for at least 6 hours. This has been shown in Table 5.

Interference:

The effect of foreign ions was studied by adding different amounts of foreign ions to 160 μg bismuth(III) and determining the bismuth following the recommended procedure. It was found that the following ions did not interfere when present in mg mentioned

in the parenthesis. Fe(III)(2), Ba(II)(2), Cu(II)(1.0), Cd(II) (1.2), Ni(II)(2.0), Ca(II)(2.0), Co(II)(2.0), Th(IV)(2.0), Sr(II)(2.0), Zn(II)(2.0), U(VI)(2.0), Hg(II)(2.0), Pd(II)(1.0), Pt(IV)(1.0), Rh(III)(1.0), Zr(IV)(2.0), Mo(VI)(2.0), Au(III)(1.5), V(V)(1.5), Ag(I)(1.0), Sn(II)(2.0), Mg(II)(2.0), Pb(II)(2.0), Cr(III)(2.0), Nitrate (4.0), fluoride (4.0), arsenate (3.0), ascorbate (3.0), tartrate (3.0), citrate (3.0), borate (3.0), thiocyanate (3.0), bromide (1.5) and phosphate (1.5). However oxalate and EDTA interfered. This has been shown in Table 6.

Determination of bismuth in synthetic mixtures :

In absence of real samples the proposed method was tested to estimate microgram amounts of bismuth from some synthetic mixtures, as shown in Table 7.

Precision and accuracy :

The proposed method was tested by analysing solutions containing a known amount of bismuth (III). From the results shown in Table 8, the method seems to be fairly precise and reproducible, requiring hardly 10-15 min. for each run. The method has also been compared with some other existing methods.

Comparison of the method

The proposed method is simple, rapid and comparable well with some other existing methods as shown in Table 9.

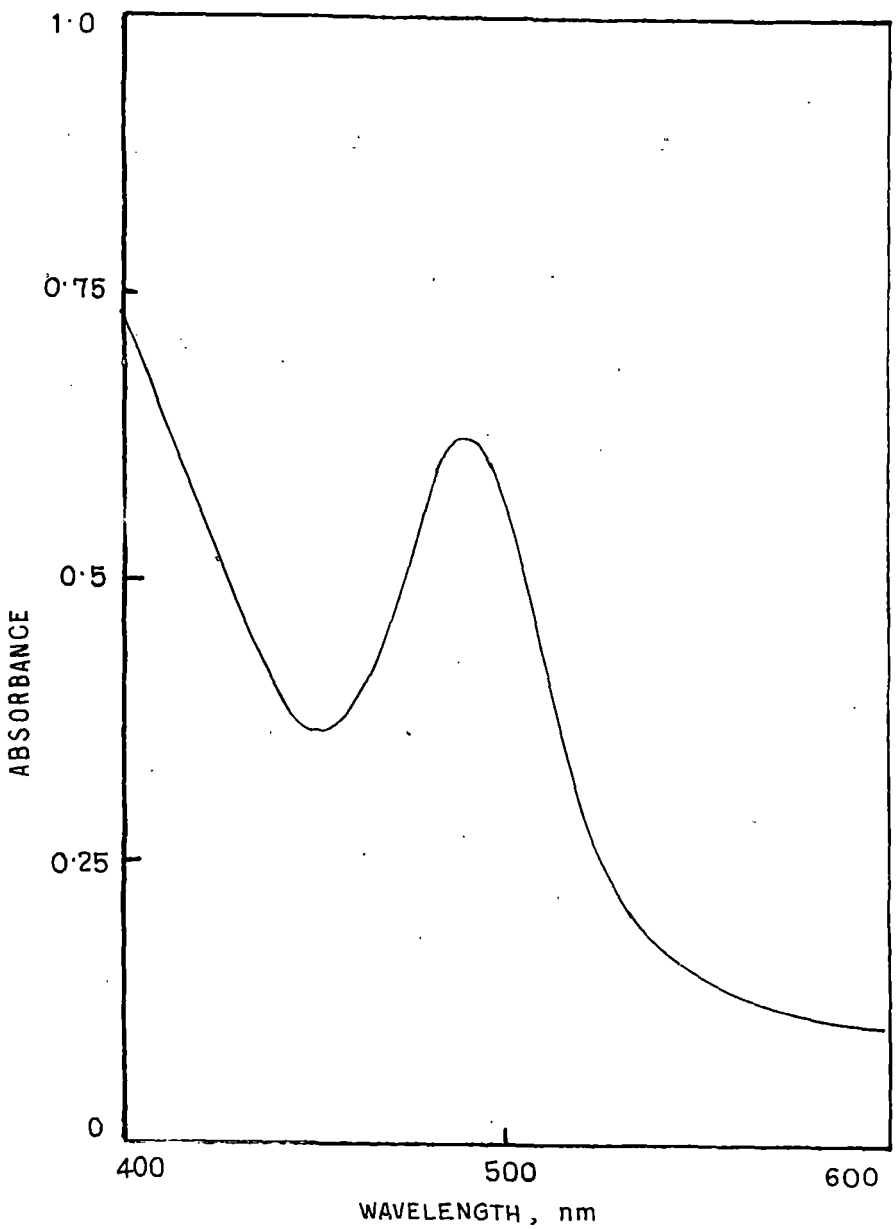

FIG. 1. ABSORPTION SPECTRUM OF Bi(III)-CTAB COMPLEX (Bi-16 ppm).

