CCLIX. INVESTIGATIONS ON THE DETERMINATION OF MICRO-QUANTITIES OF IODINE

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(Received 10 September 1937)

DURING recent years several communications dealing with micro-methods for the determination of iodine have appeared. In this connexion we have found it desirable to amplify our previous communications [Reith, 1929; 1930; 1933; 1935] with new data, in the hope that by clear definition of manipulative details we shall contribute to the attainment of that uniformity in technique, which is so much to be desired.

Knowledge of the previous papers is assumed. The azide-bromine-sulphuric acid method is employed in all the experiments to be described. Most of the reagents (0.5 *N* H_2SO_4 , 5% sodium azide, saturated bromine water, 1% NaNO_3 etc.) were prepared in the manner already described. The K_2CO_3 solution contained 780 mg. of anhydrous K_2CO_3 per ml. Modified methods of preparation were used for two of the reagents: 0.5% starch solution was rendered stable for several months by the addition of 0.8% of salicylic acid, while 0.001 *N* $\text{Na}_2\text{S}_2\text{O}_3$ was effectively stabilized by addition of 1% amyl alcohol [Meyr & Kirschbaum, 1928]. It should be mentioned that the alcoholic extracts were evaporated in a dust-free stream of nitrogen following Harvey [1935], and the residues were never heated subsequently. Heating a residue containing only 10–20 mg. K_2CO_3 could easily lead to loss of iodine (see under § 5). All experiments except those described in § 3 were carried out in porcelain dishes.

(1) *Extraction of traces of iodide from salt mixtures*

The isolation of traces of iodide from a mixture of salts (consisting chiefly of K_2CO_3 in practice) is usually carried out according to the method of von Fellenberg. This well-known method, however, is very tedious and incompletely defined. Hamilton [1936] first described an extraction method, which in our experience still possesses some slight practical objections. We prefer the technique described below, which is applicable to the determination of iodine in water, urine etc. to which 2–2.5 ml. K_2CO_3 solution have been added.

Method of extraction. The mixture of salts to be extracted is transferred with the help of a little water from the dish to a graduated 10 ml. test-tube with a glass stopper. If one repeatedly uses about six drops of water and rubs it round the dish with a glass rod or rubber swab, the material can be transferred quantitatively in a total volume of about 3.5 ml. The contents of the tube are then shaken up so that the upper layers are not too dilute and do not mix with the alcohol. If necessary the volume may be greater but it should not exceed 5 ml. 5 ml. of 93% (by weight) alcohol (sp. gr. 0.815 at 15°) are now added, the tube is stoppered and inverted fifty times, the air bubble being allowed to rise to

the top each time. The two layers are then allowed to separate for a few minutes, while the stopper is removed and placed in a small clamp to prevent the attached liquid from being lost.

The test-tube is then fitted with a doubly bored cork carrying a short and a long tube (see Fig. 1) so that the latter reaches to within 2 mm. of the aqueous layer. The alcoholic layer is then blown over into a dish. The cork with the tubes is removed and hung in such a position that none of the adhering alcoholic extract goes astray. The extraction is then repeated in the same manner with 5 ml. of alcohol and the extract blown over from a distance of 2 mm. from the aqueous layer.

From the numerous control experiments we have carried out we give a few below, which indicate the reliability of this rapid method.

Fig. 1. Apparatus for iodide extraction.

(a) 2 ml. of K_2CO_3 solution + 200 mg. of NaCl + water to 5 ml. Extracted with 93% alcohol as described. After each treatment the volumes were 5.0, 3.9 and 3.3 ml. Two extracts together contained on titration 14 mg. of K_2CO_3 and 79.5 mg. of NaCl.

(b) As (a) but extracted with absolute alcohol. After each treatment the volumes were 5.0, 3.4 and 2.4 ml. (separation of NaCl crystals). The two extracts together contained 11 mg. of K_2CO_3 and 79.5 mg. of NaCl.

