

Spectrophotometric Determination of Iodine Species in Table Salt and Pharmaceutical Preparations

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A sensitive spectrophotometric method for the determination of iodine species like iodide, iodine, iodate and periodate is described. The method involves the oxidation of iodide to ICl_2^- in the presence of iodate and chloride in acidic medium. The formed ICl_2^- bleaches the dye methyl red. The decrease in the intensity of the colour of the dye is measured at 520 nm. Beer's law is obeyed in the concentration range 0—3.5 μg of iodide in an overall volume of 10 ml. The molar absorptivity of the colour system is $1.73 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ with a correlation coefficient of -0.9997 . The relative standard deviation is 3.6% ($n=10$) at 2 μg of iodide. The developed method can be applied to samples containing iodine, iodate and periodate by prereduction to iodide using Zn/H^+ or $\text{NH}_2\text{NH}_2/\text{H}^+$. The effect of interfering ions on the determination is described. The proposed method has been successfully applied for the determination of iodide and iodate in salt samples and iodine in pharmaceutical preparations.

Key words spectrophotometry; iodine species; ICl_2^- ; methyl red

Iodine is an essential micronutrient in human growth and is very important for iodine supplementation metabolism. Deficiency of iodine causes serious delay in neurological development, goiter and hypothyroidism.¹⁾ Table salts are iodized with iodate or iodide to serve as a source of iodine. The iodized salt is recognized as the method of choice and the most successful strategy for the prevention of iodine deficiency disorders. The recommended concentration of iodate in salts is 40 ppm.²⁾ Iodine is an effective germicide for a wide range of microorganisms. Iodine is often used in conjunction with complexing nonionic surfactants or polymers (iodophors) in disinfectants that are used in dairies, laboratories and food processing plants. In addition to this iodine finds applications as dietary supplements, catalysts, pharmaceutical preparations, stabilizers and in photography. Iodine is also used in the production of motor fuels, high purity metals and in cloud seeding. The varied applications of iodine have made the determination of iodine very important.

Several methods of iodine determination have been proposed, including selective electrodes,³⁾ X-ray fluorescence (XRF),⁴⁾ inductively coupled plasma mass spectrometry (ICP-MS).^{5,6)} Trace levels of iodide have been determined by the catalytic effect usually on the cerium(IV)–arsenic(III) reaction.^{7,8)} Other reactions catalyzed or inhibited by iodide have also been described.^{9,10)} Precipitation as silver iodide, dissolution in potassium cyanide, and determination of silver in the complex by atomic absorption spectrometry has been used for the indirect determination of iodide in a flow system.¹¹⁾ Sensitive extraction photometric methods based on ion-pair formation with methylene blue,¹²⁾ or with brilliant green¹³⁾ are well known. Recently methods based on the oxidation of leuco xylene cyanol FF¹⁴⁾ or thionin¹⁵⁾ with iodate are reported. Several spectrophotometric methods have been reported for the determination of periodate and iodate.^{16–20)} El-Shahawi²¹⁾ used the ion-associate of periodate with amiloride hydrochloride for simultaneous spectrophotometric determination of periodate and iodate by liquid–liquid extraction. Most of the reported methods are not sensitive enough or require complicated and expensive instruments.

There is a need for the determination of iodine species in table salts and pharmaceutical samples. The developed method should be sensitive, simple and reliable.

This paper describes a spectrophotometric method for the determination of iodine species like iodide, iodine, iodate and periodate. The method involves the oxidation of iodide to ICl_2^- in the presence of iodate and chloride in acidic medium.²²⁾ The formed ICl_2^- bleaches the dye methyl red. The decrease in the intensity of the colour of the dye is measured at 520 nm. The system obeys Beer's law in the concentration range 0—3.5 μg of iodide in an overall volume of 10 ml. The developed method can be applied directly to samples containing iodide and iodine and after prereduction of iodate and periodate to iodide using Zn/H^+ or $\text{NH}_2\text{NH}_2/\text{H}^+$. The proposed method has been successfully applied to the determination of iodide and iodate in salt samples and iodine in pharmaceutical preparations.

Experimental

Apparatus All absorbance measurements were made using Elico SL 177 scanning spectrophotometer with 1 cm glass cells.

Reagents All reagents were of analytical reagent grade and distilled water was used for preparing all solutions.

