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The Spectrophotometric Determination of Small Amounts of Hydrogen Peroxide in Aqueous Solutions*

By T. C. J. OVENSTON and W. T. REES

Synopsis—An accurate and precise method for the determination of microgram quantities of hydrogen peroxide in neutral aqueous solutions is described. The method depends on the liberation of iodine by the action of the hydrogen peroxide on potassium iodide, the reaction being catalysed by ammonium molybdate. The iodine liberated is determined by measurement of the absorption by the periodide ion at a wavelength of 353 mμ.

The comparative merits of the periodide and the starch-iodine methods for the absorptiometric determination of liberated iodine are examined, and comparison is made with the peroxidised titanium method for the determination of hydrogen peroxide.

When hydrogen peroxide is added to a solution containing an excess of iodide, iodine is set free according to the reaction

$$H_2O_2 + 2I' \rightarrow 2OH' + I_2.$$

The use of this reaction for the determination of hydrogen peroxide was proposed by Planes.[1] The reaction is slow in neutral solution but the rate increases with fall of pH, although the presence of acid accelerates the photolysis of the unused iodide and leads to erratic results.

Of the other absorptiometric methods which have been proposed, probably the most satisfactory is that based on the formation of the yellow complex when hydrogen peroxide is added to titanium sulphate in acid solution. This method has been adapted for abridged spectrophotometry by Allsopp[2] and by Eisenberg.[3]

Preliminary experiments suggested that the iodine method was very much more sensitive than the titanium method, and the iodine method was chosen for the present investigation when it was found that the reaction in neutral solution could be accelerated sufficiently by the addition of a small amount of ammonium molybdate. This catalyst has been employed in a titrimetric procedure using the same reaction.[4]

The purpose of this paper is to assess the merits of the principal methods available for the measurement of the liberated iodine, and to present a rapid and accurate method for determining microgram quantities of hydrogen peroxide in aqueous solutions.

In earlier work, the liberated iodine has been commonly determined by adding starch solution and comparing the blue colour of the starch - iodine complex with that of standards. This method has been studied very fully and it has been shown to possess some serious drawbacks. Starch itself is a material of variable composition, its two principal constituents being amylose and amylopectin. Amylose gives with iodine (in the presence of iodide) a deep blue complex, and amylopectin gives a somewhat less intense violet colour. The colour obtained with different batches of starch is thus liable to vary. In addition, the colour intensity is dependent on the concentration of iodide and the temperature of the solution, and it also lacks stability. Nevertheless, a fair degree of precision is possible if conditions are carefully controlled.

* After this paper had been written, another paper describing a spectrophotometric method for the determination of small concentrations of hydrogen peroxide was noted (Patrick, W. A., and Wagner, H. B., *Anal. Chem.*, 1949, **21**, 1279). The method is similar in principle to that described in the present paper, except that the liberation of iodine is carried out in an acid medium similar to that used in experiment D under the heading "Effect of acidity." The present writers are of the opinion that the optimum conditions for accurate quantitative work are obtained only when using an approximately neutral medium. In further confirmation of this, ten tests were made by each method, using 8·6 μg. of hydrogen peroxide in each test. The results can be summarised in the following way—

	Blank reading		Test reading		Test corrected for blank	
Method	Mean E	Standard deviation	Mean E	Standard deviation	Mean E	Standard deviation
Ovenston and Rees	0·0077	0·00067	0·7010	0·00245	0·6933	0·00275
Patrick and Wagner	0·0282	0·00567	0·7354	0·00977	0·7072	0·01268

The adherents of the starch - iodine technique have possibly been influenced by the apparently high sensitivity of the method when the colour is examined visually. Even when using a photo-electric absorptiometer, Sendroy[5] concluded that the relative colour intensity of the starch - iodine complex was about a hundred times that of the yellow colour of the periodide (I_3') ion present in iodine - iodide solutions, which also is proportional to the iodine content. However, Sendroy had employed filter systems which were decidely favourable to the starch - iodine method. Despite this, he recognised that the measurement of the yellow periodide was more convenient and gave more accurate results, and later, with Alving,[6] he found that the sensitivity could be increased at least fiftyfold by means of filters transmitting more in the ultra-violet.

Further spectrophotometric studies of the starch - iodine method have been made by Bairstow[7] and Pieters and Hanssen,[8] who have recommended it for the determination of the iodine liberated (in an adaptation of the Winkler method for oxygen in water), provided that suitable precautions are taken to ensure temperature control and standardisation of starch supply. Gross[9] has recommended spectrophotometric measurement of the absorption by the blue complex at a wavelength of 575 mμ.

