VOLUMETRIC DETERMINATION OF PERIODATE ION AFTER THE OXIDATION OF CARBOHYDRATES

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One of the most important practical methods for studying and determining the structure of carbohydrates is periodate oxidation [1]. In spite of numerous modifications, at the present time there has been no satisfactory universal volumetric method for determining periodic acid after the oxidation of carbohydrates. In view of this, Barneby's method of determining periodate ion [2], which he proposed for mixtures of inorganic substances and is practically unused for determining carbohydrates, was of interest to us.

Taking this method as a basis, we have developed an accurate, rapid, and universal method of determining periodate ion for various types of sugars. A sample of the solution under investigation (one volume) in water or a weak acid buffer is first neutralized with a saturated solution of sodium hydrogen carbonate and then finally with pH 7.3 borate buffer (one volume) with the addition of an excess (50 times the theoretical amount) of solid potassium iodide. The iodine liberated is immediately titrated with a standard solution of sodium thiosulfate.

Table 1

pH Values of the Titrated Solutions in the Oxidation of Maltose

Excess of periodate ion		pH of the borate	pH of the titrated solution
g/*l*	% of theory		
4	50	7.3	7.6
14	175	7.3	8.3
18	225	7.3	8.3

Neutralization of the solution with sodium hydrogen carbonate is carried out, in view of results obtained in a blank experiment, in the presence of the indicator bromocresol purple which has a color change at about pH 6.2. If phenolphtalein is used, as several authors recommend, the results of the titration will depend on the time of titration, the pH always being high (about 9) at the end. Borate buffer with pH 7.3 is used to maintain the pH of the titrated solution. This buffer possesses a definite specificity in titrations of iodine with sodium thiosulfate. According to Barneby's results [2] and also to our own, other buffers, for example phosphate, acetate, and hydrogen carbonate buffers, do not give satisfactory results. In spite of the fact that in the reduction of periodic acid hydroxyl ions are formed at the same concentrations as those of the periodate ion which are being used for the analysis, the pH change observed is small. At high concentrations of periodate ion, the pH increases more considerably (Table 1).

It can be seen from Table 1 that variations in the pH do not affect the accuracy of the titration and therefore the liberated iodine can be titrated in dilute solutions and also in the fairly concentrated solutions used for analytical and preparative purposes.

The addition of a large excess of potassium iodide not only enables the titration of the liberated iodine to be carried out rapidly and the time for analysis to be shortened by, also prevents the parasitic oxidation and iodination processes that many investigators have reported [3–6]. For all compounds oxidized (maltose, lactose, deoxyribose, dextran, etc.,) we obtained the same figures on titration directly after the addition of the potassium oidide and after the solution had been left to stand in the dark for 10–15 min. When a smaller amoung of potassium iodide is used, the solution must be kept for some time before titration. According to Barneby [2], the solution may be titrated 2–3 min after the addition of the potassium iodide (a 25-fold excess over the theoretical amount), when the periodate has been reduced to iodate completely. Otherwise the periodate ion reacts with the sodium thiosulfate and inaccurate results are obtained.

Table 2

Results of the Titration of 10 ml of a Solution of $NaIO_4$ (27.8 g/*l*) at Various Dilutions with Acetate Buffer

Acetate buffer pH 3.75	Solution of sodium hydrogen carbonate	Borate buffer	Normality of the iodine solution	Sodium thiosulfate, 0.0940 N, ml	pH of the titrated solution
ml					
0	0.5	10	0.0640	27.3	8.7
10	5.5	10	0.0368	27.3	8.5
20	10.5	20	0.0216	27.3	8.2
30	15.5	30	0.0174	27.3	8.0

As can be seen from Table 2, the results of the titration of a solution in a blank experiment under the conditions described do not depend on the initial concentration of periodate ion or that of the acetate buffer in which oxidation is frequently carried out or on the normality of the solution of iodine obtained.