(c) 2.5 ml. of K_2CO_3 solution + 50% of iodide ion evaporated in a dish to crystallization. Rinsed into a graduated test-tube with portions of 6 drops of water until the volume was 3.5 ml. Extracted three times with 5 ml. portions of 93% alcohol as described but each time inverted only 30 times. Found:

1st extract	contained	45.8 γ	iodine	and	3.0 mg.	K_2CO_3 .	Vol. of aqueous layer	3.0 ml.
2nd	"	4.4	"	1.4	"	"	"	2.7 "
3rd	"	0.5	"	0.9	"	"	"	2.6 "

(d) 2 ml. K_2CO_3 solution + 50% iodide ion treated as under (c) but diluted to 6 ml. Found:

1st extract	contained	44.0 γ	iodine	and	76 mg.	K_2CO_3 .	Vol. of aqueous layer	3.8 ml.
2nd	"	6.8	"	12	"	"	"	2.7 "
3rd	"	0.4	"	1.8	"	"	"	2.2 "

(e) 2.5 ml. K_2CO_3 solution + 50% iodide ion treated as under (c) but diluted to 6 ml. Found in 1st extract 45.9%, in 2nd extract 3.8% and in 3rd extract 0.3% of iodine.

(f) 2.5 ml. K_2CO_3 solution + 5.0% iodide ion made up to 5.0 ml. and extracted according to the recipe (except that the tube was inverted 40 times). Found in two extracts combined 5.0% iodine.

Exps. (a) and (b) differ as regards the strength of the alcohol used. It appears that absolute alcohol extracts almost as much salts (at least of K_2CO_3 and chloride) as 93% alcohol: the latter is simpler to prepare and therefore was employed in all subsequent experiments.

Exps. (c), (d) and (e) differ mutually as regards the K_2CO_3 concentration in the aqueous layer. It appears that the extraction of iodide is complete even from relatively dilute K_2CO_3 . The amount of K_2CO_3 extracted along with the solvent increases rapidly with the dilution of the aqueous layer.

If the recipe is followed and 2–2.5 ml. of K_2CO_3 solution are diluted to not more than 5.0 ml., the amount of K_2CO_3 extracted by the solvent does not interfere with the subsequent titration. It has appeared that 30 inversions of the

tube are sufficient to ensure complete extraction; for safety, 50 inversions are made. From Exp. (f) it follows that a smaller amount of iodide can be extracted completely.

This method of extraction was employed in all subsequent experiments.

(2) *Some new methods for the determination of small quantities of iodide*

According to Sandell & Kolthoff [1934; 1937] it is possible by a catalytic reaction to determine 0.05–1.0 γ of iodine with a maximum error of 20 % and a mean error of 10 %. In this method nitrites must be oxidized, fluorides must be made innocuous with aluminium chloride, and cyanides interfere with the reaction. In our opinion it is doubtful whether this interesting method will find much practical application; the presence of nitrites, fluorides or cyanides along with iodides is always possible in practice and therefore a protracted procedure must always be employed. The high degree of sensitivity is certainly an advantage but nearly always sufficient starting material will be available to ensure the presence of 1–2 γ of iodine, which may be determined titrimetrically.

The colour reaction of Saifer & Hughes [1937] with dioxane, is not sensitive enough for micro-quantities of iodide ion. We have various objections to the method of Endres & Kaufmann [1936]. According to our experiments, which we need not describe in detail here, their colour reaction develops too slowly and is too weak with the smallest quantities of iodine (< 6 γ). Besides, in practice, the iodide is frequently mixed with nitrite, which makes determination by this method impossible.

The application of formic acid (according to Viebock & Brecher [1929; 1933] and according to Spitzer [1936]) to remove bromine according to the reaction

is worthy of a closer examination.