A stock solution of iodide (1000 ppm) was prepared by dissolving 0.1307 g of potassium iodide in distilled water and made upto 100 ml in a standard flask. A working solution of 1 $\mu\text{g ml}^{-1}$ was prepared by suitable dilution. A stock solution of iodate (1000 ppm) was prepared by dissolving 0.1223 g of potassium iodate in distilled water and made upto 100 ml in a standard flask. A working solution of 69 $\mu\text{g ml}^{-1}$ was prepared by suitable dilution. A stock solution of periodate (1000 ppm) was prepared by dissolving 0.1205 g of potassium periodate in distilled water and made upto 100 ml in a standard flask. A working solution of 75 $\mu\text{g ml}^{-1}$ was prepared on dilution. Iodate solution (0.04%) was prepared by dissolving 0.040 g of potassium iodate in 100 ml of distilled water. Sodium chloride solution (22%) was prepared by dissolving 22 g of sodium chloride in 100 ml of distilled water. Sulphuric acid (6 M) was prepared by the addition of 166.7 ml of concentrated sulphuric acid (Sp. Gravity 1.84) to 200 ml of distilled water, cooled and diluted to 500 ml. Methyl red solution (0.003%) was prepared by dissolving 0.1 g of methyl red dye in 1 ml of 4.5 N sodium hydroxide and diluting to 100 ml. Ten milliliters of this solution was diluted to 100 ml after acidifying it by adding 0.5 ml of 6 M sulphuric acid. Thirty milliliters of this solution was diluted to 100 ml to obtain 0.003% methyl red. Hydrazine solution (400 ppm) was prepared by dissolving 0.1626 g of hydrazinium sulphate

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in 100 ml of water. Formaldehyde solution (7600 ppm) was prepared by diluting 2 ml of formaldehyde (38%) to 100 ml with water. Suitable aliquot of this solution was diluted to obtain 1000 ppm solution. *p*-Phenylenediamine solution (0.5%) was prepared by dissolving 0.50 g of *p*-phenylenediamine in 5 ml of 6 M sulphuric acid and diluting to 100 ml with distilled water. Bromine solution (600 ppm) was prepared by dissolving 0.2143 g of potassium bromate and 2.143 g of potassium bromide and diluting to 1 l with water. Fifty milliliters of this stock solution was transferred into a 100 ml calibrated flask containing 40 ml of 4.25 M sulphuric acid and diluting to 100 ml with water (300 ppm). This solution was prepared on the day of use. Sulphuric acid (4.25 M) was prepared by adding 59 ml of concentrated sulphuric acid (Sp. Gravity 1.84) to 150 ml of water, cooled and then diluting to 250 ml. Sulphamic acid solution (1000 ppm) was prepared by dissolving 0.1 g of sulphamic acid in 100 ml of water.

Procedure. Calibration Graph To a series of 10 ml calibrated flasks, 3 ml aliquot of the sample containing 0—3.5 μg of iodide, 2 ml of 0.04% iodate, 1 ml of 22% sodium chloride and 1 ml of 6 M sulphuric acid were added. The solutions were mixed well and kept aside for 10 min. One milliliter of 0.003% methyl red was added before diluting to 10 ml with distilled water. The absorbance of the solution was measured at 520 nm against water. The plot of absorbance *versus* concentration of iodine is a straight line with negative slope.

Determination of Iodide in Salt Samples Dissolve 5—10 g of salt sample in 70—80 ml of water taken in a beaker. Filter the sample and dilute it to 100 ml in a calibrated flask. Dilute the sample suitably to get a solution containing 1 $\mu\text{g ml}^{-1}$ of iodide. Three milliliters of the sample containing not more than 3.5 μg of iodide is treated with 2 ml of 0.04% iodate, 1 ml of 22% sodium chloride and 1 ml of 6 M sulphuric acid. The solutions were mixed well and kept aside for 10 min. One milliliter of 0.003% methyl red was added before diluting to 10 ml with distilled water in a calibrated flask. The absorbance of the solution was measured at 520 nm against water. The concentration of iodide is established from the calibration graph.

Determination of Iodate and Periodate Method 1: Reduction of Iodate and Periodate to Iodide Using Zn/H^+ : One milliliter of 69 $\mu\text{g ml}^{-1}$ of iodate or 75 $\mu\text{g ml}^{-1}$ of periodate is added to 25 ml of water taken in a 50 ml beaker. To this 0.2—0.25 g of zinc metal and 1 ml of 6 M sulphuric acid were added and the contents were mixed well and kept aside till the dissolution of zinc. The solution was made upto 50 ml. Each milliliter is equivalent to 1 μg of iodide (Chart 1).

