A New Method of Spectrophotometric Determination of Iodine in Natural Waters

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Introduction

Because no appropriate method is available for the determination of a small amount of iodine found in ordinary natural waters, the determination of this element has been limited to special kinds of water which are iodine-rich. In order to fill this lack, the present method was established.

The characteristics of this method are the following:

1) By the use of silver nitrate solution, together with a large amount of silver chloride, iodide ions are precipitated as silver iodide and are completely gathered into the chloride precipitate.

2) The precipitated iodide is converted into iodate by bromine. Then the reaction between the iodate and cadmium iodide liberates the iodine, in a quantity six times that of the original sample. Thus the minimum amount of determinable iodide is lowered to one-sixth.

3) Finally, the liberated iodine is determined spectrophotometrically as starch-iodine-chromogen. Thus 0.2 μg. of iodine can be determined with an error of only ±5%.

Analytical Method

Reagents

1) Sodium chloride solution, about 0.1 N, free from iodine.

The addition of a small amount of silver nitrate solution can remove any trace of iodine in the form of silver iodide involved in a large amount of silver chloride.

2) Silver nitrate solution, about 0.1 N.

3) Sulfuric acid, about 3 N.

4) 1/2 M acetate buffer with pH 2.8 saturated with bromine.

1000 parts of 1/2 M acetic acid are mixed with 20 parts of 1/2 M sodium acetate. A suitable amount of bromine is added.

5) Cadmium iodide solution, about 5%.

Cadmium iodide crystals are dissolved in distilled water and boiled for five minutes before they are stored in a brown glass bottle.

6) Starch solution, about 0.5%.

After being prepared in the usual way, the solution is put to centrifuge at 3000 r.p.m. for ten minutes. Then it is filtered through a filter paper of fine texture.

7) Sodium acetate solution, about 25%.

8) Sodium sulfite solution, about 1%.

Procedure

1) Take a suitable amount of sample, usually

3—5 litres, depending upon the iodine content, filter it through a piece of absorbent cotton previously washed with 3 N hot hydrochloric acid and distilled water. And a sufficient amount of 0.1 N sodium chloride solution to the filtrate to adjust the chloride concentration to about 15 mg. per litre. While vigorously stirring, add an amount of silver nitrate solution equivalent to the chloride. After the silver chloride is completely precipitated, add 3 N sulfuric acid in the proportion of 1 ml. to 1 litre of the solution. Allow the solution to stand in a dark place for about twenty hours. After the precipitate has completely settled, the supernatant is siphoned off and the remaining precipitate is transferred to a small beaker (50 ml.). Rinse the precipitate with distilled water several times and pour the washings on a filter paper so that any suspended precipitate will be collected on it. Transfer the collected precipitate with a small amount of water back into the original beaker.

2) To the content of the beaker, add 2 ml. of 0.1 N sodium chloride solution and then and 10 ml. of 1/2 M acetate buffer previously saturated with bromine. Dilute the total volume with distilled water to about 25 ml. Stir and allow it to stand for one hour at a temperature below 20°C with occasional stirring. At this step, the iodine is completely oxidized into iodate.

3) Warm the beaker on a boiling water bath until excess bromine is expelled and the solution turns pale yellow. After cooling by tap water, filter the liquid through a small filter paper of fine texture. Wash the residue on the filter paper three times with small portions of distilled water. Gather the filtrate and washings into a 50 ml. beaker.

4) Warm the beaker on a boiling water bath until all trace of bromine is expelled and the solution is colorless. Leaving it to cool to room temperature, add 0.2 ml. of 1% sodium sulfite solution to remove any bromous acid which might have been formed during the above oxidation process.

5) Add 10 ml. of 1/2 M acetate buffer and keep the solution at a temperature below 20°C. Oxidation is complete within thirty minutes. Evaporate the solution on a boiling water bath to a volume of about 10 ml.

6) Cool and transfer the solution into a 25 ml. measuring flask of brown glass. Dilute the solution to about 20 ml. And 1 ml. of 0.5% starch solution and cool by tap water for five minutes. Then add 1 ml. of cadmium iodide solution, shake vigorously, and allow it to stand for fifteen minutes until a deep blue color fully develops. Adjust the pH to 4.2 by the addition of 0.3 ml. of 25% sodium acetate solution. After filling distilled water to the mark, the contents of the flask is mixed well.