The above-mentioned authors have not examined how far this reaction is applicable to micro-iodine titrations. We have investigated this point because in this way it might be possible to dispense with the boiling out of bromine. For this purpose we prepared a 5 % solution of sodium formate containing sufficient formic acid to react just acid to methyl orange (in all about 10 % formic acid) and carried out the following experiments.

(g) 2 ml. water + 2 drops H_2SO_4 + 3 drops bromine water + 0.1 ml. sodium formate: after standing for some time, potassium iodide and starch were added. No free bromine was detected after 10 min.

(h) As (g) but contained 5.0 γ of iodide ion. Found by titration 5.0 γ iodine (six determinations).

Thus the method gives accurate results with pure iodide solutions. In practice, however, it is frequently necessary to titrate mixtures of iodide and nitrite, in which the latter must be destroyed in the well-known way with an excess of sodium azide. It appeared to us that the excess of azide usually employed is an obstacle to the use of formic acid.

(k) 5.0 γ iodide ion + 3 drops azide acidified with H_2SO_4 then as (g). Found 5.0 γ .

(l) 5.0 γ iodide ion + 5 drops azide acidified with H_2SO_4 then as (g). Found 4.8 γ .

(m) 5.0 γ iodide ion + 7 drops azide acidified with H_2SO_4 then as (g). Found 4.1 γ .

From these results we concluded that in practice, the usual boiling method is to be preferred.

(3) *The reduction of iodate in alkaline media with hydrazine*

Hydrazine has already been used as a reducing agent for micro-quantities of iodate in alkaline media by Wilke-Dorfürst [1927], Harvey [1934; 1935] and Paal & Motz [1935]. The quantitative course of this reduction however is as yet incompletely known. Hamilton [1936] in a recent investigation has shown that the reduction of iodate proceeds to the extent of 97–100 % by boiling for 30 min. with 10 mg. hydrazine sulphate and then evaporating the mixture to dryness. From a single experiment it appeared that reduction was also complete by simply evaporating to dryness. The author does not state what volume is boiled and evaporated or how long this operation takes, so that it appears to us to be of interest to give an account of the following experiments.

In the nine experiments numbered (n) to (v) inclusive, below, 10 γ of iodine were introduced as iodate into a platinum dish with 1 ml. of K_2CO_3 solution and the quantities of hydrazine sulphate and water stated. After evaporation on the water-bath, the residue was extracted with alcohol and the iodide titrated. As is well known, iodate is not extracted with alcohol.

(n) 5 mg. hydrazine sulphate + 20 ml. H_2O . Time of evaporation 15 min. Found in extract 5.9 γ I ion.

(o) 20 mg. hydrazine sulphate + 20 ml. H_2O . Time of evaporation 15 min. Found in extract 9.3 γ I ion.

(p) 20 mg. hydrazine sulphate + 50 ml. H_2O . Time of evaporation 45 min. Found in extract 9.2 γ I ion.

(q) 40 mg. hydrazine sulphate + 10 ml. H_2O . Time of evaporation 10 min. Found in extract 8.9 γ I ion.

(r) 100 mg. hydrazine sulphate + 50 ml. H_2O . Time of evaporation 45 min. Found in extract 8.9 γ I ion.

(s) 10 mg. hydrazine sulphate + 10 ml. H_2O , after evaporation (10 min.), addition of the same amounts of hydrazine sulphates and water and again evaporating. Found in extract 8.5 γ I ion.

(t) 10 mg. hydrazine sulphate + 25 ml. H_2O , after evaporation (20 min.) the same amounts of hydrazine and water added and evaporated (20 min.). Found in extract 8.4 γ I ion.

(u) As (r) but 20 mg. NO_3^- added at the beginning as KNO_3 . Found 7.8 γ I ion.

(v) As (r) but 20 mg. NO_2^- added at the beginning as KNO_2 . Found 7.6 γ I ion.

