Note

The automated determination of iodate in periodate-oxidation mixtures*

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One of the methods required for the automated determination of the structure of polysaccharides is an assay for the uptake of periodate. This assay, when combined with the automated determination of formaldehyde released on periodate oxidation and an assessment of sugars remaining after periodate oxidation[1], would enable many details of the structure of the carbohydrate undergoing oxidation to be defined.

In oxidation studies, the consumption of periodate is generally measured by iodimetric titration of the unconsumed periodate[2], or by a spectrophotometric method based on the u.v. absorption of residual periodate and iodate formed in solution[3]. Since these procedures are not suitable for development into a method for the continuous monitoring of periodate in solution, attention was given to the colorimetric reactions between phenols and periodate[4,5].

The reaction of guaiacol and periodate gave a coloured product, the absorption of which in solution could be measured at 415 nm. No interference from formaldehyde and formic acid was found when the reaction was carried out in acetic acid (0.5M). However, when the method was applied to the study of periodate oxidations of carbohydrates, only a small excess of periodate could be tolerated; otherwise, the decrease in response as periodate was consumed could not be measured accurately from the chart recording.

For this reason, the method developed by Belcher and Townshend[6], whereby iodate formed by the Malaprade reaction was measured directly, was considered. In this method, the excess of periodate was masked with molybdate at pH 3 (the complex hexamolybdoperiodate being formed); the iodate was then treated with iodide to form tri-iodide, which was measured spectrophotometrically.

An automated system was developed based on the procedure of Nisli and Townshend[7], and a schematic representation is shown in Fig. 1. The absorbance of the solution at 340 nm was measured *ca.* 10 min after the mixing of the potassium iodide solution with the molybdate-masked solution. No interference from formic acid, formaldehyde, or other aldehydic products (when present in a two-fold molar excess with respect to iodate) was found under these conditions. Increase of the

*Dedicated to Professor M. Stacey, C.B.E., F.R.S., in honour of his 65th birthday.

development time to 30 min resulted in interference from formic acid and formaldehyde.

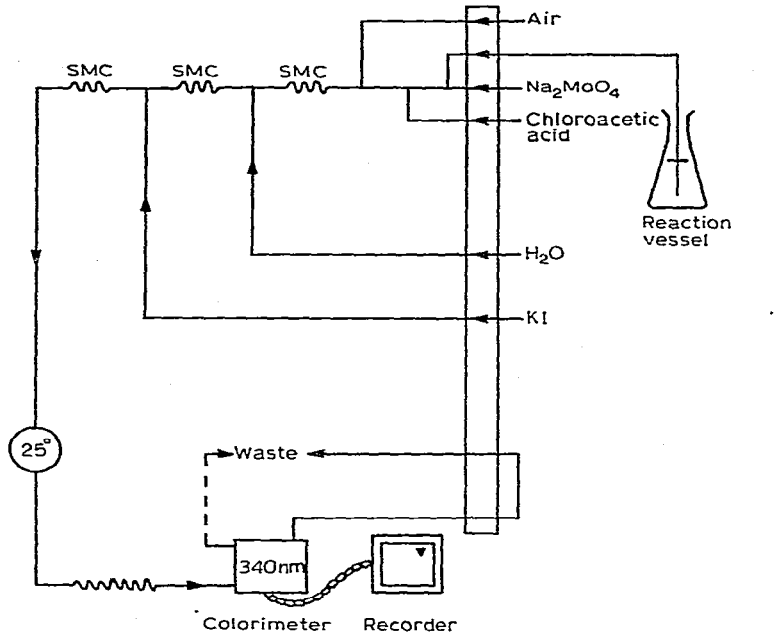

Fig. 1. Schematic representation of the automated system for the determination of iodate in periodate-oxidation mixtures. Reagent composition and flow rates: air (0.80 ml/min), sample (0.03 ml/min), sodium molybdate (20mM, 0.60 ml/min), chloroacetic acid (0.5M, adjusted to pH 3 by sodium hydroxide, 0.16 ml/min), water (1.37 ml/min), and potassium iodide (0.6 M, 0.60 ml/min).

A calibration curve must be constructed, using standard solutions of periodate and iodate, prior to the commencement of a series of oxidations. To establish an initial steady response, a periodate solution of appropriate concentration should be sampled for *ca.* 30 min prior to starting an experiment.

