[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE]

A METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF IODINE AS IODIDE AND IODATE

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RECEIVED DECEMBER 18, 1924 PUBLISHED APRIL 4, 1925

One of the reasons often assigned for the geographical distribution of goiter is that of the lack of iodine in the form of salts occurring naturally in the water supply of well defined districts. It has been thought that although the quantity might be very small indeed, yet this small quantity consumed over a long period of residence in a non-goiterous locality had a vital effect upon the body. During the course of examinations of water in this connection in this Laboratory, various methods were used to determine iodine, and it was found that the methods described in the literature were not all that could be desired. Attempts were made, therefore, to devise a method that would give accurate results with an inexperienced operator.

The use of *o*-tolidine as a reagent for the determination of chlorine and the use of iodine in the estimation of tolidine suggested the possibility of adapting it for the estimation of iodine. It was found that *o*-tolidine in a neutral solution gave a blue-green color with iodine and that a similar color was obtained with it by using hydrogen peroxide as an oxidizing agent for iodides. Various concentrations of *o*-tolidine and hydrogen peroxide were tried, holding the concentration of one constant and varying the other. In this way it was found that 0.5 cc. of a solution of 1 g. of *o*-tolidine (Eastman) in 150 cc. of 95% alcohol and 5 cc. of 3% hydrogen peroxide when added to 15 cc. of an iodide dissolved in water gave the best results. The lower limit of color development in this manner is when the 15cc. sample to be tested contains about 0.01 mg. of potassium iodide and the upper limit is at about 0.10 mg., as above this concentration the color is too intense for a satisfactory comparison with standards. Standards containing between 0.01 mg. and 0.10 mg. of potassium iodide and varying by differences of 0.01 mg. show sufficient differences in the depth of color to allow comparisons to be made very readily.

These results led to the adoption of the following procedure for the determination of iodine.

(a) **Preparation of Standards.**—Test-tubes (18 × 150 mm.) of good, clear glass are selected such that the diameters are very nearly the same; marks are made on the tubes with a file at the 15cc. volume line. A standard solution of potassium iodide is prepared by dissolving and diluting a water solution of this substance to give the equivalent of 0.01 mg. of iodine per cc. Portions of this standard solution are then run into each of ten test-tubes so that the extremes of iodine content are 0.01 and 0.10 mg. and the eight tubes of intermediate iodine content vary consecutively by 0.01 mg. The volume of solution in each test-tube is then increased to 15 cc. by the addition of water; 0.5 cc. of the tolidine solution prepared as described above is next added to each tube and thoroughly mixed by shaking.

(b) **Preparation of the Unknown Sample.**—A sample containing between 0.01 and 0.10 mg. of iodine as iodide or iodate is made slightly alkaline with sodium hydroxide, 10 cc. of hydrogen peroxide is added to oxidize any nitrites present and the mixture is evaporated to 20 cc.; after the residue has been filtered, and washed with hot water, the filtrate is made exactly neutral to litmus with sulfuric acid, evaporated to a volume slightly less than 30 cc. and divided into two equal parts. To one part in a test-tube is added 0.5 cc. of the tolidine solution and the solution diluted to 15 cc. with water. To the other portion hydrogen sulfide is added until the solution is saturated; the excess of hydrogen sulfide is then removed by boiling, the liquid cooled, 0.5 cc. of tolidine solution added, the volume made up to 15 cc. and the contents of the tube are mixed by shaking. Five cc. of hydrogen peroxide is now added from a buret as quickly as possible to each of the tubes containing the unknown and the standards so that the reaction times for all of the tubes are nearly the same. Each of the tubes is then shaken thoroughly, and after five minutes the tubes containing the unknown samples are compared with the standards. After ten minutes comparisons cannot be made because the blue color gradually changes to a brown and a precipitate of organic matter forms. The values obtained in the unknown tube which was treated with hydrogen sulfide are the values for the total iodine as both iodide and iodate; the other unknown tube gives the value for the iodide iodine only; the difference between these two values is the amount of iodine present as iodate. It is essential that all of the hydrogen sulfide be removed before proceeding with the analysis.