These experiments show that the reduction of iodate occurs to the extent of about 90 % if 20 mg. of hydrazine sulphate and 50 ml. of water are used and the mixture evaporated on the water-bath to dryness. This reduction method appears to us to be particularly useful for the determination of iodine in organic matter. The latter is destroyed by combustion in a stream of oxygen and the liberated iodide or iodine collected in wash-bottles containing alkali. At most one-sixth of the iodine can be present as iodate and if 90 % of this is reduced, the loss of iodine as iodate in the extraction cannot exceed 2 % of the total. Reduction with hydrazine is to be preferred to reduction with SO_2 after acidification with H_2SO_4 because less reagent is needed and the amount of salt is not increased.

If complete reduction of the iodate is desired, boiling is necessary. According to the following experiment boiling is sufficient:

(w) As Exp. (p) but boiled gently for 30 min. in a small Erlenmeyer flask over a small gas flame to a low volume. Found in the extract 10.2 γ iodide ion.

According to Hamilton, it is preferable to use hydrazine hydrate rather than hydrazine sulphate because the former is completely volatilized on evaporation.

(4) *Is iodate produced when mixtures of iodide and potassium carbonate are heated in presence of an oxidizing agent?*

A definite answer to this question has never been given. Riggs [1909; 1910] states that iodate is formed when iodide is heated with a large excess of nitrate and alkali but Seidell [1909] was unable to confirm these results. We considered it of practical importance to investigate this question under clearly defined conditions of time and temperature, since such conditions are sometimes employed in the micro-determination of iodine.

In the experiments described below a block furnace made of bronze was used; this instrument can be regulated very readily, and it has the great advantage that by its use it is impossible to overheat the dish locally. The furnace, which was very cheap (see Fig. 2), is cast in bronze and turned internally so that the

Fig. 2. Bronze block furnace with double asbestos wall. Dimensions in mm.

lid fits closely. The side walls and lid are provided with two layers of asbestos between which there is an air space 1 cm. wide. It is advisable not to take asbestos sheet, which has been in the laboratory for some time, but to take it straight from the warehouse, where it cannot have come into contact with iodine, and ignite it before use. The lid is removed by means of the spring (Fig. 2*b*). The furnace stands on four iron feet, which are screwed into the block. When heated with three Teclu burners it reaches 500° within an hour and can be kept at this temperature without difficulty with one burner. Temperature corrections for exposed mercury thread in the nitrogen-filled thermometer must be carefully calculated, since they may be fairly high (25–35° at 450–550°). All temperatures mentioned below are corrected.

The furnace has reached equilibrium as soon as the temperature of the metal (at *a*) and that of the interior differ by at most 5–10°.

When the furnace has reached the desired temperature, the dish is placed inside on a pipeclay triangle. The thermometer again registers the desired temperature within 5 min. of opening and shutting the furnace. We considered it necessary to check the furnace carefully to see whether any iodine was picked up at 500° by a dish containing K_2CO_3 .

The following three heating experiments were carried out with this furnace (*x*, *y* and *z*). Mixtures of 100γ of iodide ion + 2 ml. K_2CO_3 solution + 80 mg. $NaNO_3$ were placed in small porcelain dishes. The mixtures were gently dried and then heated in the furnace for 30 min. The salt mixture was then extracted with alcohol (=extract before reduction). The extracted salt mixture may

still contain iodate and was therefore treated with 20 mg. of hydrazine sulphate in the way already described, after which it was again extracted with alcohol (=extract after reduction). The results were as follows:

- (x) Heated at 400° for 30 min. Extract before reduction 97.6 γ , after reduction 1.2 γ iodine.
- (y) Heated at 450° for 30 min. Extract before reduction 99.2 γ , after reduction 0.6 γ iodine.
- (z) Heated at 500° for 30 min. Extract before reduction 98.2 γ , after reduction 1.1 γ iodine.

The small amount of iodine, which we found after reduction (about 1 % of the total) may result from incomplete extraction. Thus no iodate is formed even on long heating in presence of a large excess of oxidizing agent, or at least it is formed in undetectable quantities.

