A Quantitative Method for Determination of Iodine.

By

Arao Itano, Ph. D.

[November 4, 1933.]

On account of the physiological significance attached to iodine, there are numerous reports on the method for its determination. However to find a method which is satisfactorily applicable for a certain purpose, it is rather difficult. Previous to an investigation to determine the iodine content of agar, several methods which have been reported lately viz: McClendon[1], Andrew[2], Fellenberg[3] and McHargue[4] were examined carefully as to their applicability, and finally decided to use the closed combustion method of McClendon, and that of McHargue with certain modifications. The method thus developed gives so satisfactory results that it is reported in detail in this paper.

Experimental Procedure.

First the standard solution of potassium iodide with and without an addition of filter paper as an organic matter, was analysed by three different methods noted in Table I, and obtained the following results:

Table I.

Determination of Iodine in the KI Standard Solution.

Methods used.	Iodine (mg.) in sample and treatment.	Iodine recovered. (mg.)	Iodine recovered. %
McClendon.	0.100 Iodine.	0.081	81
	0.100 „	0.081	81
	0.100 „ + 1 g. filter paper.	0.061	61
	ibid.	0.058	58
Andrew.	0.100 Iodine. + 2 g. filter paper.	0.057	57
	ibid.	0.051	51
Fellenberg.	0.100 Iodine. + 2 g. filter paper.	0.058	58
	ibid.	0.065	65

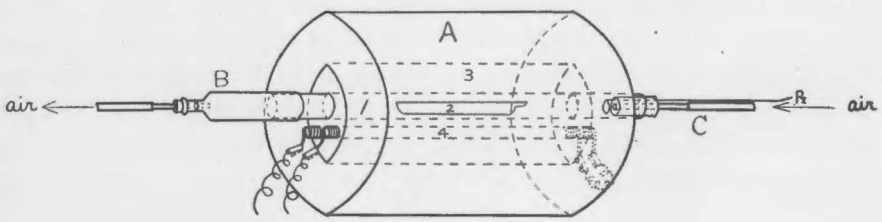
From these results, it may be noted that better results were obtained by the closed combustion method after McCLENDON than the others although some loss occured even in this method especially so where the organic matter is present. Other two open combustion methods were unsatisfactory altogether. Consequently a closed combustion method recently reported by McHARGUE and his co-workers with certain modifications was tried, as described below:

Apparatus used:

The set up of apparatus is shown in photograph (Plate III) and the inside of the furnace is shown by drawing (Figure I). The detail description of the entire apparatus is given below:

Fig. I.

Inside View of the Electric Furnace.



A. Electric furnace of which detail is shown in the drawing (Figure I).
   1. quartz tube, 3 cm. inside diameter, 0.4 cm. thick and 50 cm. long.
   2. quartz boat, 1.5 wide × 10 long × 1 cm. deep.
   3. earthen sleeve.
   4. 'Silit' heating unit, A. C.; p. v. 99—101.5; s. v. 108—181; 7.08—8.4 amp.

B. Hard glass tubing, attached to the quartz tube with gypsum paste.

C. Rubber stopper with a glass tubing; the rubber stopper is protected with asbestus and mica on the inside portion, and also the rubber stopper is covered with the cheese cloth of which end is kept immersed in water in flask so that the stopper is kept wet by the capillary water. Pt—a good size platinum wire is inserted through the stopper by which the quartz boat is pushed inward.

D. Smoke screen[5] which is made of two funnels put together inserting two sheets of filter paper between them and sealed with paraffine of high melting point round the edge. This is to prevent the black smoke arising by the combustion of organic matter through a series of absorbing bottles.

E_1, E_2, E_3 and E_4. The absorption bottles for iodine, each containing the calcium hydroxide suspension [0.5–0.7 g. $Ca(OH_2)$ in 150–200 cc. water.]. E_4 is placed on the right side to prevent the back fire when a sudden combustion may take place.

F. The wash bottle containing 5% KOH solution to catch any iodine which may come with the air current.
G. Cooling arrangement.
H. and I. Pyrometer.
J. Transformer.

