a certain percentage of the true values, and thus neither has a preeminent claim to scientific accuracy; for practical work in water analysis, however, the Seyler method, in the hands of an experienced operator, especially on account of rapidity of completion, has much to commend itself, and it is our purpose to employ it in our regular work.

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TITRATIONS WITH POTASSIUM IODATE.

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As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation:

$$KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl. \qquad (1)$$

On the other hand it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be

$$KI + Cl_2 = KCl + ICl. \qquad (2)$$

In both cases the end of the reaction is shown by the immiscible solvent becoming colorless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O, \qquad (3)$$

while if a great excess of hydrochloric acid is present the reaction runs

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O, \qquad (4)$$

the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colorless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behavior is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus,

$$ICl + H_2O = IOH + HCl, \qquad (5)$$

the iodous hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, etc., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré[1] for the titration of iodides. In order to compare the reactions of the first two equations, I titrated 5 cc. of a decinormal potassium iodide solution with chlorine water in presence of 5 cc. of chloroform. After the addition of 75.4 cc. of the latter the chloroform became colorless. The titration was now repeated with the further addition of respectively 15, 20 and 30 cc. of strongest hydrochloric acid and the amounts of chorine water required were, 25.4, 25.22 and 25.25 cc., the end reaction being of extraordinary sharpness. Nearly three times as much chlorine was, therefore, required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (equation 1) had been neutralized by the addition of calcium carbonate, the theoretical amount of 75.75 cc. of chlorine solution would have been required. In order to judge the influence of smaller quantities of acid, the titration was repeated with addition of 1, 2, 5 and 10 cc. of concentrated hydrochloric acid, when respectively 34.1, 26.9, 26.0 and 25.6 cc. of chlorine water were required.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realizing the reaction of equation 4. 9.7465 grams of acid potassium iodate were dissolved in water and made up to 1 liter. According to the theory, each cubic centimeter of this solution should be equivalent to 16.6 mg. of potassium iodide. To 10 cc. of a solution of pure potassium iodide (20.6 grams to the liter), 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (sp. gr. 1.21) were added and the mixture was titrated in a glass-stoppered bottle of 250 cc. capacity, with the iodate solution, shaking briskly, until the chloroform lost its color, the end-point being exceedingly sharp. 12.43 cc. of the iodate solution were required. Hence, 0.20634 gram potassium iodide was found against 0.20600 taken, or 100.17 per cent. In a second ex-

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[1] *Ann. Chem.* (Liebig), **94**, 365 (1855).

periment, 15 cc. of the iodide solution titrated in the same way with 33 cc. of hydrochloric acid and no additional water, required 18.62 cc. of the iodate solution, corresponding to 0.30900 gram found, against 0.30900 gram taken, or 100.00 per cent., found.

The process as described can be applied to the titration of chromates. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 cc. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36.3 mg. of potassium pyrochromate were taken and 36.8 mg. found.

The following experiment shows the applicability of the process to the titration of free iodine: 0.3447 gram of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 cc. of a potassium iodide solution containing 20.6 grams per liter, 10 cc. of fuming hydrochloric acid and 5 cc. of chloroform were added, and the titration was carried out in the usual way. Required: 19.85 cc. of standard iodate. Since 6.20 cc. are required for the iodide, 13.65 cc. remain as corresponding to the free iodine, or 0.3467 gram iodine found; 100.46 per cent.

To determine whether the method can be used for determination of chlorates, and under what conditions, the succeeding experiments were tried. Five cc. of a solution of potassium chlorate containing 70.3 mg. of the pure salt was added to 25 cc. of the potassium iodide solution mentioned above and 50 cc. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 cc. of chloroform were added and the titration completed. Required: 13.65 cc. of the iodate. As the iodide is equivalent to 31.0 cc., 17.35 cc. correspond to the chlorate, whence 70.9 mg. of potassium chlorate were found. In a second similar experiment only 40 cc. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 13.98 cc. of iodate were required, hence 69.55 mg. of chlorate were found. This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13.77 cc. of iodate were required, whence 70.41 mg. of chlorate were found.