It may also be mentioned that heating with excess NaNO_3 at 500° has not led to noticeable loss of iodine.

(5) *The destruction of organic matter in open dishes in micro-iodine determinations*

It is generally assumed that the destruction of organic materials (e.g. organs and foodstuffs) in open dishes is impossible without loss of iodine, either by actual volatilization or by mechanical entrainment in the fumes and smoke. At the same time, heating in open dishes is employed by various investigators (e.g. in the examination of drinking water) in order to destroy small amounts of organic matter mixed with large amounts of K_2CO_3 . Although the conditions are much more favourable there is reason to doubt whether a significant loss of iodine may not occur. In other words, can a temperature be found at which a small amount of organic matter may be completely destroyed and yet no loss of iodide occur by volatilization?

This question has been incompletely answered by previous investigators. Jochmann [1928] carried out heating experiments in platinum and nickel dishes in a muffle furnace; he states that porcelain and silica dishes are unsuited for this purpose. His conclusions are difficult to check since a description of his experiments with data as to the quantities of organic matter, K_2CO_3 and iodide and of the times of heating is not given.

One of us [Reith, 1929, 1, 2] carried out a series of experiments in an electric furnace and came to the following conclusions.

I. On heating iodide mixed with little K_2CO_3 solution (20 γ I + 10 mg. K_2CO_3) no loss occurs at 300° in 5 min. but loss occurs at higher temperatures. The loss already reaches 30 % in 5 min. at 470°.

II. On heating iodide mixed with a large proportion of K_2CO_3 solution (20 γ I + 250 mg. K_2CO_3) no loss occurs at 470° in 30 min.

III. On heating iodide mixed with much K_2CO_3 solution and some organic matter (20 γ I + 250 mg. K_2CO_3 + 2 mg. cane-sugar) destruction was complete in 30 min. at 470° and no loss of iodide was noticeable.

Harvey [1935], who was unacquainted with the above-mentioned dissertation, carried out similar experiments, which confirmed the conclusion reached under I; contrary to conclusion II he noted a loss of iodide up to 10 % on heating with a large amount of K_2CO_3 (1.4 g.) at 500°. On the other hand, Allot *et al.* [1932] failed to notice any loss on heating with a large proportion of K_2CO_3 at 500°.

The possession of the block furnace enabled us to carry out heating experiments in a more reliable manner than was possible with an electric furnace. Again we found it possible to heat iodide mixed with a large proportion of K_2CO_3 (12.5 γ I + 2 ml. K_2CO_3 solution) to a high temperature without loss of

iodine. On heating to 500° and even to 540° for 30 min. the whole of the added iodide was recovered when working in either porcelain or platinum dishes (see also Exps. *x*, *y* and *z*). Thus we have failed to confirm the suggestion that platinum catalytically accelerates the loss of iodine in these ignitions [Harvey, 1935].

Subsequently, a number of experiments were carried out in porcelain dishes with mixtures of K_2CO_3 with 30–50 mg. of various organic materials. It was soon apparent that after heating such mixtures for 30 min. at 500° or even at 550°, a large number of carbon particles were still present in the salt mass, which remained partly suspended in the alcohol during the extraction. These carbon-containing extracts can be filtered clear, provided that the filter papers are completely freed from alcohol-soluble material by thorough washing with 93 % alcohol. Filtration through a Schott 3 G 4 glass filter is most practicable. The residues from the filtered alcoholic extracts were, however, pale yellow and contained traces of organic matter, which made them unsuitable for titration. When these residues were again ignited with 2 ml. K_2CO_3 solution, the resultant extracts were colourless but the loss of iodine sometimes reached as much as 20 %.

Subsequently, the following method was investigated.