Another method of measuring the liberated iodine depends on extraction with a solvent such as carbon disulphide, carbon tetrachloride or chloroform to give a violet solution. The efficiency of extraction of iodine from the aqueous phase depends very much on the concentration and nature of the salts present, and methods relying on a single partition therefore tend to be unreliable. At the same time, if the iodine is removed completely by a series of extractions, the total volume of the solvent so accumulated is so large that the sensitivity of the test is seriously reduced, concentration being impracticable owing to the volatility of the iodine.

Very recently, spectrophotometric methods for the determination of liberated iodine by means of the periodide ion have been reported by Shahrokh and Chesbro[10] and by Custer and Natelson,[11] extinction measurements being made in each case with a Beckman quart spectrophotometer. The latter authors published absorption spectra of iodine in water potassium iodide solutions, benzene, toluene, alcohol and chloroform, but did not study the starch - iodine complex. Of these spectra, that for iodine in potassium iodide showed the strongest absorption bands.

Comparison of sensitivities of methods for photo-electric spectrophotometry

Measurements were made with a Beckman quartz spectrophotometer (model DUV), using the tungsten-filament source at wavelengths above 320 mμ. and the hydrogen-arc source at lower wavelengths. Absorption spectra of six solutions were plotted, the concentration of free iodine being 4·5 μg. per ml. throughout. The solutions were—

A. 0·0002 *M* potassium iodide solution containing 500 μg. of starch per ml.
B. 0·002 " " " " " " "
C. 0·01 " " " " " " "
D. 0·1 " " " " " " "
E. 0·1 *M* potassium iodide, without starch.
F. Pure chloroform.

The starch was typical material supplied by the British Drug Houses Ltd. The starch - iodine colours were all developed and measured at 20° C., and the spectra are shown in Fig. 1. The absorption due to the chloroform solution is so small in relation to the other solutions as to require no further consideration in the present work.

For this concentration of iodine, at 20° C., it appears that the most intense absorption by the starch - iodine complex occurs in about 0·01 *M* potassium iodide solution. There is an indication of the formation of a different complex at higher concentrations of potassium iodide. The largest specific extinction for the starch - iodine system at 20° C., as obtained from curve C (Fig. 1) at 605 mμ., is 0·147 per cm. per p.p.m. of iodine. The corresponding values for the periodide ion in 0·1 *M* potassium iodide, as obtained from curve E (after correction for the absorption due to the presence of iodide), are 0·107 per cm. per p.p.m. of iodine at 353 mμ. and 0·145 per cm. per p.p.m. of iodine at 289 mμ. Using photo-electric receivers of adequate sensitivity for the various wavelengths concerned, the sensitivity of the periodide method is much greater than has generally been supposed, and is, in fact, about as sensitive as the starch - iodine method if measurements are made at 289 mμ. Even if measurements are made at 353 mμ., the periodide method still possesses three-quarters of the sensitivity of the starch - iodide method. In view of the many factors which render

the starch - iodide method liable to error, the best method for photo-electric measurement is clearly that using the absorption in the near ultra-violet part of the spectrum by the periodide ion.

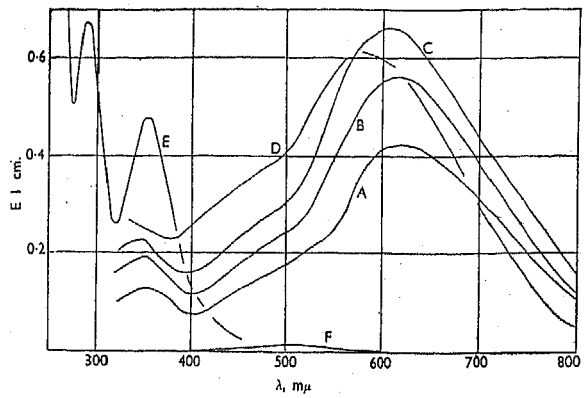

Fig. 1. Absorption spectra, based on an iodine concentration of 4·5 μg. per ml. Curves A, B, C, and D, starch - iodine complex developed with 0·0002 *M*, 0·002 *M*, 0·01 *M* and 0·1 *M* potassium iodide respectively. Curve E, I_3' complex developed with 0·1 *M* potassium iodide. Curve F, iodine in pure chloroform.

CHOICE OF WAVELENGTH—

Extinction - concentration graphs (not reproduced here) were plotted for various iodine concentrations in 0·1 *M* potassium iodide. In each case Beer's law was obeyed, but the error for measurements made at 289 mμ. was about four times as great as for those made at 353 mμ. There seems nothing to be gained by using the more intense peak, therefore, and all subsequent measurements of the periodide absorption were made at 353 mμ.