Manipulation of Apparatus.

1. The sample is air dried and powdered, and a known quantity is placed in the boat.
2. Heat the furnace so that the temperature inside the quartz tube reaches 1,100°C.
3. Attach B to the quartz tube with gypsum paste, connect E_1, E_2 and E_3; start the suction pump.
4. Place the boat with the sample at the right end of the quartz tube, then put the stopper C in place which carries a good size platinum wire pusher, and connect E_4 and F.
5. Let the sample remain in the place for a few minutes so that the moisture evaporates, and push the boat in slowly toward the centre of the quartz tube by means of the platinum wire, then plug up any space left with the gypsum paste.
6. Apply suction strongly so that a continuous stream of air bubbles come through F.
7. Stop the combustion after one hour and thirty minutes for the agar but two hours are allowed for the soil.
8. On completion of the combustion, stop the suction pump, take off B and C. Transfer the content of E_1, E_2, E_3 and E_4 into a litre beaker and wash them thoroughly with hot water. B and C are well washed and also D of which the filter paper is cut up into pieces and thrown into the beaker. The boat and the quartz tube are not washed since the temperature is so high that no iodine remains behind.[4)]
9. The solution thus obtained in the beaker is boiled for thirty minutes and filtered, washing the precipitate thoroughly with boiling water; the filtrate is evaporated down to dryness in evaporating dish on the water bath. On evaporation, the precipitate of calcium carbonate is formed so that it should be carefully washed with 95% alcohol and warm water alternatingly three times to extract the iodine completely. Further the concentrated solution is transfered to a platinum dish* of 50 cc. capacity and 1 cc. of 80% K_2CO_3 is added, and evaporated to dryness again on the water bath. The dried residue in the platinum dish is covered with a watch glass and is subjected to heating for

* Unless the platinum dish is used at this stage, it was found that a great loss of iodine takes place.

20—30 seconds until the bottom of the dish becomes dull red in order to eliminate some organic matter which might have remained and may interfere with the determination. The residue in the dish is taken up with a small amount of boiling water and placed on a filter and washed several times with boiling water, and the filtrate is used for the iodine determination.

Finally to determine iodine quantitatively, generally the colorimetric or the titration methods is used. In this case, the colorimetric method is used where the iodine content is seemingly more than 0.05 mg. and the titration method is used where the content is less since the latter is better adopted for determination of a minute quantity.

The description of both the colorimetric and titration methods are given below:

The Colorimetric Method.[6]

Reagents used: (MERCK's)

(a) Sulfuric acid solution.—(10 per cent.)
(b) Sodium nitrite.—(1 per cent.)
(c) Carbon bisulfide.—CS_2.
(d) Potassium iodide.—(1 cc. = 0.1 mg. I.)

Determination:

The last filtrate is transfered to 50 cc. separatory funnel and acidified to P_H 3.0 controlled with Brom-phenol-blue paper, by adding (a); then 1 cc. of (b) is added and shaken up so that the iodine is freed; 1—2 cc. of (c) is added and shaken vigorously for 2 minutes so that the iodine is transfered into CS_2, and CS_2 with iodine is separated into a small separatory funnel. The CS_2 portion thus separated often contain some foreign matter which must be excluded by a micro-centrifuge. The clear portion is used for comparison of color against the standard KI solution (d) which has been treated in the same manner as the sample, through the micro-colorimeter.

The Volumetric Method.[7]

Reagents used: (MERCK's)

(a) Sulfuric acid solution.—(N/5.)
(b) Methyl orange solution.—(0.01 per cent.)
(c) Bromine water.—(fresh.)
(d) Potassium iodide.—(1% solution, freshly prepared just before used.)
(e) Sodium hyposulfite.—(N/1,000 standardized against N/1,000 Potassium iodate: 1 cc. = 0.0001269 g. I.)
(f) Starch solution.—(1 per cent.)
(g) Porcelain ware, broken pieces, washed in acid and alkali alternatingly and dried.