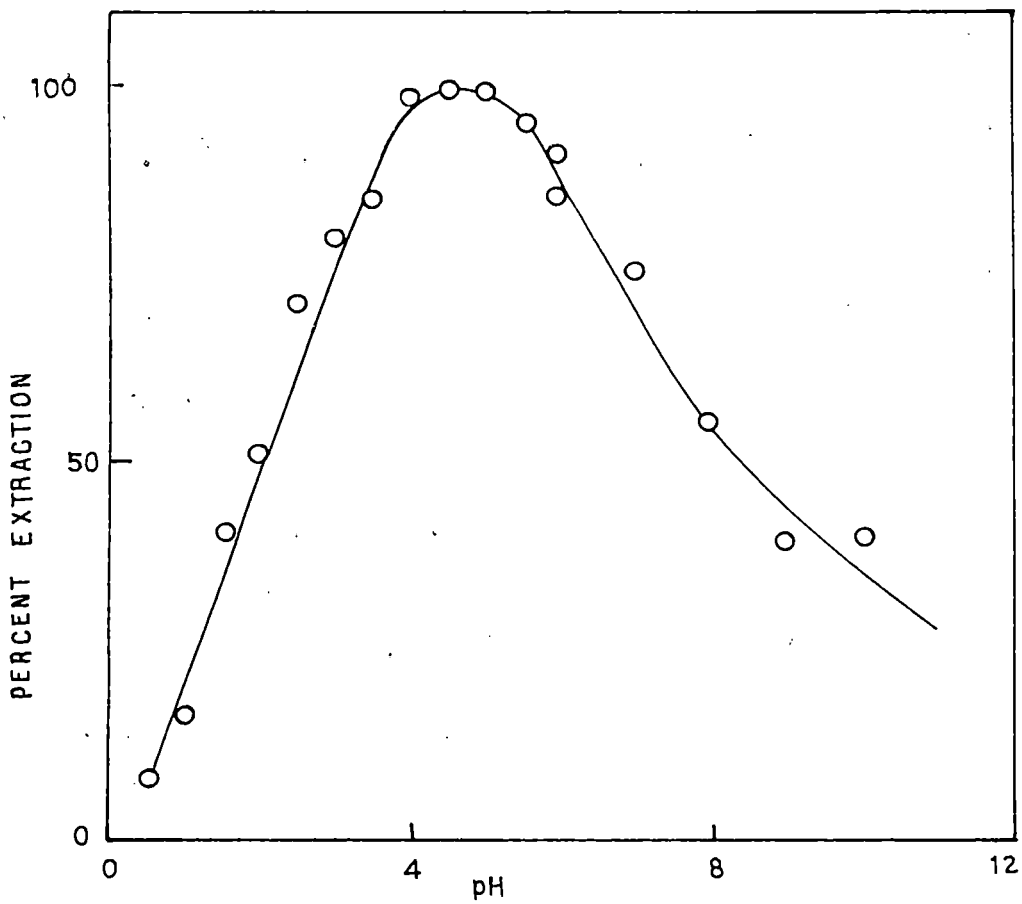

FIG. 2. EXTRACTION CURVE OF Bi(III) - CTAB COMPLEX

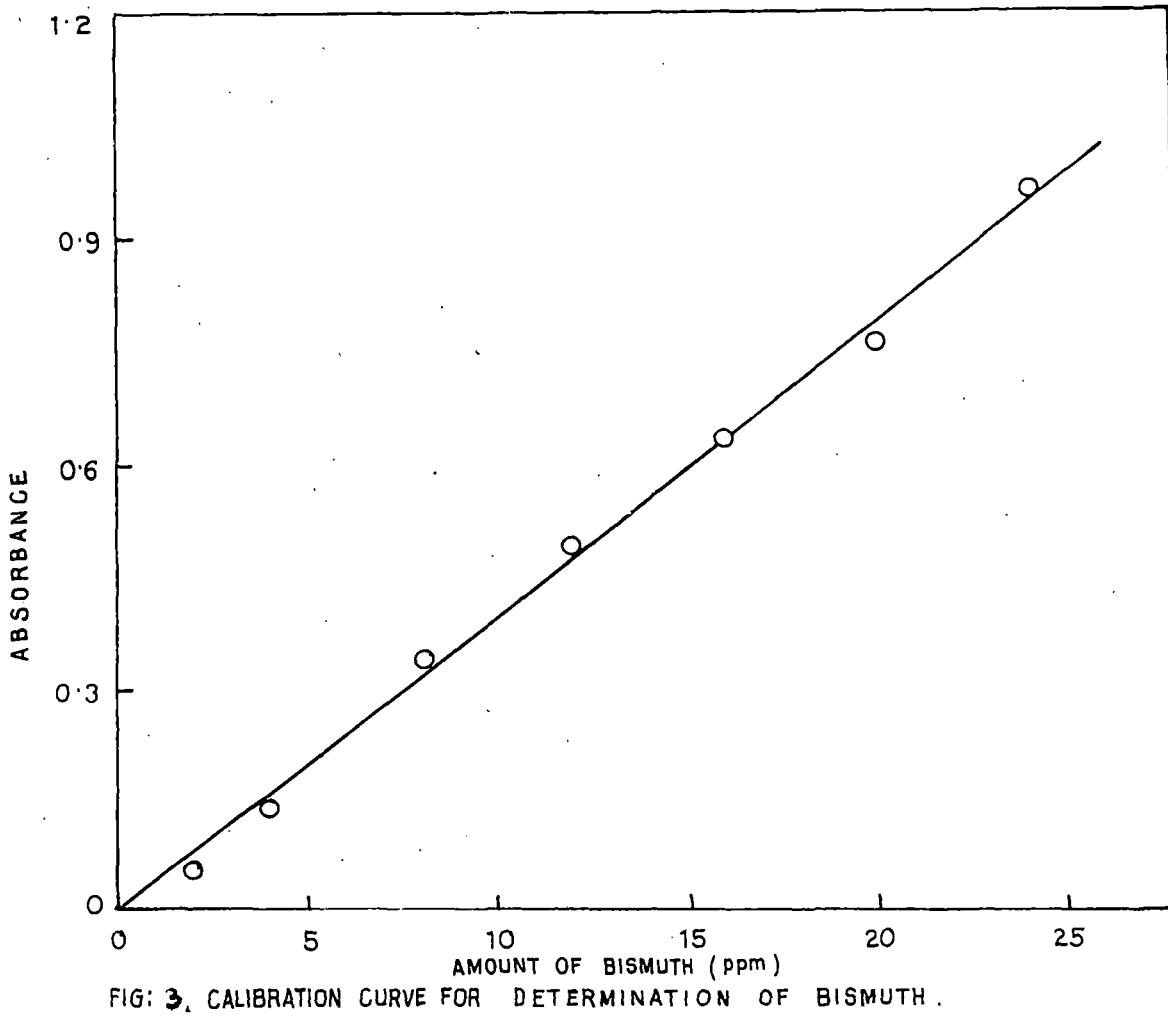

FIG: 3. CALIBRATION CURVE FOR DETERMINATION OF BISMUTH.

Table 1. Variation of absorbance with pH of the aqueous phase [The aqueous phase (10 ml) contains 160.2 μg of Bi(III), 2.5 ml aqueous solution (2%) of KI and 0.2 ml CTAB (0.1%)]

pH	Absorbance at 490 nm	pH	Absorbance at 490 nm
0.5	-	4.5	0.632
1.0	0.108	5.0	0.632
1.5	0.252	5.5	0.598
2.0	0.322	6.0	0.536
2.5	0.442	7.0	0.472
3.0	0.504	8.0	0.346
3.5	0.508	9.0	0.252
4.0	0.630		

Table 2. Effect of cetyl trimethyl ammonium bromide concentration. [The aqueous phase (10 ml) (pH-5) contains 160.2 μg of Bi(III) and 2.5 ml aqueous KI (2%)] Aqueous solution of CTAB (0.1%) was used.