Determination of Iodate in Salt Samples Twenty to twenty-five grams of salt samples containing iodate were dissolved in 70—80 ml water taken in a beaker. Filter the sample and dilute the sample to 100 ml in a calibrated flask. Ten milliliters of the salt solution is added to 15 ml of water taken in a 50 ml beaker. To this 0.2—0.25 g of zinc metal and 1 ml of 6 M sulphuric acid were added and the contents were mixed and kept aside for dissolution of zinc. The solution was made upto 50 ml. To 3 ml of this solution, 2 ml of 0.04% iodate, 1 ml of 22% sodium chloride and 1 ml of 6 M sulphuric acid were added. The contents were mixed well and kept aside for 10 min. One milliliter of 0.003% methyl red was added before diluting to 10 ml with distilled water in a calibrated flask. The absorbance of the solution was measured at 520 nm against distilled water. The concentration of iodide is established from the calibration graph. Concentration of iodate is calculated.

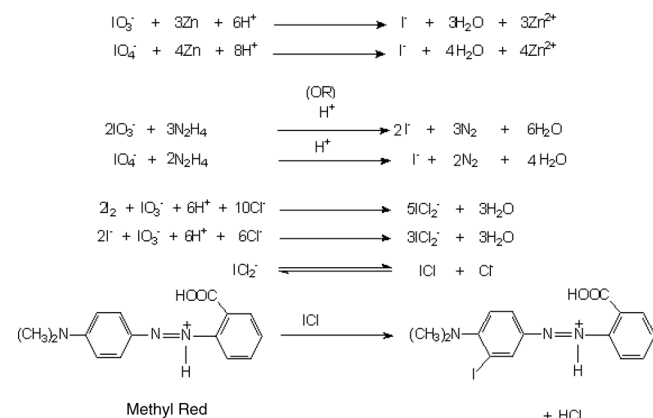


Chart 1. Reaction Scheme

concentration of iodate in 50 ml = concentration of iodide $\times 1.378 \times 50/3$

concentration of periodate in 50 ml = concentration of iodide $\times 1.5 \times 50/3$

Method 2: Reduction of Iodate and Periodate to Iodide Using Hydrazine and Acid: One milliliter of 69 $\mu\text{g ml}^{-1}$ of iodate or 75 $\mu\text{g ml}^{-1}$ of periodate is added to 25 ml of water taken in a 50 calibrated flask. To this 1 ml of 400 ppm hydrazine and 1 ml of 6 M sulphuric acid were added and the contents were mixed well and kept aside for 10 min. One milliliter of 1000 ppm formaldehyde was added mixed well and diluted to 50 ml. Each milliliter is equivalent to 1 μg of iodide (Chart 1).

Determination of Iodate in Salt Samples Twenty to twenty-five grams of salt samples containing iodate were dissolved in 70—80 ml water taken in a beaker. Filter the sample and dilute the sample to 100 ml in a calibrated flask. Ten milliliters of the salt solution is added to 15 ml of water taken in a 50 ml calibrated flask. To this 1 ml of 400 ppm hydrazine and 1 ml of 6 M sulphuric acid were added and the contents were mixed well and kept aside for 10 min. One milliliter of 1000 ppm formaldehyde was added mixed well and diluted to 50 ml. To 3 ml of this solution, 2 ml of 0.04% iodate, 1 ml of 22% sodium chloride and 1 ml of 6 M sulphuric acid were added. The contents were mixed well and kept aside for 10 min. One milliliter of 0.003% methyl red was added before diluting to 10 ml with distilled water in a calibrated flask. The absorbance of the solution was measured at 520 nm against distilled water. The concentration of iodide is established from the calibration graph. The concentration of iodate is calculated.

concentration of iodate in 50 ml = concentration of iodide $\times 1.378 \times 50/3$

concentration of periodate in 50 ml = concentration of iodide $\times 1.5 \times 50/3$

Determination of Iodine in Pharmaceutical Samples Dissolve 0.5 g of iodine containing ointment or dilute 1 ml of iodine containing pharmaceutical preparation to 50 ml. Take 1 ml of the diluted solution and further dilute it to 50 ml in a calibrated flask. Take 3 ml of sample containing not more than 3.5 μg of iodine and analyse it following the procedure recommended under calibration graph. Calculate the concentration of iodine in the sample.

Following the above recommended procedures, analysis of 5 samples containing iodine species can be completed in 60 min.

Results and Discussion

Quantitative bleaching of azo dyes by halogens like chlorine or bromine is widely used for their spectrophotometric determinations.²³⁾ The present method involves the oxidation of iodide to ICl and stabilization as ICl_2^- ($\text{ICl} + \text{Cl}^- \rightleftharpoons \text{ICl}_2^-$) in the presence of iodate and chloride in acid medium. The formed ICl_2^- bleaches the dye methyl red and the decrease in the intensity of the colour is a measure of iodide concentration.

