

Note

Iodometric determination of aldoses in the presence of magnesium oxide

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Oxidation with iodine under alkaline conditions has been widely used for the determination of aldoses^{1–4}. The reactions postulated for this oxidation are as follows.



Under carefully controlled conditions, the reaction is nearly quantitative; but with an excess of alkali and of iodine, over-oxidation of the aldose occurs. Romijn¹, who devised the method, used such buffer salts as alkaline carbonates, phosphates, and borax to control the alkalinity and avoid the over-oxidation that he found to occur with strong alkali. Later investigators have modified the method in various ways.

In the method of Willstätter and Schudel², the most widely used procedure, twice the volume of 0.05M iodine solution required for oxidation of the aldose is added. This is followed by dropwise addition of 1.5 times as much 0.1M sodium hydroxide solution. The mixture is kept for 15 min at room temperature, and the excess of iodine is then titrated, in acidified solution, with sodium thiosulfate. The iodine consumed represents that required for oxidation of the aldose, for over-oxidation, and for oxidation of other compounds present.

Under carefully controlled conditions, oxidation of the aldose to the aldonic acid takes place with relatively little over-oxidation, or oxidation of nonreducing carbohydrates. It is, however, difficult to control the amount of iodine available for reaction with the aldose, because part of the iodine is converted into iodate, which does not oxidize the aldose.



The extent of the iodate reaction varies with the experimental conditions. Thus, if the alkali and iodine are added rapidly, much of the iodine is consumed in the iodate reaction, rather than in the oxidation of the aldose. Although iodine is freed from the iodate when the solution is acidified and titrated with standard sodium thio-

sulfate, it is not available for oxidation of the aldose during the reaction period. In the analysis, a deficiency in the available iodine results in a low value, whereas an excess results in over-oxidation, and, consequently, in a high value.

In view of these considerations, we sought to make the procedure more consistent, and less susceptible to formation of iodate. The modification recommended consists chiefly in the use of the so-called "light" magnesium oxide as a buffer, to maintain the solution moderately alkaline (pH 9–10).

EXPERIMENTAL

Iodometric method for determination of aldoses. — Light magnesium oxide (~ 0.3 g) is added for every half millimole of aldose, contained in 10 mL of water. Standardized, 0.05M iodine solution is added with gentle shaking, in an amount sufficient to give, after 30 min, a back-titration of 2–5 mL of 0.05M sodium thiosulfate. After the reaction period, the mixture is acidified with 0.2M hydrochloric acid, and the unreacted iodine is titrated with the sodium thiosulfate (starch indicator). Each milliliter of iodine consumed in the oxidation represents 0.05 millimol of aldose. If the back-titration exceeds 2–5 mL of 0.05M thiosulfate, over-oxidation may have occurred. It is, therefore, advisable to repeat the determination with the amount of iodine solution suitably adjusted.

RESULTS AND DISCUSSION

Tables I to VI illustrate the advantages and limitations of the analytical method described. Table I shows that the amount of magnesium oxide in the reaction mixture is not critical, provided that some of the solid remains throughout the reaction period. The results in Table II show that the analytical method is applicable for the determination of aldoses in general. It is evident from Table III that the reaction time

TABLE I

OXIDATION OF D-GLUCOSE BY IODINE IN THE PRESENCE OF INCREASING AMOUNTS OF MAGNESIUM OXIDE^a

<i>0.05M I₂ added per 0.5 mmol of D-glucose (mL)</i>	<i>MgO (mg)</i>	<i>Back-titration with 0.05M Na₂S₂O₃ (mL)</i>	<i>I₂ consumed (mmol/mmol of D-glucose)</i>
12.50	37	4.00	0.850
12.50	75	2.71	0.979
12.50	150	2.48	1.002
12.50	225	2.58	0.992

^aReaction conditions: substrate (0.5 mmol) in water (10 mL); MgO as cited, and 0.05M I₂ solution (12.5 mL) added. Mixture kept, with gentle shaking, for 30 min at room temperature before back-titration.

TABLE II

REACTION OF VARIOUS ALDOSES WITH IODINE IN THE PRESENCE OF MAGNESIUM OXIDE^a

<i>Aldose</i>	<i>Sample (0.5 mmol) (mg)</i>	<i>I₂ consumed (mmol/mmol of substrate)</i>
D-Glucose	90	1.010
D-Galactose	90	1.000
D-Mannose	90	0.995
D-Xylose	75	1.025
D-Arabinose	75	1.005
D-Ribose	75	1.005
D-glycero-D-gulo-Heptose	105	0.990
Lactose hydrate	180	1.005
Maltose hydrate	180	0.980

^aReaction conditions: substrate (0.5 mmol) in water (10 mL); MgO (0.3 g) and 0.05M I₂ solution (12.5 mL) added. Mixture kept, with gentle shaking, for 30 min at room temperature before back-titration.