CTAB added (ml.)	Absorbance at 490 nm	CTAB added (ml.)	Absorbance at 490 nm
0.1	-	1.8	0.632
0.2	0.108	2.0	0.630
0.3	0.150	2.25	0.632
0.4	0.250	2.5	0.632
0.6	0.360	3.0	0.630
0.8	0.460	3.5	0.632
1.0	0.504	4.0	0.630
1.2	0.600	4.5	0.632
1.4	0.630	5.0	0.630
1.6	0.634		

Table 3. Effect of potassium iodide concentration [The aqueous phase (10 ml) (pH-5) contains 160.2 μg of Bi(III) and 2 ml of CTAB (0.1%)] Aqueous KI(2%) was used

KI added (ml)	Absorbance at 490 nm	KI added (ml)	Absorbance at 490 nm
0.1	0.105	1.75	0.632
0.25	0.250	2.0	0.632
0.5	0.400	2.25	0.632
0.75	0.450	2.5	0.630
1.0	0.500	3.0	0.632
1.25	0.566	3.5	0.632
1.5	0.600	4.0	0.630

Table 4. Beer's law data

Amount of Bi ppm	Absorbance at 490 nm.
2	0.055
4	0.135
8	0.345
12	0.495
16	0.630
20	0.765
24	0.965

Table 5. Variation of absorbance of the Bi(III)-CTAB complex with time

Time in hours after extraction	Absorbance at 490 nm
0.25	0.630
0.5	0.630
1	0.632
2	0.630
4	0.628
6	0.628

Table 6. Effect of diverse ions for the determination of 160 μg of bismuth (III)

Foreignion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Nitrate	4000	Th(IV)	3000
Fluoride	4000	Sr(II)	3000
Arsenate	4000	Zn(II)	3000
Ascorbate	4000	U(VI)	3000
Tartrate	4000	Hg(II)	3000
Citrate	4000	Pd(II)	1500
Borate	4000	Pt(IV)	1500
Thiocyanate	3500	Rh(III)	1500
Bromide	3000	Zr(IV)	3000
Phosphate	3000	Mo(VI)	3000
Fe(III)	3000	Au(III)	2000
Ba(II)	3000	V(V)	2000
Cd(II)	1500	Sn(II)	3000
Ni(II)	3000	Mg(II)	3000
Ca(II)	3000	Pb(II)	3000
Cu(II)	1500	Cr(III)	3000
Ag(I)	1500	Co(II)	3000

Table 7. Determination of bismuth in synthetic mixtures (average of three determinations)

Composition with amounts in (μg)	Bismuth found in (μg)
1. Bi(123.2), Fe(200), Ni(200)	122.5
2. Bi(123.2), Cu(200), Pb(200)	120.5
3. Bi(123.2), Zn(200), Mn(200)	121.0
4. Bi(123.2), Co(200), Pb(200)	124.5
5. Bi(123.2), Pd(200), Pt(200)	122.5

Table 8. Reproducibility of bismuth recovery

Bismuth taken (μg)	Bismuth found (μg)	Mean (μg)	Std. Dev. (%)
61.62	60.5, 60.5, 62.0 61.5, 62.5, 63.0	61.66	1.03
123.24	120.5, 122.5, 124.0 122.0, 121.0 123.0	122.16	1.29
160.2	161.5, 158.5, 160.5 161.0, 162.5, 160.5	160.75	1.33
221.8	220.5, 222.0, 223.0 221.0, 222.0 220.0	221.42	1.11

Table 9. Comparison of the present method

Ref.	Reagent	pH	λ_{max} (nm)	Molar absorptivity ($l\ mol^{-1} cm^{-1}$)	Interference
34.	2-mercapto-4,4,6-trimethyl-1H, 4H-pyrimidine	1.5-3.0N perchloric acid	500	12700	Nil
61.	O-nitrophenyl fluorone	1.84-2.34	532	7.08×10^4	Nil (interference of most of the cases of metal ions has been eliminated)
63.	Semixylenol orange	1.8M $HClO_4$	540	4.2×10^4	Ni^{*+2}
65.	Tribromo-chlorophosphonazo	2.4	640	1.05×10^5	-
66.	Arsenazo-DBC	1.2N $HClO_4$	632	9.0×10^4	Nil (The common ions do not interfere)
	Present method	4.5	490	8220	Oxalate, EDTA

* masking agents used

Extraction and Spectrophotometric Determination of Copper with Cetyltrimethylammonium Bromide.

Introduction

There are numerous methods which have been suggested for the separation and determination of copper by liquid-liquid extraction. The principal method used for such extraction procedures involved the utilization of various organic reagents like β-diketone, monoxime, dioxime, nitrosophenol, dithizone, dithiocarbamate and other miscellaneous reagents as the chelating agents, followed by photometric determination of the metal. The ion association system involved the utilization of thiocyanate, halide, phenanthroline and other organic reagents.

The extraction of copper by diethyl dithiocarbamate[67] was investigated at pH 8.5. The absorbance of the complex was measured at 560 nm in butyl acetate. Other well-known methods involved the utilization of neo-cuproin[68] and bis cyclohexane oxalyl-dihydrazone[69] for the determination of copper.

The reaction of copper with pyridine and thiocyanate has been investigated. The greenish-white precipitate, soluble in chloroform, carbontetrachloride and ether, gives an intense blue colour[70].

Arora H.C. et al and Talra R.K.[71] have performed the solvent extraction of Cu(II) by using 4-Isonitroso-3-methyl-1-phenyl-5-pyrazolone. The complex was extractable into benzene. Gonzaley et al[72] determined copper(II) spectrophotometrically at 680 nm as its 1:2 (metal:ligand) complex with nucic acid at pH 10.0.

Reddy et al[73] determined copper(II) by making use of 2-hydroxy acetophenone oxime. The complex was extractable into iso-Bu COMe at pH 5.5. The absorbance of the organic layer was measured at 355 nm. Copper(II) was determined spectrophotometrically using moncethyl ester of n-butyl-amino-o-hydroxy benzyl phosphonic acid[74]. The 1:1 green complex was soluble in methyl alcohol and the absorbance of the complex was measured at 400 nm.

More recently, procedures based on the formation of copper complexes with bis(4-hydroxypent-2-ylidene) diaminoethane[75], 2-(5,5-dimethyl-4,5,6,7 tetrahydrobenzthiazolyl-2-azo)-4-ethyl phenol[76], 5-methyl-1,10-phenanthroline and Eriochrome cyanine R[77], 1-phenyl-3 thiobenzoylthiocarbamide[78], ammonium (2-amino-3-hydroxy-4-pyridylazo) benzene-4-arsonate[79], citric acid or EDTA[80], biacetyl monoquinolyl hydrazone[81], substituted pyridines and thiocyanate[82], 4-methyl tetrahydrobenzofurano (6,7,6) coumarin[83], 5-(3,5-dibromo-2-pyridylazo)-2,4 diamino tolune[84], meso-tetrakis (p-sulfonyl-phenyl) porphyrin[85], 4-methyl-2-(2-hydroxy-1-naphthylazo) thiazole and 4-odamantyl-2-(2-hydroxy-1-naphthylazo) thiazole[86], 2-(5,5-dimethyl, 4,5,6,7-tetrahydro-

benzothiazolyl-2-azo)-4-chloro-5-methyl phenol[87], 2-(5,5-dimethyl-4,5,6,7-tetrahydro-2-benzothiazolylazo)-4 bromophenol[88], 2-hydroxy-1-acetonaphthoneoxime[89], bis (acetyl acetone) ethylenediamine[90], 2,2'-biquinolyl and tetrabromophenolphthaloin ethyl ester[91], 1,3-bis [di(2-pyridyl) methylene amino] urea[92], 2-(2-benzothiazolylazo)-5-dimethyl aminobenzoic acid[93], cetyltrimethyl ammonium chloride-chromal blue G[94], 2-(5-bromo-2-pyridylazo) -5-diethylaminophenol[95], N-(α-pyridyl)-2-thioquinaldinamide[96], cuprizone[97], N-(4-hydroxy-3-methoxy benzylidene) hydrazine carbothioamide[98], have been investigated for the spectrophotometric determination of copper.

