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Indirect Determination of Iodide Using Flame Atomic Absorption Spectrometry

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An indirect atomic absorption spectrometric determination of iodide has been proposed. The method involves the formation of chelate complex, [Cu(bptc)I], where BPTC, Hbptc=2-benzoyl pyridine thiosemicarbazone, within a wide pH range (4.3—8.5), extraction of the complex into butyl acetate solvent and determination of copper signal by flame AAS and hence indirectly determining iodide. The method gave a linear graph upto 10. 4 μg ml^{-1} of iodide with a limit of detection (3σ) value of 47 ng ml^{-1}. The proposed method was free of spectral interferences from large number of metal ions, anions, and organics. Hence it was successfully applied to iodide determination in laboratory chemicals and commercial grade salts.

Iodides are used extensively in the preparation of pharmaceuticals and in photography. Trace amounts of iodide are required by animals and plants. Nevertheless, iodized table salts are now available commercially. In view of this, monitoring of iodide in these samples is necessary. The separation and determination of trace amounts of iodide was reviewed by Williams,$^{1)}$ while spectrophotometric and spectrofluorometric procedures have been summarized by other authors.$^{2,3)}$ The catalytic activity of iodide has been used for its determination.$^{4)}$ Though the sensitivity for the determination of iodide by the X-ray fluorescence technique$^{5)}$ is high, but its instrumentation is costly. Hence routine laboratory analysis of iodide can be performed by indirect atomic absorption spectrometry (AAS).

Since iodide cannot be measured directly by AAS as it has principal atomic resonance lines in the vacuum ultraviolet region, indirect determination of iodide by AAS has been reported by several authors.$^{6-12)}$ The reported methods involve either by precipitation of iodide as AgI and measuring excess Ag ;$^{7)}$ sorption of excess Hg(II) on a cation exchanger and measurement of the mercury (II) complex in the solution ;$^{9)}$ measurement of interfering effect of iodide on Hg(II) signal ;$^{10)}$ extraction of ion pair with tris(1,10-phenanthroline) cadmium(II) into nitrobenzene and measuring cadmium signal,$^{6)}$ or by extraction of ion pair with bis(2,2′-bipyridyl) mercury (II) into ethyl acetate and measurement of the Hg(II) signal by cold vapor AAS.$^{11)}$ The present method proposes to form a chelate complex of iodide and copper (II) with 2-benzoylpyridine thiosemicarbazone (BPTC, Hbptc) and extraction of the complex into butyl acetate, aspiration of the solvent into flame AAS, measurement of the copper signal and hence indirectly relating it to iodide concentration.

Experimental

Reagents and Standard Solutions. Iodide solution (1035 μg ml^{-1} of iodide) was prepared by dissolving potassium iodide (Glaxo, Bombay) in double distilled water and was standardised gravimetrically.$^{13)}$ Working solutions were prepared as required. All other solutions were prepared with doubly distilled water and the chemicals used were of analytical reagent or guaranteed reagent grade, except for the salts to which iodide determination was applied, the specifications been given later.

Pure BPTC (2-benzoylpyridine thiosemicarbazone) was prepared from thiosemicarbazide (Sigma) and 2-benzoylpyridine (Sigma) by the method of De and Guha.$^{14)}$ [Cu(bptc)Cl] was obtained as shiny black crystals by refluxing a mixture of $CuCl_2 \cdot 2H_2O$ (Aldrich) and BPTC in rectified ethanol. A stock solution containing 4000μg ml^{-1} of Cu(II) was obtained in an aqueous medium and was standardised titrimetrically.$^{13)}$

Instrumentation. The atomic absorption measurements were made with a Shimadzu Model AA 646 using the following instrumental conditions : Copper hollow cathode lamp current, 7 mA; wavelength, 324.7 nm; slit width, 0.38 nm; burner height, 4 nm; acetylene flow rate, 2.0 l min^{-1}, and air flow rate, 10 l min^{-1}. Values of pH were measured with a Delta Electronics Model T-MS 30 digital pH meter.

General Procedure. The following solutions were placed in a 100 ml separatory funnel in the order given : 1.0 ml of [Cu(bptc)Cl] solution (about 200 μg ml^{-1} with respect to Cu^{II}), diluted to 10.0 ml with doubly distilled water, 0.5 ml of Na_2HPO_4-citric acid buffer solution of pH 6.5, 1.0 ml to 4.0 ml of sample solution (for the blank, 1.0 ml to 4.0 ml process blank was used accordingly), and 5.0 ml of butyl acetate solvent was added. The mixture was shaken for one min and allowed to stand for five min, in order to establish the extraction equilibrium. The extraction procedure was repeated using 4.0 ml of the solvent. The two organic extracts were combined, and the volume made upto 10.0 ml. Lastly, the absorbance measurements against process blank was done by aspirating the organic phase into an air-acetylene flame of AAS.

