A Microanalysis for Periodate Oxidations

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THE value of the assessment of composition and structure of organic compounds by oxidation using periodic acid or its salts is well-known[1,2] as must also be the limitations imposed by the usual macrotitrations for the iodimetric determination of periodate in the presence of iodate. Here we report a polarographic method sensitive enough to be used on less than 1 μmole of sample.

Polarograms were obtained on a Heathkit Polarograph for a variety of experimental conditions including supporting electrolytes, maximum suppressors, voltage ranges, current sensitivities, concentrations of sample, and pH as controlled by buffers. A supporting electrolyte 0·01N in H_2SO_4, 0·2N in K_2SO_4 with a pH $\sim$ 3 was found to be suitable for the analysis of both periodate and iodate. As a maximum suppressor Triton X 100 was found to produce irregularities so gelatin was used instead. The polarographic cell contained 25 ml. of solution for study with provision for relating the potential of the dropping mercury cathode to a calomel reference electrode (s.c.e.).

Referred to the s.c.e., the half-wave potential for the iodate reduction occurred at $-0·28$ volt under

TABLE

Sample	μmoles	μmoles KIO$_4$			μmoles KIO$_4$ consumed per μmole sugar
		added	excess	consumed	
Glucose	0·20	2·00	1·11	0·89	4·5
	0·20	1·65	0·67	0·98	4·9
	0·40	2·00	0·38	1·62	4·1
	1·00	10·00	6·00	4·00	4·0
Arabinose	0·20	1·65	0·89	0·76	3·8
	0·40	4·00	2·40	1·60	4·0
	1·00	10·00	6·10	3·90	3·9
Mannitol	0·20	1·65	0·64	1·01	5·1
	0·40	4·00	1·91	2·09	5·2
	1·00	10·00	4·98	5·02	5·0

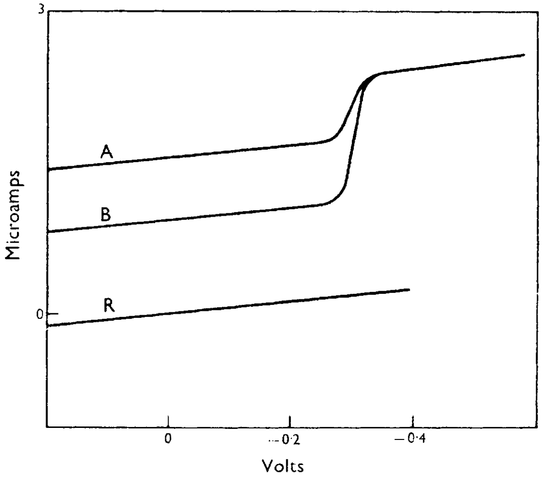
the above conditions and was more negative than this at higher pH. The half-wave potential for the periodate wave was somewhat obscured by anodic currents, occurring at about + 0·27 volt. The identities of these respective waves were substantiated by making individual additions of the appropriate species to enhance the wave heights. The wave heights were calibrated using standard solutions.

The nature of the polarograms obtained is shown schematically in the Figure, where curve A represents a polarogram for the oxidizing periodate solution alone and curve B that for the solution after oxidation of a carbohydrate sample. Curve R represents the residual current. It can be seen that the periodate current decrease owing to the loss of periodate is made up in the iodate wave so that the iodate wave remains virtually at the same absolute height on the graph; of course the iodate has increased relatively. This provides a check on the overall procedure. Incidentally, another valuable feature of this arrangement is that it does not matter if the periodate reagent solution used is not freshly made up but has undergone some decomposition (as it will on standing) to iodate which can be accounted for on the polarogram.

In the Table below are shown some results of such determinations of the periodate used on solutions to which glucose, mannitol, and arabinose were added individually in various amounts. It is interesting that an addition of KIO$_4$, nominally 2·0 μmole, turned out in fact to be 1·65 μmole on standing, but causing no particular inconvenience.

For mannitol and arabinose the agreement in number of μmoles of KIO$_4$ consumed by the vicinal hydroxyl groups determined and expected seems good enough to be decisive. In the case of glucose further investigation is required to ascertain whether it has more stability to oxidation owing to the formation of the formyl ester. This might also apply to arabinose.

Other features and possibilities of the above method are also under consideration. For example it would be possible to reduce the quantity of sample still further by a suitably designed microcell. The method could handle, for instance, the amount of sample obtained from a chromatograph. Also the addition of iodide as an intermediate or mediator to the above system has been done and appears capable of producing alternate determinations. However, the most fruitful aspect of all may be a kinetic study of the nature of the periodate oxidation itself, which will be started soon.



FIGURE

(*Received, May 15th,* 1967; *Com.* 466.)

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[1] F. Smith and R. Montgomery, "The Chemistry of Plant Gums and Mucilages", American Chemical Society Monograph 141, Reinhold, New York, 1959.

[2] R. L. Whistler, ed., "Methods in Carbohydrate Chemistry", Academic Press, New York, 1965.