Alonso Rodriguez Elia et al[99] have developed a method for the spectrophotometric determination of Cu(II) by using triethylene tetramine hexamethylene phosphonic acid. The absorbance of the complex was measured at 680 nm.

Huang Yechu[100] presented an extractive photometric technique to determine copper with 1,2-cyclohexanediamine tetra acetic acid in the pH 2.5. Phthalate-HCl buffer was used. The absorbance of the complex was measured at 700 nm.

Bajkin Dubravka P et al[101] made an investigation spectrophotometrically for the determination of copper(II) by

using 4,4'-dimethoxy-benzilmonoxime.

In the present investigation CTAB has been used for the extraction and spectrophotometric determination of copper.

EXPERIMENTAL

Apparatus and Reagents :

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer fitted with stoppered quartz cells of 10 mm optical path length.

A stock solution of copper(II) was prepared from $CuSO_4 \cdot 5H_2O$ and standardised. A working solution of copper(II) was prepared by appropriate dilution. Aqueous solution of cetyl trimethyl ammonium bromide (CTAB) (SISCO) (0.2%) and potassium iodide (BDH) (2%) were used for the purpose.

Chloroform and other solvents were distilled before use. Buffer solution (pH 2.0), prepared by the standard method was used to adjust the acidity of the aqueous phase. To study the interferences, standard solutions of respective diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of copper :

To an aliquot containing 52.5 μ g of copper(II), were added 2 ml of potassium iodide, 2 ml of cetyl trimethyl ammonium bromide followed by adequate amount of buffer (KCl-HCl buffer) to make the volume of the aqueous solution to 10 ml and left for 1 min to

ensure complete complexation. Finally it was equilibrated with chloroform (10 ml) for 30 sec. The organic layer was separated and poured over anhydrous sodium sulphate to remove any water droplets. The absorbance of the chloroform extract was read at 360 nm against a blank and the amount of copper was deduced from a calibration curve. To study the effect of interference, the desired diverse ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

In presence of potassium iodide and cetyltrimethyl ammonium bromide copper forms a yellowish complex extractable into chloroform. But separately either in presence of potassium iodide or cetyl trimethyl ammonium bromide the method does not form any extractable complex.

Absorption spectra :

The absorption spectrum of the copper(II) complex in chloroform against a blank showed absorption maximum at 360 nm (Fig. 1). The reagent blank prepared under identical condition did not absorb in the region. Hence the wave-length of 360 nm was selected for all analytical measurements.

Extraction as a function of pH :

Extraction of copper in terms of absorbance was investigated in the pH range 0-10. The complex exhibited constant and maximum absorbance in the pH range 0.5-3.5 which indicated a complete and quantitative recovery of the metal. Absorbance decreases when the extractions were carried out beyond pH 4.0 or at higher acidities. For our purpose, acidity of the aqueous phase was maintained at pH 2.0 with the buffer. The variation of absorbance with pH of the aqueous phase has been shown in Table 1.

Effect of solvent :

Apart from chloroform, some other organic solvents like carbon tetrachloride, benzene or ethylacetate were tested as extracting solvents. It was found that the complex in chloroform gives the maximum absorbance and hence this solvent was used for our purpose.

Stability of colour :

The absorbance of the Cu(II)-CTAB complex in chloroform is stable for at least 12 hours as measured at elapsed intervals of time shown in Table 4.

Reagent concentration and Beer's law :

In the process, the concentrations of potasssium iodide and cetyl trimethyl ammonium bromide were varied in order to ascertain the optimum condition for quantitative extraction of the metal. It was noted that 2 ml potassium iodide along with 2 ml of cetyl trimethyl ammonium bromide was sufficient to extract 52.5 μ g of copper(II) in a simple operation. Use of excess potassium iodide (over 4 ml) has a tendency to lower the absorbance of the chloroform extract, while higher concentration of cetyl trimethyl ammonium bromide (upto 4 ml) had no adverse effects (Fig. 2). The results have been shown in Table 2 and 3.

Different amounts of copper were extracted by the recommended procedure and absorbances of the chloroform extracts measured. The system obeyed Beer's law over a concentration of 10 ppm of copper. The molar absorptivity of the complex (based on copper content) was evaluated to be 1.064×10^4 lit $mol^{-1} cm^{-1}$ and Sandell's sensitivity 0.059 μ g/cm^2. Beer's law data have been tabulated in Table 5 (Fig. 3).

Interference :

To study the effects of diverse ions on the extraction behaviour, copper was determined as above in presence of the respective foreign ions. Deviation of not more than $\pm$ 3% from the recovery of copper was taken as the tolerance limit for the diverse ions tested. Copper (52.5 μ g) could be determined without

interference in presence of the following ions shown in Table 6.

Determination of copper in synthetic mixtures :

In absence of real samples the proposed method was extended to various synthetic mixtures to estimate microgram amounts of copper as shown in Table 7.

Precision and Accuracy :

Precision and accuracy of the method was tested by analysing solutions containing a known amount of copper. The results in Table 8 show that the method is fairly precise and reproducible requiring hardly 10-15 min for each run.

Conclusion :

The present method for the spectrophotometric determination of copper is simple and rapid. Copper can be determined without interference in presence of all the common ions tested except thiosulphate. The method is well comparable with some other existing methods as shown in Table 9.