Treatment of Samples. Five different salts were investigated for trace iodide in them : Iodized table salt (Tata Chemicals, Bombay), ordinary table salt (Grocer's shop), sodium chloride (E. Merck, Bombay, GR), potassium bromide (Sarabhai, Baroda, GR), and potassium iodate (BDH, England, LR). 2 to 20 g samples (dried previously by hot air at 40°C), according to content of iodide, was taken in a 100 ml beaker and to this was added 40 ml of acetonitrile. The mixture was warmed at 50°C and then cooled. The clear liquid was decanted, and the process was repeated twice using 10 ml of acetonitrile each time. After combining the three portions in a 100 ml beaker, 15 ml of water was added to it and acetonitrile was evaporated over a hot water bath in a fume cupboard. The aqueous part was transferred to a 25 ml volumetric flask and diluted to the mark after adjusting the pH to 6.5.

For the preparation of process blank, the steps described above for sample preparation was followed except that no salt was used.

Results and Discussion

Optimization of Different Parameters. Extraction of the chelate complex [Cu(bptc)I] was found to be maximum over the pH range 4.3 to 8.5. However, the whole work was carried out at pH 6.5 using Na_2HPO_4-citric acid buffer. Several pure solutions and mixed solvent systems were tried as possible extractant of the complex at pH 6.5; the results are summarized in Table 1. As evident from Table 1, the extraction was found to be maximum for both butyl acetate and methyl isobutyl ketone. But methyl isobutyl ketone was avoided due to two reasons: Firstly, the blank value was higher for methyl isobutyl ketone and secondly, thiocyanate did interfere strongly with extraction into methyl isobutyl ketone, when studying for spectral interferences. Variation of the aqueous phase by 1,4-dioxane, ethanol, methanol or acetonitrile was avoided to the greater extent. Because it increases the blank value of the system, as evident from our earlier work.[15]

A shaking time of 1 min and equilibration time of 5 min was sufficient for the maximum extraction to be attained. The stability of the complex was high and was stable in the organic phase for more than a day.

Choice of the Complex System. Indirect atomic absorption spectrometric determination of anions has been found to be most effective when chelate complex or ion pair of the anion is extracted into organic solvent and the solvent aspirated directly into flame AAS. Previous authors[6,11] reported iodide determination via ion pair formation ; we propose the formation of chelate complex with $[Cu(bptc)]^+$ in aqueous phase and extraction into organic phase. Before conforming to this complex, several other Schiff base systems were examined, viz. $[Co(bptc)_2]^+$, $[Ni(bptc)]^+$, $[Co(bpinh)]^{2+}$ (bpinh=2-benzoylpyridine isonicotinoylhydrazone), and other complexes like $[Fe(bpy)_3]^{2+}$ (bpy=2,2'-bipyridyl), $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline). In fact, the stability of the complexes of Schiff bases of 2-benzoylpyridine with metals have been discussed extensively by Dutta and De.[16]

Table 1. Extraction of the Iodide Complex into Various Solvent Systems

Solvent system	Extraction/%
Butyl acetate	97.6
Methyl isobutyl ketone (MIBK)	97.7
Ethyl acetate	64.5
Isopentyl acetate	41.6
Chloroform	28.9
Butyl acetate : MIBK (1 : 1)	23.5
Butyl acetate : isopentyl alcohol (5 : 1)	43.4
Butyl acetate : 1-butanol (6 : 1)	21.7

Mole-ratio method was applied to determine the composition of the extracted complex under the experimental conditions; the ratio of $I^- : [Cu(bptc)]^+$ was found to be 1.19. Hence the extracted species is presumably [Cu(bptc)I].

Analytical Performance. Several cations, anions, and organic compounds were mixed with 50 μg of iodide to form binary mixtures and then the proposed method was applied for iodide determination in those binary mixtures. The results in Table 2 show that the extraction and determination of iodide was possible with an error of ±2%.

Before applying to actual complex matrix systems, the method was applied to iodide determination in synthetic matrices. It was found that 5 μg ml^{-1} of iodide was determinable from these synthetic mixtures within an error of ±2% (Table 3).

The present method gave a linear calibration graph for 0.4 to 10.4 μg ml^{-1} of iodide. The limit of detection (3σ) and limit of quantitation (10σ)[17] values were found to be 47 ng ml^{-1} and 157 ng ml^{-1} respectively. The sensitivity (defined as the slope value of the plot