Several model compounds were subjected to oxidation in sodium periodate (10mM, 50 ml), and the results are summarised in Table I. The theoretical amounts of periodate were consumed by erythritol, D-threitol, D-mannitol, and methyl α-D-

TABLE I

Sample	*Weight (mg)*	*Oxidation time (h), at 20°*	*Uptake of periodate (mol.)*
Erythritol	0.98	2	3.06
D-Threitol	0.98	2	3.01
D-Mannitol	0.91	6	5.00
Methyl α-D-glucopyranoside	2.43	15	1.95
Lactitol	1.73	5	6.73

glucopyranoside, but lactitol underwent over-oxidation after 5 h at 20°. The oxidation curves of erythritol and D-threitol are shown in Fig. 2.

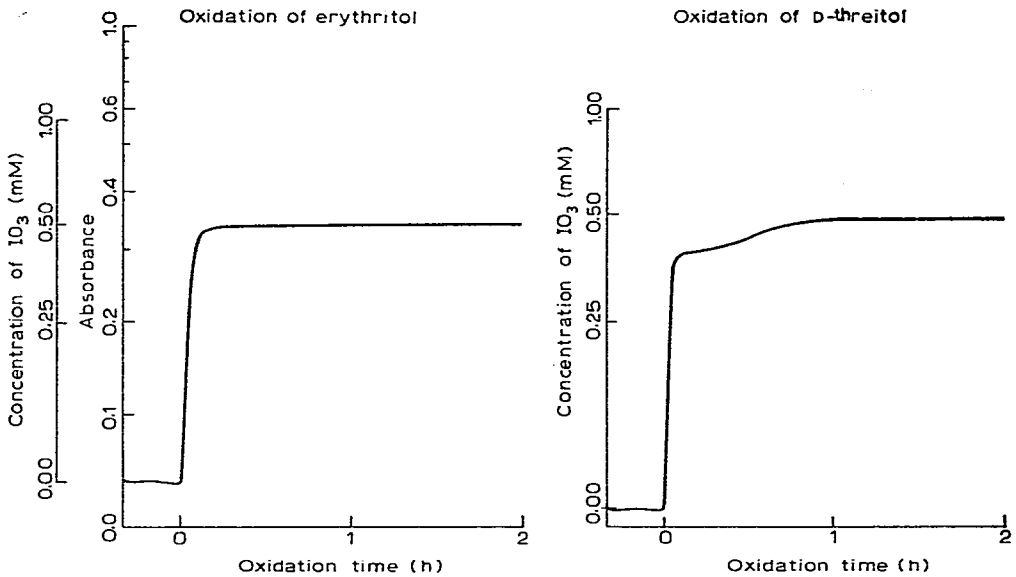

Fig. 2. Oxidation curves of the tetritols.

Although the method described is suitable for the continuous monitoring of the iodate produced in a solution undergoing periodate oxidation, it may readily be modified for determination of the periodate uptake of a series of compounds. The solution of carbohydrate is mixed with periodate solution of appropriate concentration, using air segmentation. The pumping rates of the solutions and the length of the mixing coil are suitably chosen to give a time interval sufficient for complete oxidation. The stream is then debubbled, and the solution recycled to the manifold where molybdate masking is performed.

EXPERIMENTAL

The flow diagram for the automated determination of iodate in oxidation mixtures is shown in Fig. 1. Technicon Autoanalyser modular equipment was used throughout. The periodate-oxidation mixture was sampled continuously (0.03 ml/min) from a flask equipped with a magnetic stirrer, and was mixed with sodium molybdate solution (0.60 ml/min) and chloroacetate buffer (0.16 ml/min) over a period of 3 min. Then, the air-segmented stream was mixed with water (1.37 ml/min) and aqueous potassium iodide (0.60 ml/min), and the mixture was passed through a coil maintained at 25° for 10 min. The absorption of the solution was measured at 340 nm in 15-mm flow-cells. Before the oxidation reaction of a carbohydrate was studied, the response

of the analytical system was calibrated by using standard solutions of sodium iodate and sodium periodate.

The sodium molybdate solution was clarified by filtration, and the potassium iodide solution was stored in a dark bottle to prevent decomposition by sunlight.

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