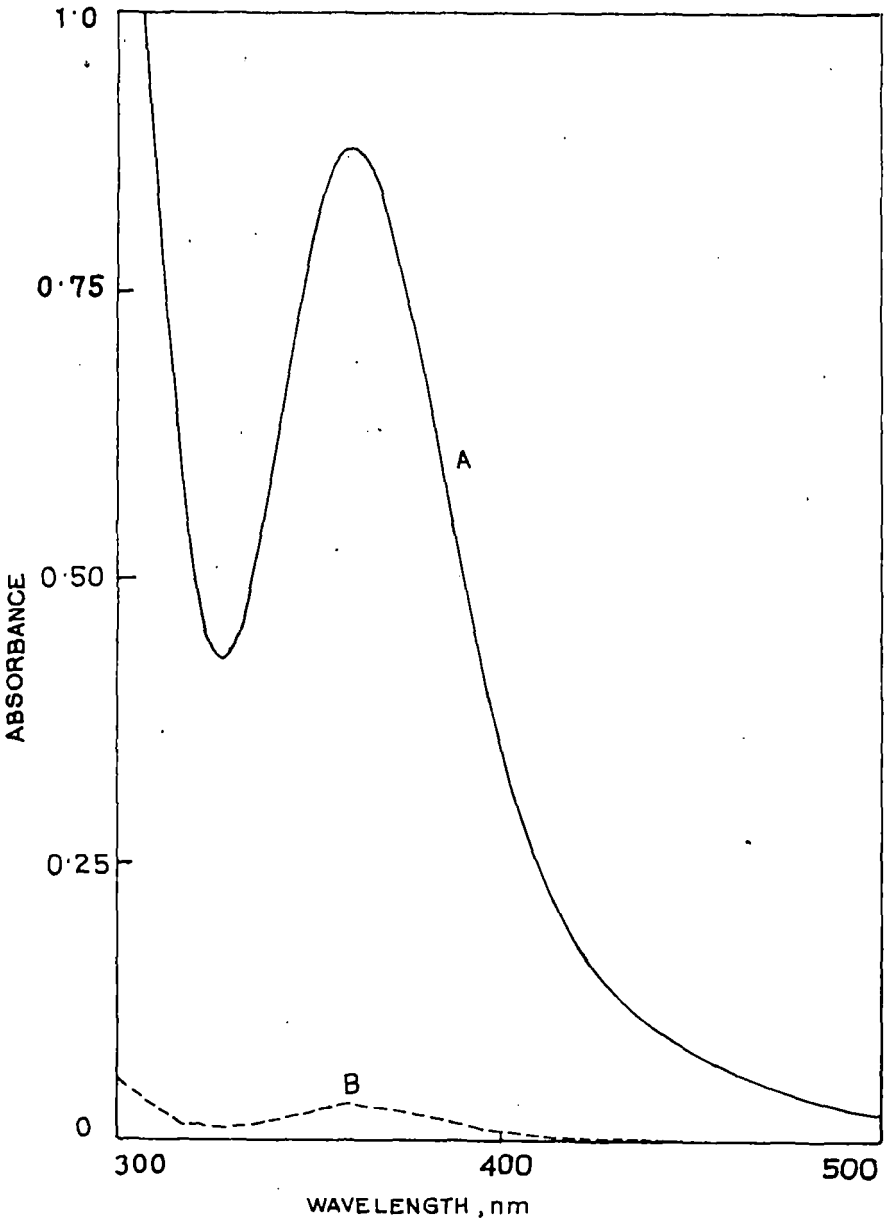

FIG: 1. ABSORPTION SPECTRUM OF Cu(II)-CTAB COMPLEX (A) AND REAGENT BLANK (B) (Cu - 5·2 ppm)