Determination :

After the sample is concentrated to 5—10 cc., it is transfered into 30 cc. Erlenmeyer flask, neutralize its reaction with (a) using (b) as the indicator, and add 0.5 cc. of (a) in excess to acidify ; 3—4 drops of (c) are added and shaken up which produces dark orange color ; boil the content on the sand bath with some (g) added, until the orange color disappears, then kept boiling for two minutes after that and cool the content in cold water immediately ; then 0.2 cc. (d) and a drop of (f) are added and titrate with (e) until the blue color disappears.

In the volumetric method, certain precautions should be taken against such factors which may influence the results as concentration of acid, potassium iodate, residue of bromine water and the loss may occur during boiling.

Standardization of Method :

With the foregoing methods, the following tests were made and obtained the results given in Table II :

Table II.

Standardization of Method for Iodine Determination.

No.	Organic Iodine.	Iodine added.	Iodine recovered.	Difference.	Iodine recovered.
	(mg.)	(mg.)	(mg.)	(mg.)	%
1.	—	0.1	0.0990	0.0010	99.0
2.	—	„	0.0971	0.0029	97.1
Average.	—	0.1	0.0980	0.0020	98.0
3.	0.1219 (0.2 g. seaweed.)	0.1	0.2151	0.0068	96.9
4.	„	„	0.2127	0.0092	95.9
Average.	0.1219	0.1	0.2139	0.0080	96.3
5.	—	0.05	0.0490	0.0010	98.0
6.	—	„	0.0476	0.0023	95.3
Average.	—	0.05	0·0483	0.0017	96.6
7.	0.1219 (0.2 g. seaweed.)	0.05	0.1666	0.0053	96.9
8.	„	„	0.1649	0.0070	95.9
Average.	0.1219	0.05	0.1657	0.0062	96.3
9.	—	0.01	0.00923	0.00077	92.3
10.	—	„	0.00961	0.00039	96.1
Average.	—	0.01	0.00942	0.00058	94.2
11.	0.1219 (0.2 g. seaweed.)	0.01	0.1282	0.0037	97.1
12.	„	„	0.1250	0.0069	94.7
Average.	0.1219	0.01	0.1266	0.1266	96.0

Note: No. 1—8 inclusive were determined by the aid of colorimetric and No. 9—12 inclusive, by the titration method at the last stage.

Table II indicates that the error increases with the amount of iodine decreases. But where 0.01—0.2 mg. iodine present, very satisfactory results were obtained as a whole. The accuracy of method lies between 94.2—99.0 per cent depending upon the amount of iodine and also the organic matter present in the sample.

Summary.

1.) A quantitative method for iodine determination based on McCLENDON's, and McHARGUE's closed combustion method with certain modifications was devised.

2.) The accuracy of the method is 94.0—99.0 per cent depending upon the amount of iodine and also the organic matter present.

3.) The minimum quantity of iodine which can be determined by this method is 1×10^{-8} g.

The author wishes to acknowledge with thanks the assistance given by Mr. Y. TSUJI of this laboratory, and also kind accommodations rendered by Shimadzu Seisakusho, Kyoto where the apparatus was manufactured.

Literature.

1.) McCLENDON, J. F., A System of Microchemical Analysis, p. 2—3, 1932.
2.) ANDREW, R. L., Analyst, 55: 269, 1930.
3.) FELLENBERG, von T., Biochem. Z. 152: 116, 1924.
4.) McHARGUE, J. S., YOUNG, D. W. and ROY, W. R., J. Ind. Eng. Chem., Analytical edition 4: 214—216, 1932.
5.) WEBER, H. C., J. Ind. Eng. Chem., 16, 1239, 1924.
6.) A. O. A. C., 3rd Edition, 9, 1930.
7.) ALLOT, E. N., DAUPHINEE, J. A. and HURTLEY, W. H., Biochem. J. 26, No. 5, 1932: BAUMANN, E. J. and METZGER, N. J., Biological Chem., 98: 405—416, 1932.

PLATE III.

The Photograph of the Apparatus used.