It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 cc. of another potassium chlorate solution containing 33.46 mg. of the pure salt was allowed to stand for ten minutes with 10 cc. of iodide solution and 20 cc. of fuming hydrochloric acid, then 5 cc. of chloroform were added, and the titration was performed. Required: 4.23 cc. of iodate. Calculated for the iodide, 12.40 cc., whence 33.39 mg. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a chlorate can be prescribed as follows.

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the volume of the solution. Close the bottle tightly and allow it to stand fifteen minutes after shaking, then add 5 cc. of chloroform. On now shaking, the chloroform must become deep violet. If the color is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colorless, which point can be estimated with the utmost precision. Each cubic centimeter of a decinormal iodate solution is equivalent to 2.782 mg. of $(ClO_3)'$.

Solutions of arsenious acid or chloride can be titrated in the same way as iodides, the reaction being expressed by the equation

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl.$$

In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent. of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent. does not. On the other hand, the minimum limit is in theneighborhood of 12 to 15 per cent. of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken: 25 cc. arsenious solution (243.8 mg. As_2O_3) and 50 cc. of fuming hydrochloric acid. Required: 24.45 cc. decinormal=242.1 mg. of arsenious oxide. Taken :5 cc. arsenious solution, 5 cc. hydrochloric acid, and 10 cc. water. Required: 4.91 cc. of iodate = 48.6 mg. Found: 48.8 mg. by iodine titration. Taken: 20 cc. arsenious solution and 40 cc. hydrochloric acid. Required: 19.69 cc. iodate = 194.9 mg. arsenious oxide. Found: 194.7 mg. by iodine titration. Taken: 15 cc. arsenious solution and 30 cc. hydrochloric acid. Required: 14.79 cc. iodate = 146.4 mg. arsenious oxide. Found: 146.3 mg. by iodine titration.

To summarize: Add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent. of the entire mixture at the end of the titration, and 5 cc. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite, shake well and continue titrating with the iodate until the chloroform is colorless. Each cubic centimeter of the standard solution corresponds to 9.9 mg. arsenious acid or 7.5 mg. arsenic.

The determination of antimony is precisely like that of arsenic. A solution was prepared of pure recrystallized potassium antimonyl tartrate, containing 31.251 grams per liter. Twenty-five cc. of this were mixed with 30 cc. hydrochloric acid and 20 cc. water, and titrated as usual. 23.62 cc. of the iodate were required, equivalent to 784.6 mg. tarter emetic found as against 781.3 mg. taken. In this determination the amount of hydrochloric acid should have been greater by 15 cc. In the next experiment, 25 cc. of the antimonious solution with 25 cc. of hydrochloric acid required 23.50 cc. of iodate, equivalent to 780.6 mg. of antimony salt found (781.3 taken). Twenty-five cc. antimony solution with 35 cc. fuming hydrochloric acid required 23.54 cc. of iodate, whence is calculated 781.2 mg. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the arsenic in Paris green directly without preliminary separation. Thus, 20 cc. of a sodium arsenite solution with 20 cc. of fuming hydrochloric acid required 8.95 cc. of iodate; the same, plus 1 gram of copper sulphate, required 9.00 cc. of iodate. For the analysis of Paris green, 0.5 gram of the substance is dissolved in 15 cc. of water and 25 cc. of fuming hydrochloric acid, and directly titrated with 5 cc. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken: 2.0874 grams ammonium ferrous sulphate. Required: 26.06 cc. iodate, equivalent to 297.6 mg. iron found, or 14.26 per cent. Theory: 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with thisdetermination. Taken: 2.0843 grams ammonium ferrous sulphate and 1 gram oxalic acid. Required: 25.95 cc. iodate, equivalent to 296.3 mg. iron, or 14.22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA, May 5, 1903.

THE PERMANENT PROTECTION OF IRON AND STEEL.[1]

BY MAXIMILIAN TOCH.

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The question of the permanence of modern steel structures, whether the iron and steel used therein is slowly corroding and will in time cause great calamity by the collapse of these structures, has led chemists and engineers to make extensive researches into

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[1] Read before the New York Section of the American Chemical Society.