Methyl red, an azodye, shows two absorption bands at 520 nm and 315 nm. The intensity of the band at 315 nm is very weak compared with the band at 520 nm (Fig. 1).

It was observed that with increasing ICl_2^- concentration, absorption decreases for the band at 520 nm whereas it in-

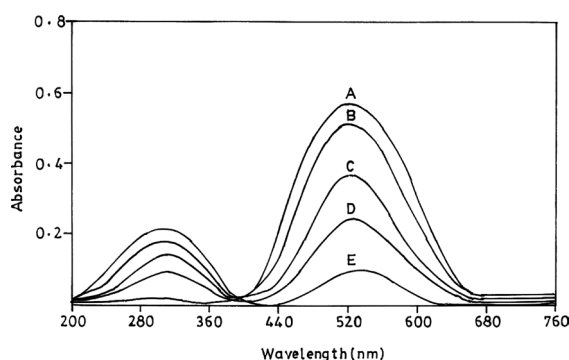


Fig. 1. Absorption Spectra of Methyl Red Measured against Water

A, blank; B, 0.5 μg of iodide; C, 1.5 μg of iodide; D, 2.5 μg of iodide; E, 3.5 μg of iodide.

creased for the band at 315 nm (Fig. 1). The reaction of ICl_2^- with methyl red involves competition between aromatic ring substitution and azo link cleavage resulting in the bleaching of colour at 520 nm. The bleaching of the colour of methyl red by strong oxidizing agents like MnO_4^- , Ce^{4+} and $\text{Cr}_2\text{O}_7^{2-}$ is by oxidative destruction of azo linkage. The proposed scheme of bleaching of methyl red by ICl is similar to the bleaching of colour of methyl orange by chlorine or bromine.²³⁾ In the case of chlorine (stronger oxidizing agent compared to bromine) the bleaching is carried upto 70% by oxidation of azo linkage and 30% by aromatic ring substitution.

In the case of bromine the bleaching of methyl orange is greater than 95% by aromatic ring substitution. This was clearly established by the synthesis and spectral characterization of relevant compounds.²³⁾ ICl is a good iodinating agent compared to iodine.²⁴⁾ Iodination of dyes like dichlorofluorescein and thymol blue with ICl were used for the spectrophotometric determination of ascorbic acid²⁵⁾ and sulphur dioxide.²⁶⁾ Based on this, the major pathway of bleaching of methyl red by ICl is by aromatic ring substitution by iodine (Chart 1). The system obeys Beer's law in the concentration range of 0—3.5 μg of iodide in an overall volume of 10 ml.

Experimental conditions were optimized for the formation of ICl using 2 μg of iodide. The effect of variation of iodate was studied. It was established that a minimum of 1 ml of 0.04% iodate was required for the formation of ICl . Further addition upto 1 ml of 0.12% of iodate showed no change in the formation of ICl for a given concentration of iodide. Hence 2 ml of 0.04% is recommended as optimum concentration.

The amount of chloride required for the reaction was studied. It was found that a minimum of 1 ml of 15% sodium chloride is sufficient for the formation of ICl and stabilization as ICl_2^- . Addition upto 1 ml of 30% sodium chloride showed no change in the formation of ICl with 2 μg of iodide. Hence the use of 1 ml of 22% sodium chloride is recommended.

The effect of variation of acidity required for the reaction was studied. It was established that a minimum of 1 ml of 4 M sulphuric acid is sufficient for the formation of ICl and its stabilization as ICl_2^- . Further addition upto 1 ml of 7 M sulphuric acid showed no change in the formation of ICl . Hence 1 ml of 6 M sulphuric acid is recommended as the optimum concentration of sulphuric acid.

The effect of methyl red concentration required for bleaching by ICl_2^- was studied. One milliliter of 0.003% methyl red solution is recommended as optimum concentration to have maximum absorbance at 520 nm in an overall volume of 10 ml.

Samples containing iodate or periodate require reduction to iodide in acidic medium prior to determination. This was achieved by using zinc and acid or with hydrazine solution. The unreacted hydrazine should be removed prior to the conversion of iodide to ICl with iodate. The effect of excess hydrazine was masked by the addition of 1 ml of 1000 ppm formaldehyde solution. Reduction of iodate or periodate to iodide by both methods gave excellent results. Samples containing iodine can be directly used for its determination like iodide without the reduction step.