The titrations, which we carried out at 26 and 4°C, gave identical results for all the substances investigated, while titration by other methods [5–7] frequently becomes more accurate at 4°C. This indicates that processes of oxidation and iodination by the iodine do not take place under the analytical conditions described. Thus, we previously studied the periodate oxidation of 4-O-carbobenzoxyglycyl-D-arabinose, for which accurate results are obtained only at 4°C when titration is carried out with sodium arsenite in a hydrogen carbonate medium, which is unnecessary for the proposed method.

Thus, the method of determining the periodate anion that has been described is a universal one in cases of the oxidation of many carbohydrates, including oligosaccharides, deoxy sugars, and other substances which, on being oxidized, give derivatives of malonaldehyde sensitive to free iodine.

In place of sodium thiosulfate it is possible to use a standard solution of sodium arsenite. However, in solutions of periodate ion with concentrations greater than 6 g/*l* a borate buffer with a higher pH must be used to bind the protons resulting from the equilibrium reaction

$$AsO_2^- + I_2 + 2H_2O \rightleftharpoons H_2AsO_4^- + 2I^- + 2H^+$$

Experimental

General method. The sample (weighed with an accuracy of ±0.1 mg) was dissolved in water or in acetate buffer with pH 3.7–3.8 (0.2 M acetic acid and 0.2 M sodium acetate), was treated in the dark with an excess of an aqueous solution of sodium metaperiodate, and was brought to a predetermined volume. The temperature of oxidation was 26–28°C. Samples (5 or 10 ml) of the oxidized solution were taken periodically and neutralized with a saturated solution of sodium hydrogen carbonate to pH 6.2 in accordance with results obtained in the neutralization of the solution in a blank experiment with the indicator bromocresol purple (pH of the color change about 6.2). Finally, the solution was neutralized with 5 or 10 ml, as the case may be, of borate buffer with pH 7.3–7.4 (50 g of borax and 50 g of boric acid in 1 *l* of water). Then a large excess of potassium iodide (50 times the theoretical amount) was added, the mixture was shaken, and the liberated iodine was immediately titrated with sodium thiosulfate solution (0.094 N). For each substance titration temperatures of 26–28°C and about 4°C were used. For titration at 4°C a sample of the oxidation solution was cooled with ice and neutralized with cooled solutions.

Lactose hydrate (1.012 g) was oxidized in 250 ml of a solution of sodium metaperiodate (20 g/*l*)

Oxidation period, hr	1	5	9	22	30
$NaIO_4$/lactose, molar ratio	3.30	3.62	3.74	4.08	4.38;

Maltose hydrate (0.5106 g) was oxidized in 200 ml of a solution of sodium metaperiodate (26 g/*l*) and 50 ml of acetate buffer at 14°C

Oxidation period, hr	3	20	48
$NaIO_4$/maltose, molar ratio	3.65	4.20	4.20;

Dextran (0.521 g containing 13% of moisture) was oxidized in 25 ml of a solution of sodium metaperiodate (18 g/*l*) and 75 ml of water

Oxidation period, hr	1	2	5	7
$NaIO_4$/anhydroglucose unit, molar ratio	1.82	1.83	1.86	1.86;

2-Deoxyribose (0.0315 g) was oxidized in 5 ml of a solution of sodium metaperiodiate and 45 ml of water

Oxidation period, hr	1	2	3
$NaIO_4$/substance, molar ratio	2.9	3.1	3.3;

(The consumption of a larger amount of periodate than might have been expected for 2-deoxyribose agrees with [8]).

α-Methyl-D-glucopyranose (0.195 g) was oxidized in 250 ml of a solution of sodium metaperiodate (10 g/*l*)

Oxidation period, hr	0.5	1	2
$NaIO_4$/substance, molar ratio	1.73	1.86	1.89;

4-O-Carbobenzoxyglycyl-D-arabinose (0.0201 g) was oxidized in 35 ml of acetate buffer, 10 ml of sodium metaperiodate solution (5.5 g/*l*), and 5 ml of water.

Oxidation period, min	20	30	60
$NaIO_4$/substance, molar ratio	1.6	1.85	2.05.

Summary

On the basis of a method previously known for inorganic mixtures, an accurate, rapid, and universal volumetric method for determining periodate ion after the oxidation of carbohydrates, including oligosaccharides and deoxy sugars, has been developed.

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