The optical density of the solution is determined spectrophotometrically, using a wavelength of 580 mμ.

Discussion

1) The usual evaporation method[1] for iodine enrichment has many tedious dfficulties which are accompanied by unavoidable loss in iodine and by contamination with other interfering elements. The proposed silver iodide method is absolutely free from such difficulties and moreover, gives a result of 100% accuracy for a tenth mg. of iodine from a sample of 3–5 litres as will be shown later. The addition of sulfuric acid perfects the coagulation of silver iodide.

2) The idea introducing the iodide-bromine reaction for minimizing the least determinable iodine to one-sixth, originally occurred to H. Ballczo[2] who recommended that the oxidation of iodide by bromine be carried out at pH 4.3. The authors obtained a satisfactory result when steps from the iodide oxidation by bromine up to the addition of starch solution and cadmium iodide are processed at pH 2.8 and then the pH is adjusted to 4.2 for colorimetry.

3) In some cases samples are left for a long time without further treatment after silver nitrate solution was added, when some amount of metallic silver may be produced due to photochemical decomposition. This silver reacts with bromine at a later step by the following equation

$$Ag^+ + Br_2 + H_2O = HBrO + AgBr + H^+$$

with the production of hypobromous acid. This hypobromous acid liberates iodine in the cadmium iodide treatment, causing a considerable error in the final colorimetry. The treatment by sodium sulfite is naturally given whereby hypobromous acid and iodate are reduced to bromide and iodide. Thus in the second oxidative treatment by bromine, iodate alone is produced.

4) For the liberation of iodine, cadmium iodide was preferred to the potassium iodide currently used[3,4] because the latter compound tends in an acid medium to liberate iodine even in the absence of iodate, thus causing a considerable error in the precise determination at which the authors are aiming.

Cadmium iodide solution keeps for at least two months without any liberation of iodine when it is stored in a brown glass bottle after being boiled for five minutes.

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[1] American Public Health Association, "Standard Methods for the Examination of Water and Sewage", New York, (1946), 9th Ed., p. 47.

[2] H. Ballczo und G. Mondl, *Mikrochem. ver. Mikrochim. Acta*, 39, 247 (1952).

[3] W. G. Gross, L. K. Wood and J. S. McHargue, *Anal. Chem.*, 20, 900 (1948).

[4] F. G. Houston, *Anal. Chem.*, 22, 493 (1950),

5) Starch-iodine-chromogen gives a maximum absorption at a wave length of 580 mμ. (See Fig. 1) and strictly obeys the Beer's law covering a range of 0.00–120 μg. of iodine.

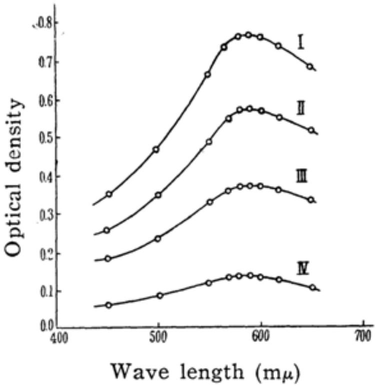

Fig. 1. Absorption curves.
I: 100 μg. of I in 25 cc.
II: 75 μg. of I in 25 cc.
III: 50 μg. of I in 25 cc.
IV: 20 μg. of I in 25 cc.

When the authors use Coleman Model 14 Universal Spectrophotometer with an accessory "round cuvette" of an effective cell thickness 13.06 mm., the following relation holds:

$$X=\frac{E-0.006}{0.0074},$$

where X is the amount of iodine in 25 ml. and E is the optical density for 580 mμ.

The amount of iodine in the original sample can be calculated by dividing X by 6[5].

Starch species and temperature affect somewhat the standard curve. Therefore, the curve sometimes should be constructed for several starch species and at various temperatures (See Fig. 2).

