A New Micro-analytical Method for Iodine.

By

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In the determination of iodine, it is essential to destroy completely the organic components in a sample without loosing iodine especially when the amount of iodine present is very minute. Previously an electric closed combustion method[1] was reported from our laboratory, which was later found that the method is very expensive consuming a great quantity of electric current and also it is difficult to control the rise of temperature locally to destroy a large amount of organic components fractionally and satisfactorily, and also it produces so much black smoke in the course of combustion that necessiates the smoke screen, as described in the previous report, which should be treated carefully later for the extraction of iodine sustained by it. Further it is difficult to prevent the black soot remain attached to the inside of the quartz combustion tube. In view of these difficulties involved in the previous method, the senior author devised a new method and developed by his co-workers, as shown in Plate VIII, Fig. 1 and 2, and which is applicable for the plant and animal materials, rich with organic matter and containing a minute amount of iodine. The description of method together with some analytical results are presented as follows :

1. Description of Apparatus :

A. — Gas combustion furnace,—
The furnace is made of a piece of asbestus cement chimney (9 cm. diameter and 45 cm. long) of which the upper and lower sides are cut open 1 cm. and 2 cm. wide longitudinally respectively so that the gas flame burns through the opening and heat the quartz combustion tube (3 cm. × 50 cm. and 0.4 cm. thick) which is placed inside of the chimney and held by means of the metal collars at both ends.

B. — A small quartz tube (1 cm. × 40 cm. and 0.15 cm. thick) through which a fine platinum wire, consists of several funnel like coils, is placed as shown in Plate VIII, Fig. 2.

C. — A piece a small quartz tube as B of 15 cm. long which can be removed for washing.

D. — Electric resistance (15 Ω adjustable).

E & F. — Nickel joints which connects A, B and C.

G. — Hard glass tube specially made to connect the combustion tube with absorption bottle a_3, and the joint is sealed with plaster.

a_1, a_2 and a_3 — The absorption bottles for iodine, of which size is 150 cc. except a_3 being 80 cc. and placed there to catch any smoke which may escape backward otherwise.

H.— A wash bottle with saturated K_2CO_3 to eliminate iodine which might come from air.

I. — A suction flask to which a water pump is connected.

2. Procedure :

a.) Treatment of samples,— the plant materials such as stems, leaves and roots are dried and powdered ; the grains and seeds are subjected to the analysis directly ; the animal matter is liquefied by means of sodium hydroxide, and acidified with sulfuric acid to slight acid under cooling. The sample thus treated is placed in three porcelain boats which are transported into the combustion tube, as in Plate VIII, Fig. 2.

b.) Sixty cubic centimeters of K_2CO_3 solution (60 cc. H_2O + 3 cc. of 10 % K_2CO_3 generally) are placed into a_1 and a_2 ; 30 cc. of water with a small quantity of 10 % K_2CO_3 are placed in a_5. These absorption bottles are connected up respectively as shown in Plate VIII, Fig. 1, and all the joints are sealed up with Plaster of Paris and the same with E and F.

c.) Next the suction by means of a water pump is applied to eliminate the air in the system ; the electric current is passed thru B having it red-heated ; light the burner at E in full and the combustion tube is heated with small gas flame for the first 30 minutes so that a larger portion of organic materials is carbonized, then gradually more heat is applied and as a rule the combustion begins within half an hour. It is necessary to burn the sample gradually since too rapid combustion sends the black smoke over into the absorption bottles which gives trouble for the determination ; heating at E may be eliminated after the combustion is completed in A because no smoke remains smeared there then ; also the electric current passing thru B may be reduced as the combustion in A advances. The time for combustion varies somewhat according to the nature of sample but about 30 minutes are sufficient in most cases. After the combustion is completed which can be judged looking at the sample thru G, the heating is stopped, gas and electric, but the suction is continued for five minutes longer. Then C, a_1, a_2 and a_3 are taken away and the contents are washed very carefully into 500 cc. volume beaker with hot water, evaporated over the hot water bath into a small volume, 40 cc. or so ; transferred to 50 cc. platinum dish and evaporated to solid on a steam bath ; the platinum dish is then placed in a dry oven at 150°C. for 20 to 30 minutes to assure complete dryness ; cover the platinum dish with a watch glass and is subjected at 500°C. heating for 2 minutes to burn up any trace of organic matter might have still remained ; dissolve the remaining ash in a small amount of hot water and 2 cc. of 10 per cent sodium bisulfite is added, then 2 cc. of 20 per cent sulfuric acid is slowly added and heated on hot water bath for 1—2 minutes. Then the acid is neutralized with 20 per cent potassium carbonate added, drop by drop, in a slight excess over the neutrality,