TABLE III

EFFECT OF REACTION TIME ON CONSUMPTION OF IODINE BY D-GLUCOSE^a

<i>0.05M I₂ added (mL)</i>	<i>Reaction time (min)</i>	<i>Back-titration with 0.05M Na₂S₂O₃ (mL)</i>	<i>I₂ consumed (mmol/mmol of D-glucose)</i>
12.50	15	4.37	0.813
12.50	25	2.90	0.960
12.50	30	2.40	1.010
12.50	45	2.33	1.017
12.50	60	2.10	1.040
12.50	120	1.90	1.060

^aReaction conditions: same as for Table II, except for the reaction times cited.

must be controlled, in order to obtain a satisfactory value for the aldose content. At room temperature, with a 5–20% excess of iodine, reaction times of 15–30 min give almost stoichiometric values, whereas longer times give higher values.

The results in Table IV show that, with an excess of iodine, sucrose and D-fructose *alone* consume appreciable amounts of iodine under the prescribed conditions. However, as indicated in Table V, D-fructose and sucrose interfere only slightly in the determination of aldoses. Apparently, the aldose consumes iodine rapidly, leaving little for reaction with other constituents in the solution.

The measurements shown in Fig. 1 and Table III show that the reaction of D-glucose with the iodine–magnesium oxide reagent is diphasic. An initial, almost stoichiometric, oxidation of the aldose to the aldonic acid is followed by a slow

TABLE IV

RESPECTIVE CONSUMPTION OF IODINE BY SUCROSE AND BY D-FRUCTOSE IN THE PRESENCE OF MAGNESIUM OXIDE^a

0.05M I ₂ added per 0.5 mmol of substrate (mL)	0.05M I ₂ consumed	
	by sucrose (mL)	by D-fructose (mL)
2.00	0.29	0.24
4.00	0.38	0.26
6.00	0.46	0.32
10.00	0.54	0.40
14.00	0.62	0.43

^aReaction conditions: same as for Table II, except for the quantities of iodine added.

TABLE V

OXIDATION OF D-GLUCOSE BY IODINE IN THE PRESENCE OF D-FRUCTOSE OR SUCROSE^a

D-Fructose in substrate (mmol)	0.05M I ₂ consumed (mmol/mmol of D-glucose)	Sucrose in substrate (mmol)	0.05M I ₂ consumed (mmol/mmol of D-glucose)
0.0	1.010	0.0	1.010
0.1	1.016	0.1	1.005
0.2	1.026	0.2	1.005
0.3	1.006	0.3	1.005
0.4	1.006	0.4	1.015
0.5	1.006	0.5	1.020

^aReaction conditions: same as for Table II, except that the substrate was 0.5 mmol of D-glucose plus the amount of D-fructose or sucrose indicated herein.

TABLE VI

CONSUMPTION OF IODINE BY MAGNESIUM D-GLUCONATE IN THE PRESENCE OF MAGNESIUM OXIDE^a

0.05M I ₂ added per meq of Mg D-gluconate (mL)	Reaction time (min)	Back-titration 0.05M Na ₂ S ₂ O ₃ (mL)	I ₂ consumed (mmol/meq of Mg D-gluconate)
12.5	15	11.85	0.65
12.5	30	11.30	1.20
12.5	45	10.80	1.70
12.5	60	10.40	2.10
12.5	120	8.90	3.60

^aReaction conditions: same as for Table II, except for the reaction times cited. The substrate was magnesium D-gluconate trihydrate.

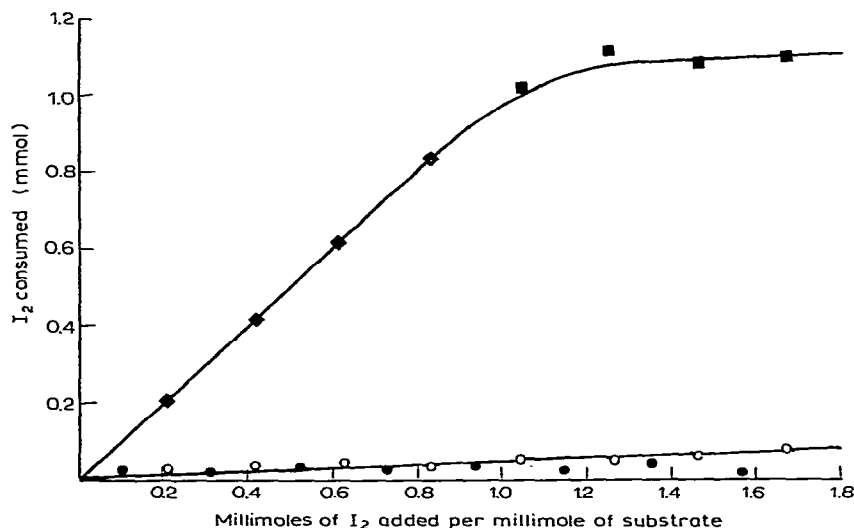


Fig. 1. Consumption of iodine by various substrates. [Reaction conditions as described in the iodometric method proposed, but with increasing amounts of iodine solution. ■, D-Glucose; ●, D-fructose; ○, sucrose.]

process involving oxidation of the primary oxidation product (magnesium D-gluconate). The results in Table VI show that magnesium D-gluconate is, in fact, slowly oxidized by iodine in the presence of magnesium oxide.

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