

SCIENTIFIC SECTION

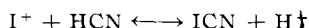
THE MICROTITRATION OF IODIDES WITH IODATE AND THE DETERMINATION OF THE IODIDE AND FERROUS IRON CONTENT IN SYRUP OF FERROUS IODIDE.*

BY I. M. KOLTHOFF.

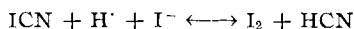
The following is a summary of an investigation on the above-named subject which was published in detail in the *Pharm. Weekblad*. Within the past few years R. Lang¹ published some new iodometric methods which are based on the formation and titration of iodine-cyanide. In principle the method is based on the fact that iodide is oxidized by a strong oxidant to iodine, whereas in the presence of hydrocyanic acid the oxidation goes further to the colorless iodine-cyanide. The reaction may be represented by the following electro-chemical equations:



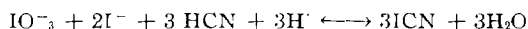
The positive iodine ion reacts with HCN:



In reality the reaction is much more complicated. We have during the titration present in the liquids the following: iodine-cyanide, iodide and hydrogen ions, which react in the following manner:



Hence during the titration of an iodide in the presence of hydrogen-cyanide with a strong oxidant, the liquid contains iodide as well as iodine, and it will produce a blue coloration with starch solution. This blue color disappears just at the end-point where all the iodide is oxidized to iodine-cyanide. The most suitable oxidant for the titration, even for traces of iodide, is iodate. Potassium iodate is readily obtainable in pure state by recrystallization from water, and serves as an ideal standard. The reaction between iodate, iodide and cyanide in acid solution may be represented by the equations:



Hence in this case the equivalent weight of iodate is half the molecular weight, whereas in the ordinary iodometric titration it is $\frac{1}{6}$ of the molecular weight. The titration gives the best results when it is carried out in a medium that contains 1 to 1.2 normal hydrochloric acid.

To 10 cc. of a 0.1 molar iodide solution is added 80 cc. of water, 20 cc. 25% hydrochloric acid and 4 to 5 cc. 10% potassium cyanide solution. The titration is performed in a long neck, glass-stoppered flask, $\frac{1}{60}$ molar (or more dilute) iodate is added until the blue color of the added starch solution just disappears. The color change is extremely sharp.

* Scientific Section A. PH. A., Des Moines meeting, 1925.

¹ R. Lang, *Z. anorg. allgem. Chem.*, 122, 332 (1922); 142, 229, 279 (1925); 144, F5 (1925).

Taken cc. KI.	Added bromide.	Used $\frac{1}{60}$ molar KIO_3 .	Calculated.
		30.00 cc.	
10 cc. 1/10 molar	—	29.98 cc.	30.00
		29.98 cc.	
10 cc. 1/10 molar	1 Gm.	30.02 cc.	30.00
10 cc. 1/10 molar	2 Gm.	30.02 cc.	30.00
10 cc. 1/10 molar	10 Gm.	30.03 cc.	30.00

These results agree with those of Lang. I find absolute correct results in the presence of large amounts of bromide, though the end-points in the case of bromines were somewhat slowly reached.

For the titration of more dilute iodide solutions, the above method does not give very accurate results, especially in the presence of bromides. In very dilute iodide solutions the color change appears too early.

Therefore, I improved the method and did not use starch as an indicator, but added carbon tetrachloride (or chloroform). The iodate was added until the violet color in the carbon tetrachloride layer just disappeared. Under these conditions the method gives absolutely correct results, even in the presence of large quantities of bromide.

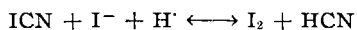
I succeeded in titrating 100 cc. of liquid that contained as little as 0.127 mg. iodide with an accuracy of 1%. As far as I know, we have at present no method that gives such accurate results in these high dilutions.

Since the determination of traces of iodine is of considerable importance with respect to goiter, I suggest trying the method given above for the titration of iodides in salts, brines, water, foodstuffs and so forth.