Influence of Various Elements and Acid Radicals

It was found that as little as 0.02 mg. of sodium nitrite per 15 cc. of solution gave with tolidine the same color as an iodide under the conditions of the test as stated above, but when nitrite solutions are boiled with hydrogen peroxide before making the test the nitrite is oxidized to a nitrate which does not interfere. Sulfates were found to have no effect on the results. Bicarbonate (temporary hardness—calcium bicarbonate) gives a color with the reagents, but when the solution is previously boiled the results of the analysis are correct and, as a sample for analysis would ordinarily have to be evaporated, any temporary hardness originally present would not interfere. A decided acidity or alkalinity interferes with the analysis; the solution must be made neutral to litmus with sulfuric acid or sodium hydroxide. When the concentration of chlorides or bromides is below 1500 parts per million there is no observed error in the results. Above this amount, however, chlorides and bromides increase the depth of color given by the reagents, causing high results for the iodine. The formation of the color due to chlorides and bromides is not directly proportional to their concentration and also varies with the amount of iodide mixed with them. It was found in the determination of samples of known concentration of iodide, that when 0.05 g. of sodium chloride or bromide was added to a 15cc. test sample the values for iodine were about 0.02 mg. high. That this color production is not due to traces of iodide in the chloride and bromide was determined by the preparation and testing of samples of these salts, using a variation both in their synthesis and in their purification. Where it is desired to determine merely the presence or the approximate quantity of iodine in a sample of drinking water, no attempt is made to remove the interfering chlorides or bromides the test being made directly on the sample of water and the result reported as a quantity of iodine "not more than" the amount shown by the test; such determinations would at least show the absence of iodine to an amount equivalent to the sensitivity of the test. Where an accurate determination is to be made of salt brines, the iodine is readily removed from the chlorides and bromides by adding ferric sulfate to the sample, acidifying with sulfuric acid and steam distilling the liberated iodine into a receiver containing dil. sodium hydroxide solution to which has been added a quantity of hydrogen peroxide to reduce the sodium hypo-iodite to sodium iodide, evaporating to dryness and neutralizing to litmus with sulfuric acid. The distillate thus obtained from sodium chloride and bromide salt solutions gave no test for iodine, and brines containing mixtures of chlorides and bromides with known amounts of iodides gave accurate results on determination of the iodine.

Iodates do not give any color in this test and therefore a sample can be analyzed for both iodides and iodates by running one determination for the former in the ordinary manner and reducing the iodates in the other sample with hydrogen sulfides, removing the excess of the latter by boiling and again making the test as described; the difference between the two results is the iodine present as iodate.

Salts of metals such as iron, copper, mercury, etc., must be removed from the sample before testing for iodide, as they cause precipitation of the tolidine.

The results of some analyses of known samples which were submitted to us as unknown are given in Table I; the sample marked "Brine" is one used by a firm of manufacturing chemists and the value found by this method is compared with the value determined by their analysts using the older methods. A sample of drinking water supplied to Cleveland gave results that indicate less than 0.002 mg. of iodine in 10 liters.

TABLE I

SAMPLES CONTAINING POTASSIUM IODIDE AND IODATE EXPRESSED AS EQUIVALENT TO MG. OF POTASSIUM IODIDE PER CC.

Observed			Present		
Total	KI	KIO_3	Total	KI	KIO_3
0.08	0.08	0	0.08	0.08	0
.10	.06	0.04	.10	.06	0.04
.10	.10	0	.10	.10	0
.03	0	.03	.03	0	.03
.01	0	.01	.01	0	.01
.02	.01	.01	.02	.01	.01

TABLE II

SAMPLES CONTAINING POTASSIUM IODIDE EXPRESSED AS MG. OF POTASSIUM IODIDE PER CC.

									Brine
Found	0.0125	0.007	0.0015	0	0	0.05	1.00	0.0012	6 p.p.m.
Present	.0130	.0075	.0025	0	0	.05	1.00	.00125	6 p.p.m.

Summary

A method is described for the determination of iodine as iodides and iodates which gives accurate results when the concentration of iodine is between 0.01 and 0.10 mg. per 15cc. sample and in which a variation of 0.01 mg. is readily distinguished. The lower limit of the test is 6 to 7 parts per million. The method is made applicable to solutions which contain interfering substances by the introduction of a preliminary steam distillation in acid solution with ferric chloride.

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PHOTOCHEMICAL STUDIES. III. THE REACTION BETWEEN NITROGEN AND HYDROGEN IN THE PRESENCE OF MERCURY VAPOR, AND THE RESONANCE RADIATION OF MERCURY

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RECEIVED DECEMBER 22, 1924 PUBLISHED APRIL 4, 1925

For certain reactions, even for those which involve a decrease in free energy, a catalyst seems necessary in order that the reaction may take place; that is, the action of the catalyst may be such as to increase the rate of a reaction which otherwise is immeasurably slow, or a catalyst may be necessary in order that a reaction may take place appreciably even during a long period of time. When the rate of a reaction is so small that only a few molecules react in unit time, then the ordinary laws of kinetic