bittern deposits contain also the elements, cesium and rubidium, which are rarely found in springs. Forty-five liters of the water were evaporated to a small volume, removing the great quantities of salt as they separated. When the volume was reduced to less than fifty cc. this solution as well as the lixiviated salts that had separated during evaporation were carefully examined in the spectroscope. But not a trace of rubidium nor cesium could be detected. It is therefore safe to conclude that the bittern deposits from the ancient sea do not contain these rarer elements.

It may not be out of place to remark that the chemical composition of this water explains the remarkable therapeutic qualities especially for rheumatism and nervous diseases that it has been found to possess.

SOME ANALYTICAL METHODS INVOLVING THE USE OF HYDROGEN DIOXIDE.[1]

BY B. B. ROSS.

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THE use of hydrogen peroxide as a laboratory reagent, although originally restricted to a few operations of minor importance, has within recent years met with a much wider extension, and its numerous applications in both qualitative and quantitative analysis, render it at present almost indispensable in every well-equipped analytical laboratory.

Among the more interesting applications of this substance in quantitative estimations are those which are based on the reaction which takes place when an excess of hydrogen dioxide is brought in contact with an acid solution of chromic acid, and Baumann[2] several years since described quite fully a number of analytical processes growing out of the reaction referred to.

In the process for the estimation of chromic acid in soluble chromates as outlined by Baumann, the substance under examination is first brought into a state of solution, and the not too concentrated liquid is transferred to a generating flask of special construction.

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[1] Read at the Buffalo meeting, August 22, 1896.

[2] *Ztschr. anal. Chem.*, **31**, 436.

Ten cc. of dilute sulphuric acid are next added, after which from five to ten cc. of commercial hydrogen peroxide are run in from a small closed vessel connected with the generating flask, while the oxygen which is evolved, after the vigorous shaking of the contents of the flask, is collected over water in an azotometer.

The following equations given by Baumann illustrate the chemical changes connected with the above described reaction :

$$K_2Cr_2O_7 + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + Cr_2O_7 ;$$
$$Cr_2O_7 + 3H_2SO_4 + 4H_2O_2 = Cr_2(SO_4)_3 + 7H_2O + O_8.$$

From these equations it will be seen that for two molecules of chromic acid or one molecule of potassium dichromate, there are evolved eight atoms of oxygen, giving an equivalent of 445.3 cc. of oxygen (measured at 0° C. and 760 mm. pressure) for each gram of chromic acid which may be present.

The writer, soon after the appearance of the original article by Baumann, made a number of experimental tests of this method with a view to applying it to some other analytical processes, and still more recently has conducted a series of tests for the purpose of determining the adaptability of Baumann's method to the indirect volumetric estimation of iron.

In the dichromate method for the volumetric determination of iron, as commonly employed, the end point of the oxidation process is ascertained by the reaction with potassium ferricyanide.

As the end of this reaction is almost invariably difficult to determine, particularly if zinc has been employed as a reducing agent, the dichromate process has met with but limited application.

In order to apply the principle of the chromic acid method of Baumann to the estimation of iron, an excess of dichromate solution was employed in all of the tests and experimental determinations, the amount of the excess of chromic acid being determined by the volume of oxygen evolved upon treatment with hydrogen dioxide.

The mode of procedure adopted was as follows :

A dichromate solution was prepared by dissolving 4.913 grams of C. P. crystallized potassium dichromate in water and diluting to a bulk of one liter.

The iron solution employed in standardizing the dichromate and permanganate solutions was obtained by dissolving iron wire in dilute sulphuric acid, the solution being reduced with metallic zinc, as usual, previous to titration.

The dichromate solution was also titrated against a freshly prepared solution of ammonium ferrous sulphate, the strength of which had been determined by titration with permanganate solution, which had also been carefully standardized by means of iron wire.

In order to ascertain the strength of the dichromate solution by the hydrogen dioxide method, about fifteen cc. of the dichromate solution is run into the generating flask above referred to, and there is also added an amount of ferric sulphate solution (free from ferrous sulphate) equivalent to about 0.06 to 0.10 gram of iron. The object of employing the ferric sulphate in this standardization is to supply approximately the same conditions as obtain in the process for the actual determination of iron.

The amount of oxygen given off from chromic acid in the presence of ferric sulphate is slightly less than that evolved when ferric sulphate is absent, but the amount of ferric iron present may vary considerably without affecting the volume of oxygen liberated.

To the contents of the generating vessel about ten cc. of dilute sulphuric acid are now added, and the flask is then connected by means of a rubber tube with a Schulze's azotometer, which has been filled with water to the zero point.

From five to ten cc. of hydrogen dioxide are next run in from a small closed vessel connected with the generating flask and the mixed liquid is then shaken, at first gently, and afterwards vigorously. The tube leading from the flask to the azotometer should be provided with a stop-cock, which should be closed before and opened immediately after each shaking.