Under these conditions the system obeys Beer's law in the

Table 1. Effect of Some Interfering Species in the Iodide Determination (Iodide=2 μg)

Species	Amount tolerated (μg)
Phosphate, oxalate, citrate, tartrate, borate, carbonate, bicarbonate, fluoride, oxalate, sulphate	1000
Br^-	2
Ba(II) , Pb(II) , Mg(II) , Co(II) , Cd(II) , Bi(III) , Ni(II) , Li(I) , Mn(II) , Sr(II) , Cr(III) , NH_4^+	1000
NO_3^-	100
NO_2^-	10
NO_2^- ^{a)}	100
Sulphamic acid	1000
SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$	1
Hydrazine	1
Hydroxylamine	1
Hydrazine ^{b)}	400
Hydroxylamine ^{b)}	400
HCHO	1000
Fe(II)	10
Fe(III)	2
Hg(II) , Cu(II)	5
Glucose, acetone	100

a) Treated with 1 ml of 1000 ppm sulphamic acid solution prior to the addition of iodate to form ICl_2^- . b) Treated with 1 ml of 1000 ppm HCHO solution prior to the addition of iodate to form ICl_2^- .

concentration range 0—3.5 μg of iodide. The detection limit of iodide (3σ) is 0.22 μg in an overall volume of 10 ml. The molar absorptivity of the system was found to be $1.73 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. A calibration graph was obtained with a negative slope and the equation being $Y = -0.1342X + 0.5718$ where Y is the absorbance and X (μg) is the concentration of iodide. The correlation coefficient was -0.9997 and the relative standard deviation was 3.6% ($n=10$) for 2 μg of iodide.

Interferences The interfering effect of anions and cations, which may co-exist with iodide were studied. Any deviation in the absorbance value of ± 0.01 to that obtained in the absence of other interfering ions in iodide determination was taken as a sign of interference. Varying concentration of interfering species were introduced along with 2 μg of iodide and the absorbance values were compared to that in the absence of interference. Tolerance limit of various ions studied in iodide determination are summarized in Table 1.

Hydrazine and hydroxylamine were tolerated upto 400 ppm by the addition of 1000 ppm HCHO prior to the addition of iodate to form ICl_2^- . Nitrite was tolerated upto 100 ppm by treating with 1 ml of 1000 ppm sulphamic acid prior to the addition of iodate to form ICl_2^- .

Applications In order to evaluate the analytical applicability of the proposed method sample of table salts containing iodide or iodate and pharmaceutical preparations containing iodine were analysed. The salt samples from the local market, U.S.A., U.K. and Germany were analyzed. *p*-Phenylenediamine method²⁾ was used as reference method to compare results. The method is based on the oxidation of *p*-phenylenediamine with iodate in acid medium. Tables 2 and 2A show the results obtained for the analysis of iodate in iodized salt from India and Germany by both the proposed and reference method.²⁾ In the reference method, a 10 ml aliquot of sodium chloride solution (25%), 0—5 ml of 80 ppm iodate, 4 ml of 0.5% *p*-phenylenediamine (ppda) in

Table 2. Determination of Iodate in Iodized Salt

Salt sample (Manufacturer)	Manufacturer's claim	Amount of iodate present (ppm) Developed method ^{a)}		Amount of iodate present (ppm) <i>p</i> -Phenylene diamine method ^{b)}	Amount of iodate present (ppm) BIS method ^{c)}
		Zn/H ⁺	NH ₂ NH ₂ /H ⁺		
Annapurna (Hindustan Lever Ltd., Mumbai, India)	Minimum 30 ppm of iodine ≡iodate 41.34 ppm	41.34	39.62	38.40	39.66
		39.62	39.62	41.60	39.13
		38.47	39.04	40.00	40.19
		39.81 ^{d)}	39.43 ^{d)}	40.00 ^{d)}	39.66 ^{d)}
Aashirvaad (ITC Ltd., Kolkata, India)	Minimum 30 ppm of iodine ≡iodate 41.34 ppm	37.34	39.62	41.60	40.72
		41.34	42.20	41.60	40.72
		41.34	40.19	40.00	39.66
		40.01 ^{d)}	40.67 ^{d)}	41.07 ^{d)}	40.37 ^{d)}
Udhayam (GHCL Ltd., Thirupporor, Tamilnadu, India)	Minimum 30 ppm of iodine ≡iodate 41.34 ppm	40.19	39.62	41.60	39.66
		39.04	39.62	40.00	38.60
		39.91	40.19	40.00	40.72
		39.71 ^{d)}	39.81 ^{d)}	40.53 ^{d)}	39.66 ^{d)}
Tata iodized salt (Tata Chemicals Ltd., Mumbai, India)	Greater than 15 ppm of iodine ≡iodate greater than 20.67 ppm	41.05	41.34	40.00	40.77
		40.19	40.48	38.40	40.72
		40.77	40.19	40.00	39.66
		40.67 ^{d)}	40.67 ^{d)}	39.47 ^{d)}	40.72 ^{d)}
i-shakti crystal (Tata Chemicals Ltd., Mumbai, India)	Greater than 15 ppm of iodine ≡iodate greater than 20.67 ppm	40.19	40.19	41.60	42.30
		39.62	40.19	38.40	40.72
		40.38	40.19	40.00	40.72
		40.07 ^{d)}	40.19 ^{d)}	40.00 ^{d)}	41.25 ^{d)}