evaporate to dryness on the hot water bath and moistened with a small amount of distilled water. The paste thus obtained is subjected for extraction of iodine with 95 per cent alcohol for 4—5 times by adding about 2 cc. alcohol at a time, and all the extracts are placed in a platinum dish of 10 cc. volume. To the extract a small amount of 20 per cent potassium carbonate is added, evaporate to dryness, heated for 5 minutes at 150°C. and then 1 minute, at 500°C. ; 1—2 drops of distilled water are added and stirred with a glass rod into a paste, and the paste is treated with alcohol for extraction of iodine as done previously. Again the extract is evaporated down to dryness after a small amount of 20 per cent potassium carbonate is added, and heated at 150°C. for 2 minutes to drive out all alcohol. Then the residue is washed repeatedly several times into ERLENMEYER flask of 25 cc. volume with a small amount of hot water used at a time so that the final volume reaches to about 10 cc.

Thus all the iodine contained in the sample is transformed into an inorganic form which is determined quantitatively as follows :

The Volumetric Method used.

Reagents used : (MERCK's.)

1.) Sulfuric acid solution.....(20 %.)
2.) Methyl orange solution....(0.01 %.)
3.) Saturated Brom water. ...(Prepared freshly.)
4.) Potassium iodine.....(5 % solution, freshly prepared just before used.)
5.) Sodium hyposulfite.....(N/1,000 standard solution which is prepared everytime from N/10 solution by dilution according to the titration value determined at the time.)
6.) Starch solution.....(0.5 %.)
7.) Porcelain ware.....(broken pieces, boiled in dilute nitric acid, burned and washed thoroughly, and dried.)

A drop of methyl orange is added to the solution under the test and titrated with 20 % H_2SO_4 to the neutral point, and then 0.05 cc. of the acid is added in excess to make the solution acid ; 3 drops of brom water are added and shaken vigorously so that the solution becomes dark orange color to which a piece of porcelain is added and brought to boiling on the sand bath with occasional vigorous shaking until the yellow color is lost, and the boiling is continued for five minutes after that. Then 0.1 cc. of 5 % KI and 3 drops of 0.5 % starch solution are added, and titrated with N/1,000 $Na_2S_2O_3$ through a burette which is graduated to 0.01 cc. until the blue color disappears, and the iodine contents is calculated as usual.

3. Analytical Results :

a.) In order to determine the accuracy of the method, a known various amount of iodine mixed with filter paper was analysed, and obtained the following results as noted in Table 1.

Table 1.

Determination of Accuracy of the Method.

Filter paper used.	Iodine added.	Iodine found.	Difference.
	(γ)	(γ)	
1 g.	2.0	2.11	+0.11
„	„	2.18	+0.18
„	„	2.06	+0.06
„	5.0	5.07	+0.07
„	„	4.96	−0.04
„	„	5.14	+0.14
„	10.0	10.18	+0.18
„	„	10.04	+0.04
„	„	10.00	0.00

As Table 1 indicates, the error becomes larger as the quantity of iodine decreases, for example, where 2 γ of iodine originally added, the error amounted to 3—10 % while in other cases the error was almost negligible. In a majority of cases, more iodine was found than it was added which may be due to the probable presence of iodine in K_2CO_3 used but chiefly the error in the titration is responsible for it. Consequently by more strict check on the manipulation and the apparatus used, the error could be reduced although the method as described serves the purpose very satisfactorily in most cases.

b.) Determination of iodine in meat: the determination of iodine in the animal matter has been considered very difficult owing to various factors involved especially its complete combustion, so that the beef was analysed by this method to ascertain its applicability, and the results obtained are shown in Table 2.