A mixture of 2.5 ml. K_2CO_3 solution + 50 mg. of organic matter + iodide ion was dried in a porcelain dish, gently carbonized at 250–300° over an Argand burner and heated in the furnace at 500° for 15 min. The mixture was then taken up in 30 ml. of hot water and the carbon filtered through a 3 G 4 Schott glass filter after which it was washed three times with 10 ml. of hot water and twice with 5 ml. of 93 % alcohol. The filtrates and washings were evaporated to a small volume, 10 mg. $NaNO_3$ were added (to oxidize traces of organic matter) and the resultant mixture again dried on a water bath and ignited, first over an Argand burner and finally in the furnace for 15 min. at 500°. The pure white product was then extracted with alcohol and worked up in the usual way.

We give here the results of a series of experiments carried out by this method; many others were carried out and showed the same effect.

Series A.

- (1) 50 mg. sugar without iodide. Found 0.5 γ iodine.
- (2) 50 mg. sugar + 20 γ I-ion. Found 20.0 γ iodine. Loss 0.5 on 20.5 = 2 %.
- (3) 50 mg. gelatin without iodide. Found 1.0 γ iodine.
- (4) 50 mg. gelatin + 20 γ I-ion. Found 18.8 γ iodine. Loss 2.2 on 21.0 = 11 %.

From these determinations it appears that the destruction of sugar in the way described above takes place without appreciable loss of iodine. The carbon does not adsorb iodide to any noticeable extent, which confirms the conclusions of Hercus & Purves [1936] and of Harvey [1935]. The destruction of gelatin involves greater loss of iodine (11 %). Probably the results obtained with sugar and gelatin may be extended to carbohydrates and proteins respectively, in general, and thus confirm the opinion that it is impossible to destroy biological material in open dishes without a loss of iodine [*vide e.g.* Allott *et al.* 1932].

If a small amount of organic material must be destroyed, it is possible to accomplish this destruction at once with an excess of $NaNO_3$ without appreciable loss of iodine. If, after one ignition, the carbon is not completely burnt (especially with insoluble organic substances), the salt mass is dissolved in water, the carbon particles are rubbed fine with a glass rod, and the mixture again ignited after drying, when the carbon completely disappears. In this way the filtration of the carbon is avoided. It is worthy of note, that very little

nitrite is observed in the residue to be titrated; this is apparently decomposed. The following series of experiments (series B) gives an idea of the utility of this method of oxidation:

Series B (always 2.5 ml. K_2CO_3 solution).

- (1) 50 mg. sugar + 100 mg. $NaNO_3$ without I. Heated $\frac{1}{4}$ hr. at 500° . Found 0.2 γ I.
- (2) 50 mg. sugar + 100 mg. $NaNO_3$ + 25 γ I. Heated $\frac{1}{4}$ hr. at 500° . Found 24.3 γ I.
- (3) 50 mg. gelatin + 100 mg. $NaNO_3$ without I. Heated twice for $\frac{1}{4}$ hr. at 500° . Found 0.7 γ I.
- (4) 50 mg. gelatin + 100 mg. $NaNO_3$ + 25 γ I. Heated twice for $\frac{1}{4}$ hr. at 500° . Found 25.0 γ I.

Thus the loss of iodine by this method amounts to only 3 % with both sugar and gelatin so that the addition of nitrate is to be recommended for the determination of iodine in materials which contain a relatively small amount of organic matter, e.g. drinking water.

SUMMARY

Some new methods have been tested for the micro-determination of iodine.

The extraction of iodide from salt mixtures by shaking with alcohol, appears to be a practical method, which can be clearly defined.

The application of formic acid in the micro-iodide titration led to objections.

The reduction of iodate in alkaline media with hydrazine has been investigated further.

No detectable amount of iodate is formed on heating a mixture of iodide, nitrate and carbonate.

Small amounts of organic matter (of the order of 50 mg.) can be destroyed with practically no loss of iodide by heating with excess of nitrate; this method is recommended, for example, for the analysis of drinking water. A simple and cheap bronze block furnace for igniting dishes to temperatures up to 550° , is described. By using this furnace, platinum dishes can be replaced by porcelain.

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