a) 1 g of the salt sample dissolved in 25 ml of water was subjected to reduction by Zn/H⁺ or NH₂NH₂/H⁺. Volume was made upto 50 ml. 3 ml of this solution was used for the analyses by the proposed method. b) Volume of salt sample used: 10 ml of 25% salt solution. c) 20 g of the salt sample was dissolved in 100 ml. To this solution 10 ml of 10% KI and 5 ml of 2 N sulphuric acid were added. The contents were titrated against 0.05 N sodium thiosulphate solution using starch as indicator. d) Average of three determinations.

Table 2A. Determination of Iodate in Iodized Salt

Salt sample (Manufacturer)	Manufacturer's claim	Amount of iodate present (ppm) Developed method ^{a)}		Amount of iodate present (ppm) <i>p</i> -Phenylene diamine method ^{b)}	Amount of iodate present (ppm) BIS method ^{c)}
		Zn/H ⁺	NH ₂ NH ₂ /H ⁺		
Marken Jodsatz ^{d)} Reines Alpensalz aus Natursole+Fluorid+ Folsaure (Sudsalz GmbH, Ridlerstr. 75, 80339 Munchen)	Iodate 20.4 µg ≡potassium iodate 0.0025%	21.19	21.19	21.67	21.86
		21.01	21.19	21.67	20.40
		21.01	21.01	22.50	21.86
		21.07 ^{d)}	21.13 ^{d)}	21.95 ^{d)}	21.37 ^{d)}
		0.00257%	0.00258%	0.00268%	0.00261%
Altlander ^{e)} Jodsatz mit Fluor (Akzo Nobel Salt bv, Den Niederlanden)	Iodate 20.4—32.5 µg ≡potassium iodate 0.0025—0.0042%	21.70	21.70	20.83	21.87
		21.53	21.53	20.00	21.13
		21.53	21.53	20.00	20.40
		21.59 ^{d)}	21.59 ^{d)}	20.28 ^{d)}	21.13 ^{d)}
		0.00264%	0.00264%	0.00248%	0.00258%

a) 2.5 g of the salt sample dissolved in 25 ml of water was subjected to reduction by Zn/H⁺ or NH₂NH₂/H⁺. Volume was made upto 50 ml. 3 ml of this solution was used for the analyses by the proposed method. b) Volume of salt sample used: 16 ml of a 30% salt solution. c) 20 g of the salt sample was dissolved in 100 ml. To this solution 10 ml of 10% KI and 5 ml of 2 N sulphuric acid were added. The contents were titrated against 0.05 N sodium thiosulphate solution using starch as indicator. d) Marken Jodsatz contain ingredients such as calcium carbonate, magnesium carbonate, sodium fluoride 0.047—0.064% as additives in addition to iodate. e) Altlander Jodsatz contain ingredients such as potassium fluoride 0.065—0.087%, sodium hexacyanoferrate(II)[E535] and silicon dioxide[E551] as additives in addition to iodate. f) Average of three determinations.

sulphuric acid were added. The contents were mixed well and the volume made upto 25 ml with water. The colour developed was measured at 525 nm. A calibration graph was obtained by plotting absorbance *versus* amount of iodate. Salt samples were analysed by the *p*-phenylenediamine (ppda) method by taking 10 ml of 25% salt solution, 6 ml of water, 4 ml of 0.5% ppda solution in sulphuric acid in a 25 ml calibrated flask. The contents were mixed well and the volume was made upto 25 ml. The colour developed was measured at 525 nm. The amount of iodate present in the salt sample was established from the calibration graph. Samples containing

iodide or iodine were converted to iodate using bromine water and removing excess bromine with formic acid.²⁷⁾ The formed iodate was determined by *p*-phenylenediamine (ppda) method.

Table 3 shows the results obtained for the analysis of iodide in iodized salt from U.K. and U.S.A. There is a good agreement between the results obtained by the proposed and reference method.²⁾ Iodophore is a weak complex of iodine and carrier polymer. It has a prolonged microbial action and used as an antiseptic and disinfectant. It is mainly used for cleaning the contaminated wounds, preoperative skin and

disinfection of equipments. Pharmaceutical preparations containing iodine were purchased from the local market and analyzed for iodine content by the proposed and *p*-phenylenediamine (ppda) method. Table 4 shows the results obtained for the analysis of iodine in pharmaceutical preparations.