However, when there are present other substances, which are oxidized by iodate in strongly acid solution, the method cannot be applied directly. Use of the reverse titration to oxidize the iodine to iodate and to titrate the latter with iodide is suggested.

The oxidation of iodide to iodate is done rapidly with a solution of hypochlorous acid in a medium of acetic or succinic acid. The excess of chlorine is boiled off and the liquid is ready for titration. Hydrochloric acid is added until the concentration is about 1 *N*; and there is titrated with a standardized iodide solution, until the carbon tetrachloride layer is just colored violet. Under these conditions I was able to titrate as little as 0.1 mg. of iodine in 100 cc. liquid with an accuracy of 1 per cent.

The method described above cannot be applied for the determination of iodide in syrup of ferrous iodide, as the ferrous iron is slowly oxidized by the iodate. Instead of using the latter oxidant we may advantageously employ potassium permanganate. When starch is used as an indicator, the coloration appears (about 1 or 2%) too early in the presence of iron. Therefore, it is better to titrate, until the pink color of permanganate is visible. Under these conditions the iodide is oxidized to iodine-cyanide and the ferrous to ferric iron. Hence we find the sum of both. The iodine-cyanide itself also is an oxidant, and it reacts in acid solution with iodide in forming iodine.



In order to prevent a disturbing action of the ferric iron, this titration must be

done in a medium of phosphoric acid. In this solution the ferric ions are bound in a complex form, and do not react with iodide.

Therefore, if we wish to titrate iodide and ferrous iron together, the titration is done in the following way.

To 10 cc. of the liquid to be titrated is added a mixture of 80 cc. water, 10 cc. 25% phosphoric acid and 5 cc. 10% potassium cyanide.¹ Then 0.1 *N* potassium permanganate is added, until the liquid appears pink colored.

Then an excess of iodide is added, and the liberated iodine is titrated with thiosulphate, using starch as an indicator. If the permanganate number is *A* cc. 0.1 *N*, and the thiosulphate number *B* cc. 0.1 *N*, we have:

$$\begin{array}{ll} \text{Iodide Content:} & B \times 12.69 \text{ Mg.} \\ \text{Ferrous Content:} & (A - B) \times 5.58 \text{ Mg.} \end{array}$$

Sucrose has but a very small disturbing effect in the titration with permanganate and therefore the method is recommended for a simple, rapid method for the titration of iodide and ferrous iron in syrup of ferrous iodide. Especially in scientific investigations, where the air and light decomposition is studied of a liquid containing ferrous iron and iodide, the method given above is of distinct advantage.

SUMMARY.

(1) The method of Lang is improved for the determination of traces of iodide with iodate as a reagent.

(2) The method of Lang is applied for the titration of iodide and ferrous iron in syrup of ferrous iodide.

PHARMACY LABORATORY OF THE UNIVERSITY,
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ISOPROPANOL AS A SUBSTITUTE FOR ETHANOL I. THE DETERMINATION OF SAPONIFICATION NUMBERS.*

BY H. A. SCHUETTE AND LOYD E. HARRIS.

Isopropanol is a member of the alcohol family whose appearance in the commercial field, either as a contribution from the petroleum-refining industry or as a foreign-made synthetic product,¹ has some interest to the pharmacist.

Fuller reported that not only is it superior to ethyl alcohol as a solvent but that it has greater antiseptic and disinfectant properties as well. He suggested² that the pharmaceutical profession has access to a solvent that might be capable

¹ The potassium cyanide must not be added to the acidified mixture, which contains the ferrous iron, as there is formed a local excess of ferro-cyanide, and the liquid turns blue by air oxidation.

* Read before Scientific Section, A. PH. A., Des Moines meeting, 1925. A contribution from the Laboratory of Foods and Sanitation, Department of Chemistry, University of Wisconsin.

¹ Anon, *Ind. Eng. Chem.*, 17, 822 (1925).

² *Jour. A. Ph. A.*, pp. 1081-4, (December 1923).