The last trace of the oxygen liberated will not be disengaged until after the lapse of about five minutes, but it is not necessary to continue the shaking during the whole of this period. After equalizing the height of the water in the two tubes of the azotometer, the volume of oxygen is noted and is easily corrected for temperature and pressure by reference to proper tables.

In order to test the strength of the dichromate solution by means of iron wire, a given weight of the wire is dissolved in dilute sulphuric acid, the solution reduced with zinc, as usual, and rapidly transferred to the generating flask (filtering, if necessary).

An excess of dichromate solution is now run in, hydrogen dioxide is added, and the oxygen is set free and collected as before described.

If a large excess of dichromate has been used in the preliminary test, duplicate tests should be made with employment of a small excess, say from two to three cc., of the dichromate.

The strength of the solution can then be readily calculated by difference, and, if necessary, the results can be checked by still further tests.

In the determination of iron in ores by this process, the solutions of ferric iron are reduced by zinc, as in the common permanganate method, and the remainder of the process is conducted just as described for the standardization of the dichromate by means of iron wire.

In addition to numerous tests of solutions of pure iron, several estimations of iron in iron ores were made by this process, the results obtained being compared with those secured by the permanganate method.

The following are the results of the tests of the iron ores referred to:

	Permanganate method. Mean of several determinations.	Dichromate method.
Iron ore No. 1	40.92	40.59
		41.25
		55.35
Iron ore No. 2	54.71	55.43
		55.50

In the determination of iron in ores by this process, it is best, as in the case of the tests with iron wire, to employ only a small excess of the dichromate solution, after making a preliminary determination, as the results are much more accurate with a small than with a large excess of chromic acid.

While a sufficient number of determinations have not been made to ascertain the probable value of this method as an independent process for the estimation of iron, nevertheless some of the results secured would seem to warrant the conclusion that it might prove of utility as a check method, it being easy of execution and not at all time-consuming.

The following equation represents the changes which take place when the dichromate is brought in contact with the iron solution after reduction :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

The writer has also attempted to apply the principle of the chromic acid method above described to the estimation of invert sugar, or rather to the determination of the amount of cuprous oxide thrown down from Fehling's solution in the process commonly employed for estimating reducing sugars.

The following equation represents the changes which take place when cuprous oxide is brought in contact with potassium dichromate in the presence of dilute sulphuric acid :

$$3Cu_2O + K_2Cr_2O_7 + 10H_2SO_4 = 6CuSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 10H_2O.$$

The cuprous oxide thrown down from the sugar solution under examination is brought upon an asbestos filter connected with a filter pump and thoroughly and rapidly washed with hot water. The filter and contents are next transferred to the generating flask of the apparatus before described, and after the addition of dilute sulphuric acid, an excess of dichromate is run in.

Very thorough and long continued agitation of the contents of the flask is necessary in order to effect the complete oxidation and solution of the cuprous oxide, and the hydrogen peroxide must not be added until the solution is complete.

The oxygen liberated on the addition of the hydrogen dioxide is collected and the volume noted as before described. The equivalent amounts of chromic acid, cuprous oxide and invert sugar can be easily calculated from the data thus secured.

This method, while apparently satisfactory from a theoretical standpoint, has so far failed to give sufficiently uniform results, one of the chief objections to the process being the difficulty attendant upon the solution of the cuprous oxide.

With improvements in the details of manipulation of the process, however, it is quite possible that more satisfactory results could be obtained.

SECOND INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

By H. W. Wiley.

Received September 15, 1896.

At the first congress held in Brussels, in 1894, it was decided to hold the meetings bi-annually and Paris was selected as the most desirable place for the reunion this year. As has already been announced to the readers of the Journal, the present congress is organized under the patronage of the French government and under the immediate direction of l'Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. The late Professor Pasteur had accepted the honorary presidency of the congress, and all delegates from foreign countries have felt an especial regret that his death has prevented them from listening to his words of welcome and from forming his personal acquaintance.

To promote the interests of the congress, committees were organized in most countries. The personnel of the one in the United States has already been published in this Journal. Through the French Foreign Office all the principal governments were invited to send delegates to the congress. Official representatives were present from Belgium, Germany, Italy, Russia, Switzerland, Austria, Portugal, Denmark, and the United States. So far as I can learn, and the fact is worthy of remark, there is no representative in attendance from England, either official or otherwise. The official delegate from the United States is Mr. C. A. Doremus, of New York, while the writer has a commission as a delegate from the Department of Agriculture, and one from the American Chemical Society, sent through the courtesy of the president and council. Belgium has the largest representation of any foreign country, and, since these gentlemen are all French in their language, the congress, as is natural, is essentially French.

The congress was formally opened July 27, at 10 A. M., in the grand amphitheater of the Sorbonne. Perhaps there is no other spot in the whole world so well suited by its history and tradi-