1. Determination of Iodate in Iodized Salt: a) Salt samples containing iodate from the local market and Germany were analysed by Zn/H^+ and NH_2NH_2/H^+ reduction methods. Salt samples were dissolved in water and made up to known volume. Salt solutions containing insoluble additives such as magnesium carbonate, calcium carbonate and silicon dioxide

Table 3. Determination of Iodide in Iodized Salt

Salt sample (Manufacturer)	Manufacturer's claim	Amount of iodide present ($\mu g/g$) Developed method ^{a)}	Amount of iodide present ($\mu g/g$) <i>p</i> -Phenylene diamine method ^{b)}
Cerebos Extra fine iodized table salt ^{c)} (Cerebos, Middlewich, Chechire, England)	Iodide 8.8 $\mu g/g$ ≡(Potassium Iodide 1150 $\mu g/100 g$)	8.375	8.063
		8.625	8.868
		8.500	8.868
		8.500 ^{e)}	8.600 ^{e)}
Diamond Crystal iodized salt ^{d)} (Cargill Incorporated, Minneapolis, MN-55440)	Iodide 49 $\mu g/g$ ≡(Potassium Iodide 0.0064%)	49.000	49.930
		51.001	48.770
		48.500	49.930
		49.500 ^{e)}	49.540 ^{e)}
		(1111 $\mu g/100 g$) ^{e)}	(1127 $\mu g/100 g$) ^{e)}

a) Volume of sample used: Cerebos salt, 2 ml of 10% salt solution; Diamond Crystal salt, 1 ml of 5% salt solution. b) Volume of sample used: Cerebos salt, 12 ml of 30% salt solution; Diamond Crystal salt, 10 ml of 25% salt solution. c) Cerebos Iodized salt contain ingredients such as magnesium carbonate, sodium hexacyanoferrate(II) as anticaking agents in addition to iodide. d) Diamond Crystal iodized salt contain ingredients such as silicon dioxide, tricalcium phosphate, dextrose and sodium bicarbonate as additives in addition to iodide. e) Average of three determinations.

Table 4. Determination of Iodine in Pharmaceuticals

Sample (Manufacturer)	Manufacturer's claim	Developed method ^{a)}		<i>p</i> -Phenylenediamine method ^{b)}	
		Concentration of iodine in sample (μg)	% of iodine in sample	Concentration of iodine in sample (μg)	% of iodine in sample
Wokadine ointment (Wockhardt Ltd., New Delhi, India)	Available iodine 0.5% w/w	2.975	0.496	98.694	0.494
		2.950	0.492	101.597	0.508
		3.000	0.500	98.694	0.494
			0.496 ^{c)}		0.498 ^{c)}
Betadine solution (G.S. Pharmbutor Pvt. Ltd., Uttarakhand, India)	Available iodine 0.5% w/v	2.975	0.494	101.597	0.508
		2.975	0.496	101.597	0.508
		2.950	0.492	98.694	0.494
			0.494 ^{c)}		0.503 ^{c)}
Betadine ointment (G.S. Pharmbutor Pvt. Ltd., Rajasthan, India)	Available iodine 0.5% w/w	2.950	0.492	98.694	0.494
		2.950	0.492	101.597	0.508
		2.975	0.496	98.694	0.494
			0.493 ^{c)}		0.498 ^{c)}
Collosol iodine oral solution (Solvay Pharma India Limited, Ahmedabad, India)	Available iodine 8 mg/5 ml	2.425	8.082 mg/5 ml	98.694	8.225 mg/5 ml
		2.475	8.250 mg/5 ml	95.791	7.983 mg/5 ml
		2.475	8.250 mg/5 ml	95.791	7.983 mg/5 ml
			8.195 mg/5 ml ^{c)}		8.063 mg/5 ml ^{c)}

a) Wokadine and Betadine ointment (0.5 g of ointment dissolved in 50 ml water, 1 ml of this solution was diluted to 50 ml, 3 ml of this solution was used), Betadine solution (0.5 ml dissolved in 50 ml, 1 ml of this solution diluted to 50 ml, 3 ml of this solution was used.), Collosol iodine oral solution (2.5 ml dissolved in 100 ml of water, 1 ml of this solution was diluted to 50 ml, 3 ml of this solution was used.) b) Wokadine and Betadine ointment (0.5 g of ointment dissolved in 250 ml water, 10 ml of this solution was used), Betadine solution (1 ml dissolved in 250 ml water, 5 ml of this solution was used), Collosol iodine oral solution (2.5 ml dissolved in 250 ml of water, 6 ml of this solution was used). c) Average of three determinations.