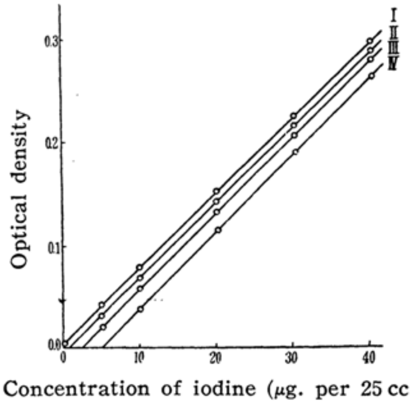

Fig. 2. Effect of temperature on color intensity at a wavelength of 580 mμ.
I: at 10–20°C III: at 25°C
II: at 23°C IV: at 28°C

The color undergoes no measurable change for at least two hours if the pH of the solution is adjusted to 4.2 after the color developed at pH 2.8. Fig. 3 shows the effect of pH on the rate of color development.

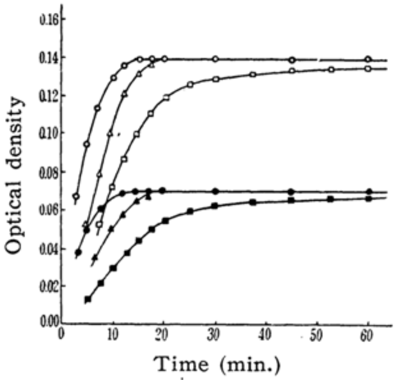

Fig. 3. Fffects of pH on rate of color development at a wave length of 580 mμ.
—○— pH: 2.8 —○— 20 μg. of I in 25 cc.
—△— pH: 3.6
—□— pH: 4.2 —●— 10 μg. of I in 25 cc.

6) Among common elements in ordinary natural waters, chloride, bromide, nitrate and sulfate cause interference which at least is not up to the concentrations 200, 10, 30 and 30 mg., respectively.

TABLE I

ACCURACY OF THE METHOD

Cl added mg.	I used μg.	I found μg.	Error %
17.5	0.00	0.00	—
17.5	0.20	0.19	−5.0
17.5	0.20	0.20	0.0
17.5	0.20	0.21	+5.0
17.5	0.99	0.95	−4.0
17.5	0.99	0.96	−3.0
17.5	0.99	1.03	+4.0
17.5	1.98	1.95	−1.5
17.5	1.98	1.91	−3.5
17.5	1.98	1.99	+0.9
17.5	4.95	4.99	+0.8
17.5	4.95	4.92	−0.6
17.5	4.95	4.98	+0.6

7) The accuracy of the proposed method was tested using various amounts of a standard solution of potassium iodide. Table I gives the result.

The fact that the oxidation of silver iodide is complete was also shown by the following experiment: Various amounts of the standard solution of potassium iodide were similarly processed and the iodine liberated at pH 2.8.

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[5] L.W. Andrews, *J. Am. Chem. Soc.*, 25, 756 (1903).

was determined using standard solution of thiosulfate. Table II shows the result.

TABLE II

OXIDATION OF SILVER IODIDE BY BROMINE*

Cl added mg.	I used mg.	I found mg.	Recovered %
35.5	0.00	0.00	—
35.5	0.19	0.19_2	101.0
35.5	0.19	0.19	100.0
35.5	0.19	0.19_1	100.5
35.5	0.39	0.39	100.0
35.5	0.39	0.38_9	99.7
35.5	0.39	0.38_9	99.7
35.5	0.49	0.49_1	100.0
35.5	0.49	0.48_6	99.2
35.5	0.49	0.48_6	99.2
35.5	0.49	0.48_9	100.0

* Determination was carried out volumetrically.

Table III shows examples of the result from natural waters to which the present method was applied.

TABLE III

EXAMPLES OF ANALYSIS

Description	Sample taken 1.	I found μg./1.	Cl found mg./1.
Rain water collected at Higashiyama area, Nagoya City (June, 1954)	4.0	0.9_0	0·18
	4.0	1.3_1	0.89
	2.0	1.1_5	0.58
	2.0	1.0_5	0.36
Ground water from a well in the campus of Nagoya University (June, 1953)	5.0	0.8_5	3.83
Surface water of Lake Biwa-ko, Shiga Prefe- (Oct., 1953)	5.0	1.3	4.69
Surface water of Lake Gongen-ike, Mt. Norikura, Gifu Prefecture (Sept., 1953)	10.0	0.2	0.13
A spring water from Higashiyama area, Nagoya City (Aug., 1954)	3.0	2.2	5.58

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