Table 2.

Determination of Iodine in Beef.

Samples.	Iodine found.
	(γ)
Fresh beef, 5 g.	1.35
Ibid.	1.06
Ibid + 2 KI.	2.96
Fresh beef, 10 g.	1.90
Ibid.	2.01

The above results indicate that the good comparable data were obtained by this method. Many attempts to determine the iodine content in the beef were made without success by the electric combustion method[1] owing to the following factors: (1.) the iodine content in beef is very minute, (2.) it was very difficult to bring about the complete combustion of beef without any loss of the smoke

produced because the local control of temperature in the electric furnace was not possible and caused an explosin in the furnace which may be contributed to the presence of gelatinous and fatty substance in the beef. Again a large amount of black soot passed over to the smoke screen and some remain smeared at various joints of the apparatus which could not be removed easily. These difficulties were removed in this new method which enables the control of local heating as well as all parts of the apparatus and allows no black smoke pass over beyond the platinum coil which brings about the complete combustion nor any soot is allowed to remain in any part of the apparatus.

Summary.

A new micro-analytical method for the determination of iodine which is applicable to various samples, plant as well as animal matter and others, is presented. The merits of the method may be summarized as follows:

1.) A minute quantity of iodine in comparatively small sample can be determined.

2.) The combustion of organic constituents in the sample is completed and no black smoke passes over to the absorption bottle nor any soot remain smeared in any part of the apparatus.

3.) By liquefying the animal matter with caustic soda, and slightly acidifying it under cooling just before subjected to combustion, prevents any explosion may occur in the course of combustion as well as vaporization of iodine at comparatively lower temperature is made possible.

4.) By this method it was found that the beef used in this investigation contained about 0.2 P.P.M. as the dry matter.

Literature.

1.) Itano, A., Berichte d. Ōhara Inst. f. landw. Forsch., VI: 54—58, 1933.

PLATE VIII.

Fig. 1. Complete Apparatus.

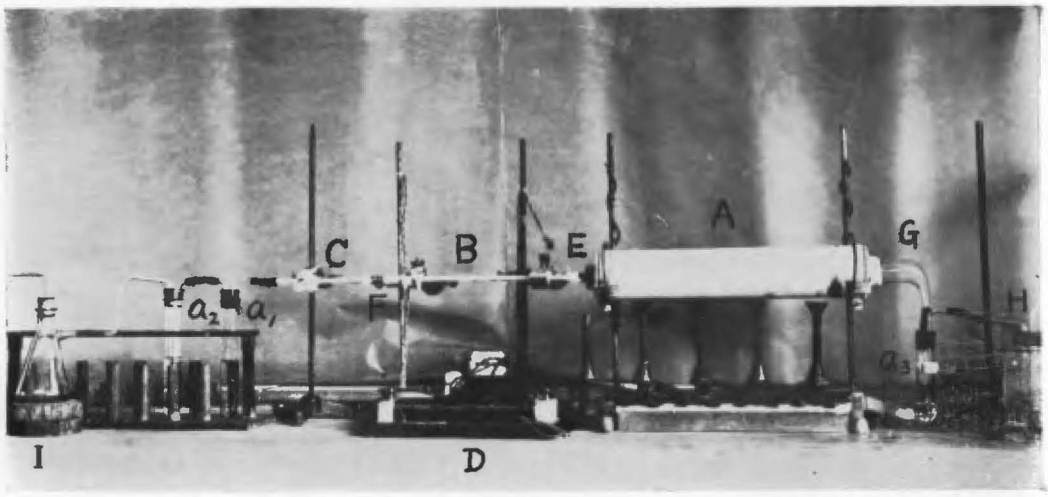

Fig. 2. Cross Section of Apparatus.