were filtered before diluting to known volume. One gram of salt sample from local market and 2.5 g of salt sample from Germany were used for the reduction of iodate to iodide with Zn/H^+ or NH_2NH_2/H^+ . A 3 ml aliquot containing not more than 3.5 μg of iodide was used for the analysis by the proposed method. The results were also compared with the reference method²⁾ and BIS (Bureau of Indian Standards-IS 7224: 1985) method.²⁸⁾ In the BIS method, 20 g of salt sample was dissolved in 100 ml of water, to this 10 ml of 10% potassium iodide solution and 5 ml of 2 N sulphuric acid were added. The liberated iodine was titrated against 0.05 N sodium thiosulphate solution, adding 1 ml of 1% starch solution near the end of titration. The results are summarized in Tables 2 and 2A.

b) Salt samples containing iodide one each from U.K. and U.S.A. was analyzed. Ten grams of the salt sample (Cerebos Extra fine iodized salt from U.K.) and 5 g of the salt sample (Diamond Crystal iodized salt from U.S.A.) were dissolved in 100 ml of water. Suitable aliquot of the salt solution containing not more than 3.5 μg was used to determine the amount of iodide by the proposed method. The results (Table 3) were compared with the *p*-phenylenediamine (ppda) method after oxidation of iodide to iodate with 2 ml of 300 ppm bromine solution. The excess bromine was destroyed by the addition of 1 ml of 85% formic acid.

2. Determination of Iodine in Pharmaceutical Preparations: a) Wokadine ointment: About 0.5 g of the Wokadine ointment was dissolved in 50 ml of water. One milliliter of this solution was diluted to 50 ml. A suitable aliquot containing not more than 3.5 μg of iodine was withdrawn from this solution and analyzed to determine the amount of iodine by the proposed method. The results were compared with the *p*-phenylenediamine (ppda) method after oxidation of iodine to iodate with 2 ml of 300 ppm bromine solution. The excess bromine was destroyed by the addition of 1 ml of 85% formic acid. The results are shown in Table 4.

b) Betadine ointment: About 0.5 g of the Betadine ointment was dissolved in 50 ml of water. One milliliter of this solution was diluted to 50 ml. A suitable aliquot containing not more than 3.5 μg of iodine was withdrawn from this solution and analyzed to determine the amount of iodine by the proposed method. The results were compared with the *p*-phenylenediamine (ppda) method after oxidation of iodine to iodate with 2 ml of 300 ppm bromine solution. The excess bromine was destroyed by the addition of 1 ml of 85% formic acid. The results are tabulated in Table 4.

c) Betadine solution: One milliliter of Betadine solution was diluted with 50 ml of water. One milliliter of this solution was diluted to 50 ml. A suitable aliquot of iodine containing not more than 3.5 μg was withdrawn from this solution and analyzed to determine iodine by the proposed method. The results were compared with the *p*-phenylenediamine (ppda) method after oxidation of iodine to iodate with 2 ml of 300 ppm bromine solution. The excess bromine was destroyed by the addition of 1 ml of 85% formic acid. The results are shown in Table 4.

d) Collosol: Collosol solution 2.5 ml was diluted with 100 ml of water. One milliliter of this solution was diluted to 50 ml. A suitable aliquot containing not more than 3.5 μg of iodine was withdrawn from this solution and analyzed to determine iodine by the proposed method. The results were compared with the *p*-phenylenediamine (ppda) method after oxidation of iodine to iodate with 2 ml of 300 ppm bromine solution. The excess bromine was destroyed by the addition of 1 ml of 85% formic acid. The results are shown in Table 4.

Conclusion

The developed method is simple, precise and sensitive for the determination of iodine species like iodide, iodine, iodate or periodate. The system obeys Beer's law in the concentration range of 0–3.5 μg of iodide in an overall volume of 10 ml with the molar absorptivity of $1.73 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. The developed method is more sensitive compared to the spectrophotometric methods based on the oxidation of leuco xylene cyanol FF¹⁴) ($\epsilon = 1.7 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and thionin¹⁵) ($\epsilon = 2.7 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) with iodate. The molar absorptivity of the developed method is comparable to the extraction method based on the ion pair with brilliant green¹³) ($\epsilon = 3.0 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) or methylene blue¹²) ($\epsilon = 3.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). The application of proposed method to the determination of iodide and iodate in salt sam-

ples and iodine in pharmaceutical preparations demonstrate the utility of the method to serve as alternate to the existing methods.

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