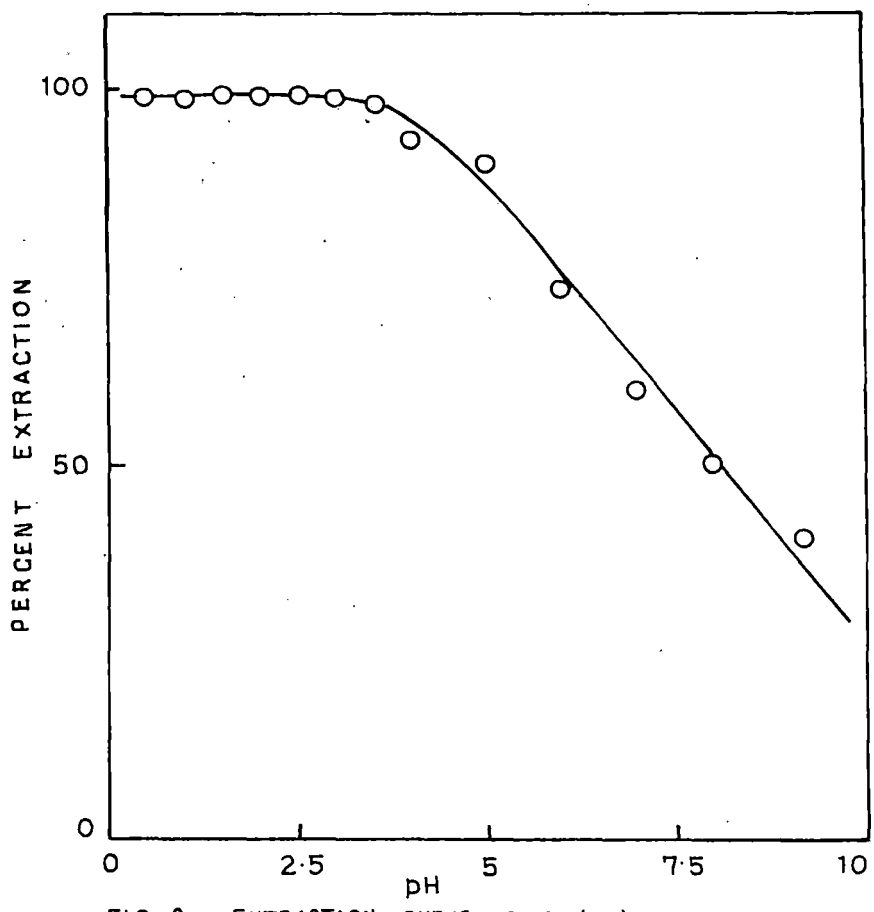

FIG. 2. EXTRACTION CURVE OF Cu(II)-CTAB COMPLEX

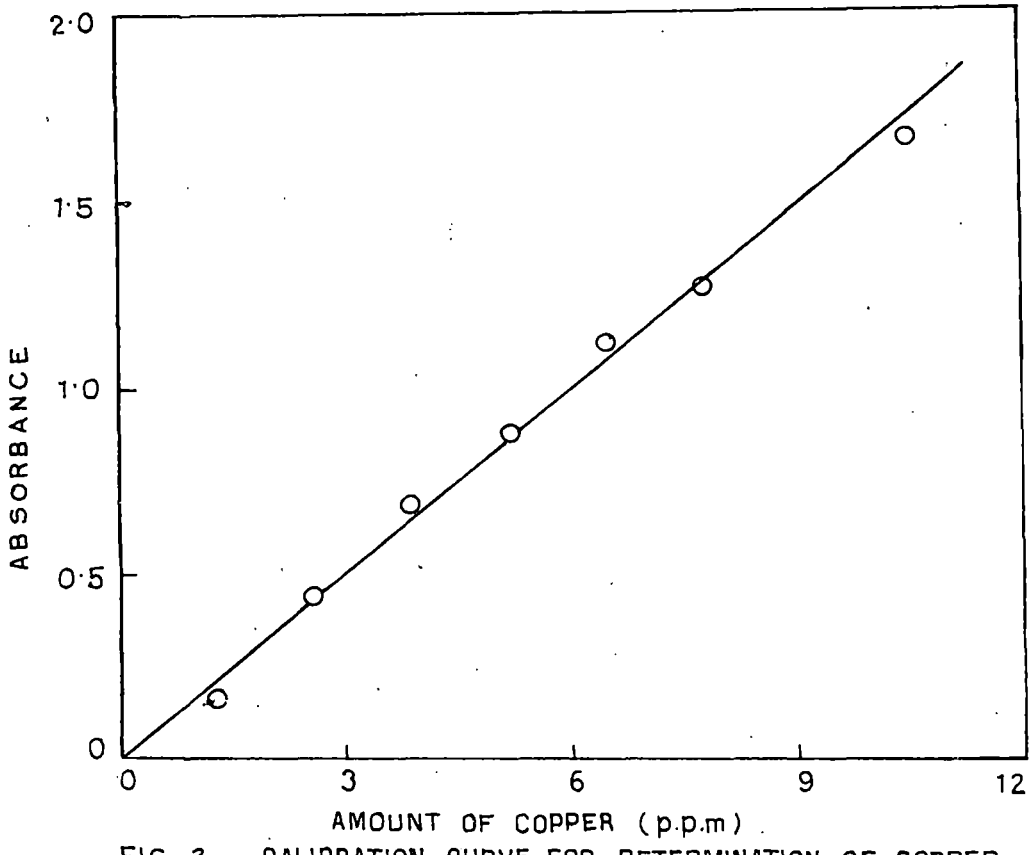

FIG. 3. CALIBRATION CURVE FOR DETERMINATION OF COPPER

Table 1 . Variation of absorbance with pH of the aqueous phase [The aqueous phase (10 ml) containing 52.5 μg of Cu(II), 2 ml of KI(2%) and 2 ml of CTAB (0.2%)]

pH	Absorbance	pH	Absorbance
0.5	0.878	4.5	0.800
1.0	0.880	5.0	0.792
1.5	0.882	6.0	0.650
2.0	0.880	7.0	0.528
2.5	0.882	8.0	0.440
3.0	0.882	9.0	0.352
3.5	0.860		
4.0	0.878		

Table 2. Effect of potassium iodide concentration [The aqueous phase (10 ml) (pH 2) contains 52.5 μg of Cu(II), 2 ml of CTAB (0.2%)] 2% KI solution was added for the purpose.

KI solution added, ml	Absorbance at 360 nm	KI solution added, ml	Absorbance at 360 nm
0.1	-	2.0	0.882
0.25	0.140	2.25	0.880
0.5	0.262	2.5	0.882
0.75	0.600	2.75	0.880
1.0	0.650	3.0	0.878
1.25	0.710	3.5	0.878
1.75	0.780	4.0	0.865
		5.0	0.860

Table 3. Effect of cetyltrimethyl ammonium bromide concentration [The aqueous phase (pH 2) containing 52.5 μg Cu(II) and 2 ml of KI (2%) was maintained at 10 ml in volume] 0.2% of cetyl trimethyl ammonium bromide was used.

CTAB added ml	Absorbance at 360 nm	CTAB added, ml	Absorbance at 360 nm
0.25	0.150	1.75	0.840
0.5	0.352	2.0	0.882
0.75	0.515	2.5	0.880
1.0	0.616	3.0	0.882
1.25	0.680	3.5	0.880
1.5	0.800	4.0	0.880

Table 4. Variation of absorbance with time

Time in hours after extraction	Absorbance at 360 nm
0.25	0.882
0.5	0.880
1	0.880
2	0.880
4	0.880
8	0.882
12	0.880
16	0.870
24	0.850

Table 5. Beer's law data

Amount of copper, ppm	Absorbance at 360 nm
1.3	0.180
2.6	0.422
3.9	0.682
5.2	0.880
6.5	1.120
7.8	1.260
10.5	1.672

Table 6. Effect of diverse ions on determination of 52.5 μg of copper

Foreign ion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Thiocyanate	3000	Calcium	2000
Fluoride	3000	Cobalt	2000
Nitrate	3000	Thorium	2000
Ascorbate	3000	Strontium	2000
Tartrate	3000	Palladium	500
Citrate	3000	Platinum	500
Phthalate	3000	Rhodium	1000
Phosphate	3000	Zirconium	2000
Bromide	3000	Molybdenum	2000
Borate	60	Gold	2000
Oxalate	60	Vanadium	2000
Thiosulphate	nil	Bismuth	2000
Barium	2000	Iron*	1000
Cadmium	2000	Mercury	500
Nickel	2000	Uranium	2000
Lead	2000	Tin	2000
Chromium	2000	Magnesium	2000
		Silver	500
		Zinc	1000

* Masking agents used.

Table 7. Determination of copper in synthetic mixtures

Composition with amounts in (μg)	Copper found in (μg)
1. Cu(52.5), Fe(200) Ni(200) + F(2000)	50.5
2. Cu(52.5), Pb(200) Bi(200)	52.0
3. Cu(52.5), Ni(200) Co(200)	52.0
4. Cu(52.5), Zn(200) Pb(200)	53.0
5. Cu(52.5), Pb(200) Pt(200)	53.5

Table 8. Reproducibility of copper recovery

Copper taken (µg)	Copper found (µg)	Mean (µg)	Std. Dev. %
1. 13.12	12.0, 15.5, 12.5 13.0, 13.0, 14.0	13.33	1.25
2. 26.25	25.0, 26.5, 28.5 29.0, 25.0, 26.0	26.66	1.72
3. 52.50	50.5, 52.5, 53.5 53.5, 50.5, 53.5	52.16	1.32
4. 78.74	80.0, 78.0, 77.5 77.0, 81.0, 80.5	79.0	1.70

Table 9. Comparison of the Present Method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
102.	Diphenylthio-carbazide	4-8	540	5.04×10^4	Pd*, Pb*, Bi*, Borate and nitrite
103.	4-nitroso-resorcinal and pyridines bases	1.5-2.5	365-375	0.71×10^4 0.45×10^4 0.89×10^4 1.06×10^4 0.21×10^4	Hg, Co(II), Pd(II), Fe(III), Zr(IV), SCN, S_2O_3, C_2O_4, EDTA, tartrate, citrate, F and ascorbate.
104.	Pyridine bases and bromide/ Iodide	1.5-2.5 and 0.5-1.5	320-355 and 350-360	2.17×10^3 3.07×10^3 3.23×10^3 2.33×10^3 5.13×10^3 and 2.38×10^3 2.65×10^3 4.28×10^3 4.76×10^3 6.77×10^3	Pd(II), Pt(IV), S_2O_3, EDTA, F, C_2O_4, tartrate, citrate, ascorbate and SCN

Contd..

Table 9 (Contd..)