Table 2. Determination of 50 μg Iodide from Binary Mixtures

Anion	Tolerance limit (μg)	*Error* %	Cation	Tolerance limit (μg)	*Error* %
NO_3^-	5000	−1.92	Mn^{2+}	5000	−1.03
SO_4^{2-}	3000	−1.48	Mg^{2+}	4000	+0.73
F^-	2000	+0.23	Zn^{2+}	3000	−1.23
$Cr_2O_7^{2-}$	2000	+0.65	Cd^{2+}	2500	−1.92
CH_3COO^-	2000	+1.82	Ba^{2+}	2300	−1.48
WO_4^{2-}	2000	−0.86	Co^{2+}	2100	−1.21
Urea	2000	+1.46	Ni^{2+}	2000	−0.22
BrO_3^-	2000	−0.92	Cr^{3+}	1500	−1.03
MoO_4^{2-}	1500	−0.43	Pb^{2+}	1000	−0.54
Oxalate	1500	−0.92	Sb^{3+}	1000	−1.36
PO_4^{3-}	1400	−0.42	Al^{3+}	1000	−1.86
VO_3^-	1300	−0.82	Fe^{2+}	800	−1.94
IO_3^-	1000	+0.46			
S^{2-}	1000	−1.62			
ClO_4^-	500	−0.86			
Cl^-	250	+0.66			
Br^-	250	+0.62			

Table 3. Determination of 50 μg of Iodide in Synthetic Mixtures

Composition (μg)	Error (%)
1. $Mg^{2+}(2000)+Mn^{2+}(5000)+Co^{2+}(5000)$	+1.96
2. $Zn^{2+}(1500)+Ni^{2+}(2000)+Cd^{2+}(2900)$	−0.32
3. $NO_3^-(5000)+IO_3^-(1000)+PO_4^{3-}(1400)$	+0.05
4. $CH_3COO^-(2000)+SO_4^{2-}(1450)+ClO_4^-(500)$	+1.88
5. $S^{2-}(1000)+F^-(1000)+Cr_2O_7^{2-}(500)$	−1.83
6. $Fe^{2+}(500)+Sb^{3+}(250)+Pb^{2+}(500)$	+1.26

Table 4. Determination of Iodide in Table Salt Samples and Laboratory Chemicals

Description of samples	Amount taken	Iodide found (μg/g)		Iodide reported
	g	Present method	Spectrometric method [3]	μg/g
NaCl (Iodized, Tata salt)	20.0	23.88	24.08	15[a]
NaCl (commercial, grocery shop)	20.0	3.15	3.43	—
NaCl (GR, Merck, Bombey)	20.0	13.74	15.78	10[b]
KBr (GR, Sarabhai, Baroda)	2.0	509.02	529.20	500[b]
KIO_3 (LR, BDH, England)	10.0	13.39	13.77	10[b]

a) Guaranteed minimum content as on the label. b) Guaranteed maximum content as on the label.

Table 5. Recovery of Iodide from Various Samples

Sample	Iodide added (μg)	Iodide found (μg)	Recovery (%)
	0.0	20.88	—
NaCl (Tata salt)	40.0	59.80	97.3
	60.0	81.62	100.2
	0.0	40.72	—
KBr	30.0	71.71	101.4
	50.0	90.22	99.0
	0.0	10.71	—
KIO_3	15.0	25.31	97.3
	50.0	60.16	98.9

of absorbance versus iodide concentration) was found to be 14.6 ml μg^{-1} which was better than the methods proposed by De Almeida et al.[7] and Kuldvere.[10] The relative standard deviation (RSD) for 10 determinations of 5 μg ml^{-1} of iodide in commercial sodium chloride (iodized) was found to be 3.2%, and for 10 determinations of the blank, it was 2.5%.

Application. The proposed method was applied for determination of iodide in commercially available table salt, both iodized and noniodized, and to several laboratory chemicals. The procedure adopted for extraction of iodide into acetonitrile medium and then stripping into aqueous phase is based upon the differences in solubilities of chloride, iodate, bromide, and iodide in acetonitrile and water given in literature.[18] This procedure of extracting out iodide from the salts was successful, as evident from recovery studies (Table 5). The amount of iodide found was further verified spectrophotometrically using *o*-tolidine[3] and the results are presented in Table 4. As evident from Table 5, apparent recoveries of 97.3 —101.4% were obtained for the determination of iodide in various samples spiked with 15—60 μg of iodide.

Conclusion. The possibility of the Schiff base [Cu(bptc)I] for routine determination of iodide in table salts and laboratory chemicals has been proposed. The present method is free from interference due to various cations, anions and organic compounds. Since the dry ashing or wet ashing procedures are not suitable for determination of volatile elements like iodine, the solubility difference of the various salts at a particular temperature has been used. Fractional solubilization and crystallization yields the analyte of interest with minimum of other matrix elements being extracted. An examination of Table 4 indicates that the spectrophotometric method[3] always gave higher values of iodide than the present method. This may be attributed to the positive interferences in the latter method caused by chloride and bromide ions. The spectrophotometric method also suffers strong interference due to iron, as it gives precipitate with the spectrophotometric reagent, *o*-tolidine. Thus the present method gives more reliable results than the routinely used spectrophotometric method which has been substantiated by the recovery studies (Table 5).

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