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
105.	N-(4-hydroxy-3-methoxybenzylidene) hydrazine carbothioamide	11.2	410	1.23×10^4	-
106.	3-thiobenzoyl-1-p-tolyl thiocarbamide		520	1.0×10^4	Co, Ni
	Present method	0.5-3.5	360	1.064×10^4	Fe*, S_2O_3

*masking agents used

REFERENCES

1. Kirov A.I., Golentovskaya I.P. and Vlasov N.A., Zavod. Lab., 1975, 41(5), 523.
2. Vasilev Kh., Karagosov L., Kunev D. and Chimbulev M., God. Vissu. Khim., Tekhnol. Inst, Sofia, 1976, 24(1), 135.
3. Jadhav S.G. and Venkateswarlu C., Indian J. Chem., 1978, 16A(3), 263.
4. Shaulina L.P., Kirrilov A.I., Depposited Doc., 1980, SPSTL 776 Khp-D80, 9.
5. Ravi Kant., Om Prakash, Sanjay Kumar and S.P. Mushran, Proc. Natl. Acad. Sci., India, Sect A, 1981, 51(2), 221-227.
6. Mamzenko Zygmut, Krasiejko Maria, Stec. Judviga; Chem. Anal., 1981, 26 (6), 1051.
7. Gorduva M.N. and Meshcheryakova D.N., Prcbl Sovrem, Anal. Khim., 1981, 3(16).
8. Shen Hanxi, Wang Zhenquing, Huaxue Shiji; 1982, 4(5), 257.
9. Xu. Guanghui, Shen Hanxi, Fenxi Huaxue, 1982, 10(5), 334.
10. Shen Hanxi, Huaxue Shiji, 1982, (2), 79.
11. Wang Huaxue, 1983, 11(4), 291.
12. Xia Daopei, Fenxi Huaxne, 1983, 11(11), 845.
13. Xu. Qiheng, Huaxin Shiji, 1984, 6(3), 191.
14. Pilipenko A.J., Demutskaya L.N., Ryabuskno O.P., Zh. Analkhim. 1984, 39(b), 1081.
15. Li Weiwu, Xi. Gangquing. Dexin, Kuangye. Gongcheng, 1983, 3(3), 48.
16. Xue Guang; Fenxi Huaxue., 1984, 12(10), 928.

17. Ten. Zhe, Wu. Shuisheng; Huaxne Shiji, 1985, 7(6), 319.
18. Zhang Zengrui, Yang Qi, Huaxne Shiji, 1985, 7(6), 311.
19. Li Shaoqing, Guo Tongzhang, Hu. Wengqing, Fenxi Huague, 1986, 14(2), 129-31.
20. Hu. Shouun, Shu. Changhua; Li Qingyi; Cheng Shlin Yin Anzhong, Fenxi Huaxne, 1987, 15(9), 814.
21. Jiang Shufa, Jie Nianquin, Cheng Chuange, Fenxi Huaxne, 1988, 16(3), 236.
22. Chen. Ziruo, Kuangye Gongcheng, 1989, 9(2), 45.
23. Den. Huixiang, Huanjing Wuran Yu Fangzhi, 1989, 11(4), 40.
24. Yang Suqing & Tan. Dahua, Lihua Jianyan, Huaxue Fence, 1989, 25(5), 311-12
25. Hu. Shorkun, Huang Mei, Zeng Zhongzhi, Sichuan Daxue Xuebao, Ziran Kexueban, 1989, 26(3), 336-9.
26. Ishii Hayime, Odashima Tsugikatsu, Kawamonzen Yoshiaki, Bull. Chem. Soc., Jpn., 1990, 63(12), 3405-9.
27. Zhou Nan., Yu. Renqing, Yao. Xuzhang, Fenxi Shiyanshi, 1990, 9(5), 25-6, 44.
28. Paria P.K., Thokdar T.K., Majumdar S.K., J. Indian Chem. Soc., 1990, 67(6), 532.
29. Mo. Weiming, Li Shengyi, Yu. Ximao, Chem. Abst., Vol. 114, No. 13, p. 835.
30. Tang Yangqiang, Chem. Abst., Vol. 114, p. 870.
31. Haddock L.A., Analyst, 59, 163, 1934.
32. T. Moeller, Ind. Eng. Chem., Anal. Ed., 1943, 15, 346.
33. Cheng K.L., Bray R.H. and Meloted S.W., Anal. Chem., 1955, 27, 24.
34. Singh Ajai K. and Singh R.P., Ind. J. Chem., 1977, 15A, pp 257-258.

35. Kotelyanskaya, L.I., Shestidesyanaya N.L., Zh. Anal. Khem, 1978, 33(6), 1095-8.

36. Gorenc D., Kosta L., J. Radio anal. Chem., 1978, 44(2), 279-84.

37. Cano Pavon J.M., Garcia de Tornes A., Pino F., An. Quim., 1978, 74(1), 24-27.

38. Nenova P., Kantcheva D. and Karadakov B., Talanta, 1978, 25(11-12), 691-2.

39. Satake Masatada and Suzuki Tsutomu, Fukui Daigaku Kogakubu Kenkyu Hokoku, 1979, 27(1), 1-10.

40. Mise Teruyoshi, Miyakonoyo Kogyo Koto Semmon Gakko Kenkyu Hokoku, 1980, 14, 73-7.

41. Chang Tao-kun, Chiang Tse-Mei and Kao Li-Chun, Fen Hsi Hua Hsueh, 1978, 6(4) 268-71.

42. Khor'kova M.A., Degtev M.I. and Zhivopistsev V.P., Izv. Vyssh. Uchebn., Zaved., Khim. Khim., Tekhonol., 1981, 24(9), 1102-5.

43. Wang, Zhenpu and Cheng K.L., Talanta, 1982, 29(7), 551-6.

44. Rojas J., Lopez Fernandez J.M. and Valcarcel M., Microchem. J., 1982, 27(3), 445-53.

45. Liu. Shaopu, Liu. Zhongfang, Fenxi, Huaxue, 1982, 10(6), 321-4.

46. Shijo Yoshio, Shimizu Tokuo, Sakai Kaoru., Bull. Chem. Soc., Jpn., 1983, 56(1), 105-7.

47. Chem. Kuochem, Qian. Quizhang, Huaxue Xuebao, 1981, (Zengkan), 120-4.

48. Vakhrysheva L.E. and Sayun M.G., Tsv. Metallurgiya, 1984, 137, 44-6.

49. Serrot F. Bosh, Perez M.J. Sayall, Diaz. Hernandez and Vinuesa J. Manes, Afinidad, 1984, 41(394), 546-8.

50. Agrawal Yadvendra Kand Bhatt Viney J., Analyst (London), 1984, 109(10), 1287-9.

51. Salim Rodi, Suraydeh Bassem, Microchem. J., 1985, 32(1), 83-8.

52. Guseinov I.K., Azerb. Khim. Zn., 1984, (1), 146-52.

53. Shchemeleva G.G., Chechushkova N.E., Bagdasarov K.N and Shelepin N.E., Izv. Vyssh. Uchebn. Zaved, Khim. Khim. Tekhnol, 1985, 28 (10), 41-5.

54. Zhang Rende and Wang Huaigang, Lanzhau Doxue Xuebao, Ziran Kexueban, 1986, 22(2), 71-75.

55. Mulik G.N., Kuchekar S.R., Chavan M.B., Ind. J. Chem., Sect. A, 1986, 25A(II), 1073-4.

56. Presnyak I.S., Antonovich V.P. and Nazarenkov A., Zavod. Lab., 1987, 53(1), 13.

57. Burns D. Thorburn and Tungkananuruk K., Anal. Chim. Acta., 1987, 197, 285-9.

58. Rakhmatullaev K., Giyasov A. Sh. and Zakirov B.G., Uzb. Khim. Zh., 1988, (6), 10-13.

59. Singh Ishwar and Kadyan Pratap Singh, Bull. Chem. Soc., Jpn., 1988, 61(10), 3689-92.

60. Honova Dagmar, Nemcova Irena and Suk Vaclav, Talanta, 1988, 35(10), 803-4.

61. Zuo. Shiyu, Guo. Jingman and Liu. Hong., Yejin Fenni, 1988, 8(1), 18-20.

62. Zhang Guang, Liu Bin and Li. Kejuan, Yejin Fenxi, 1989, 9(2), 43-4.

63. Zhou Nan, Yu. Renqing, Yao. Kuzhang and Lu. Zhiren., Huaxue Shiji, 1990, 12(5), 280-2, 311.

64. Nonova D., Vasibva E. and Mincheva V., God Sofii Univ. 'Kliment Okhridski', Khim. Fak., 1985 (Pub. 1990), 79, 373-98.

65. Sun Xi and Yi Youhang, Yejin Fenxi, 1990, 10(3), 10-12.

66. Yang Dailing, Wang Hon Wei and Yu Ximao, Wuhan Daxue Xuebao, Ziran Kexueban, 1986, (3), 68-72.

67. Hague J.L., Brow E.D. and Bright H.A., J. Research Nath. Standards, 1951, 47, 380; Classen A. and Bastings, L., Z. anal Chem., 1956, 153, 30.

68. Gaher A.R., Anal Chem., 1954, 26, 577.

69. Vogel I., Text book of Quantitative Inorganic Analysis, EIBS, London, 1978.

70. Gordieyff V.A., Analyt. Chem., 1950, 22, 116.

71. Malik Wahid V. and Salahuddin, Ind. J. Chem., 1963, 1, 203-207.

72. Gonzalez Portal, Aurora Bermejo Marinez F., Baluza Santos C., Act. Quim. Compostelena, 1978, 2(2-3), 54.

73. Reddy T., Sreenivasula and Rao S. Brahmaji, Current Science, 1979, 48 (10), 439.

74. Zuchi Gand Rev. Roum. Chim., 1979, 24(3), 497.

75. Kafor O., Emmanuel Chakwuemeka, Talanta, 1980, 27(11A), 887.

76. Kandrae J., Chem. Zvesti, 1980, 34(5), 645-52.

77. Ishidu Ryoei, Tonosaki Koichi, Sci. Rep. Hirosaki Univ., 1980, 27(2), 123-9.

78. Ilyas Q.R. & Joshi A.P., Mikrochim. Acta., 1980, 2(3-4), 263.

79. Varma Yashbir Singh, Barua Sudarshan, Singh Ishwar, Garg Bhagwan Singh, Singh Rajendra Pal, Ann. Chim., 1981, 71(5-6), 343.

80. Zaki M.T.M., Alquasmi R. and Fresenius Z., Anal. Chem., 1981, 306, 5, 400.

81. Anipindi A.R., Jain P. & Singh R.P., J. Chin. Chem., Soc., 1981, 28 (3), 165.

82. Chattopadhyay Partha and Majumdar Santosh Kumar, Ind. J. Chem., 1982, 21A, 857-858.

83. Tyagi Ani., Tyagi R.P., & Joshi B.C., Bull. Inst. Chem. Acad. Sin., 1982, 29, 47.

84. Ma. Zhicheng Rang. Qingxin & Pan Qinyhong, Yankuangeeshi, 1983, 2(1), 61-2, 24.

85. Chen. Bingrong, Fenxi Huaxue, 1983, 11(6), 459-61.

86. Pilipenko A.T., Karetnikova E.A. and Trachevskii V.V., Zh. Anal. Khim., 1983, 38(10), 1787-92.

87. Kandrac J. and Zalo A., Acta. Fac. Rerum-Nat. Univ. Comenianae Chim., 1984, 31, 95-104.

88. Szalo Anton and Kandrac Jan., Fiz. - Khim. Issled. Ravnovesii, V. Rastvorakh, Yaroslavl, 1983, (202), 83-9.

89. Reddy K.V. and Hussain R.C., Curr. Sci., 1984, 53(15), 798-99.

90. Gamberov D.G. and Babaev A.K., Zn. Anal. Khim., 1984, 39(5), 801-3.

91. Sakai Tadao., Ohno Noriko., Tsuruboshigekazu, Tanaka Masaya and Horigome, Analyst (London), 1984, 109(8), 1043-5.

92. Gomez Ariza J.L., Barragan de la Rasa F.J. and Montana Gonzalez M.T., Mikrochim. Acta, 1984, 2(5-6), 407-16.

93. Katami Takeo, Hayakawa Tomokuni, Furukawa Maramichi and Shibata Shozo, Analyst (London), 1984, 109(11), 1511-12.

94. Yesugi Katsuya, Miyawaki Mitsuo and Nagahiro Tohru, Microchem. J., 1985, 32(3), 332-7.

95. Sakai Yukio, Anal. Sci., 1985, 1(4), 373-6.

96. Chakraborti Anil K., Ind. J. Chem., Sect. A., 1986, 25A (9), 886.

97. Rudometkina T.F., Chernova I.B. and Orlov V.V., Zavod Lag, 1987, 53(9), 18-20.

98. Gowda H. Sanke, Ahmed S. Maqbool and Jagadeesh K.S., J. Indian Chem. Soc., 1989, 66(12), 915-7.

99. Alonso Rodriguez Elia., Rermejo Barrera Adela and Bermejo Martinez F., An. Quim, 1990, 86(4), 436-8.

100. Huang Yechu, Yejin Fenxi, 1990, 10(3), 54-5.

101. Bajkin Dubravka P., Perisic-Janjic Nadav and Nikolic Aleksander D., Zb. Rad. Pris-Mat Fak, Univ. Nov., Sadu. Ser. Hem. 1989 (Pub. 1991), 19, 19-24.

102. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Ind. Chem. Soc., 1990, 67, 263-264.

103. Sarkar A., Thokdar T.K., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, LXV, 742-743.

104. Thokdar T.K., Sarkar A., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, LXV, 386-388.

105. Hu. Shcukun, Huang Mei, Zeng Zhongzhi, Sichuan Daxue Xuebao, Ziran Kexueban, 1989, 26(3), 336-9.

106. Ambhore D.M. and Joshi A.P., J. Ind. Chem. Soc., 1991, 68(3), 175-7.