EFFECT OF POTASSIUM IODIDE CONCENTRATION—

The effect of potassium iodide concentration on the specific extinction at 353 mμ. was briefly examined. Fig. 2 shows the relation between the concentration of the potassium iodide and extinction for an iodine concentration at 6·3 μg. per ml. The slope of the curve is very slight for 0·1 *M* potassium iodide, and this strength was used for the determination of hydrogen peroxide.

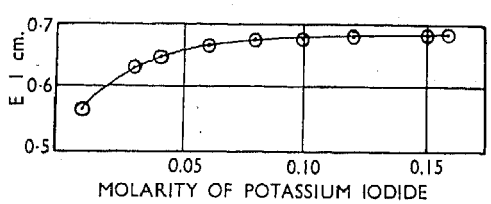

Fig. 2. Effect of concentration of potassium iodide on the development of the I_3' complex (extinction measurements at 353 mμ).

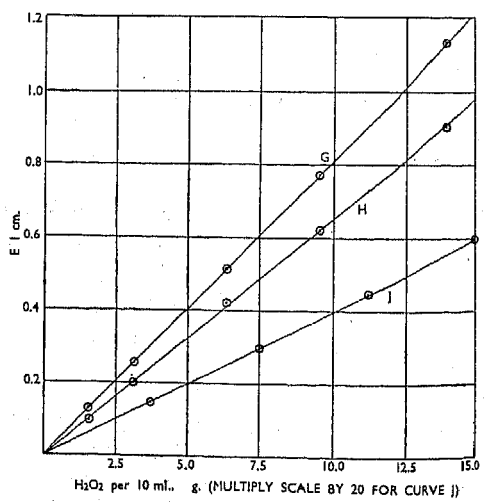

Fig. 3. Standard curves. Curve G, I_3' method at 353 mμ. Curve H, I_3' method adapted for Spekker absorptiometer. Curve J, Titanium method at 410 mμ.

Recommended method

Reagents—

Potassium iodide—0·2 *M* solution. If stored in the dark this will last at least a week. An increase in the extinction of the reagent blank indicates that it requires renewal; this value was normally about 0·010 in the present investigation.

Ammonium molybdate—0·5 per cent. w/v solution.

Hydrogen peroxide—0·0003 per cent. w/v solution. This is used for preparation of the calibration graph, and may be prepared by volumetric dilution of 0·03 per cent. w/v hydrogen peroxide which has been standardised against permanganate after thousandfold dilution of purest 30 per cent. reagent.

Procedure—

Take a volume of the neutral sample solution not exceeding 4 ml., containing not more than about 12 μg. of hydrogen peroxide, in a 10-ml. calibrated flask. Add 5 ml. of 0·2 *M* potassium iodide solution and 0·1 ml. of 0·5 per cent. w/v ammonium molybdate solution and dilute to the mark at 20° C. Allow to stand in the dark for 5 minutes and then measure the extinction of the solution at 353 mμ. using a 1-cm. cell. Correct this reading for actual cell thickness and subtract the extinction reading of the reagent blank, prepared similarly and at the same time, but with 4 ml. of water in place of the sample. Derive the hydrogen peroxide content of the sample by reference to a calibration graph prepared in the usual way by taking known amounts of 0·0003 per cent. w/v hydrogen peroxide covering the desired range, and plotting the weight against the extinction measurements after correction for the extinction of the reagent blank.

Adaptation of method for use with a Spekker photo-electric absorptiometer

Although the best results are obtained with a prism spectrophotometer, it is possible to use a photo-electric filter absorptiometer with very little loss of sensitivity. Using a mercury-arc lamp as source, a suitable filter combination consists of Calorex heat absorbing filters together with Wood's glass filters to isolate the 365-mμ. mercury line.

Effect of acidity

In order to demonstrate the advantage of using an approximately neutral medium for the liberation of the iodine, a series of five experiments, A, B, C, D and E (Table I), were conducted in which various amounts of sulphuric acid were added, the determinations being otherwise as described in the recommended method. The same amount of hydrogen peroxide, 8·9 μg., was present in each test, and a blank was run in the absence of peroxide in every experiment. The acid included in each experiment was sufficient to render the normality of the final 10 ml. of solution equal to the following values—

Experiment	A	B	C	D	E
Final normality of H_2SO_4 ..	nil*	0·01	0·1	0·2	1·0

* No acid added.

Extinction readings at 353 mμ. were taken over a period of time, the solutions being kept in the dark, and the results obtained are given in Table I.

It is clear from these experiments that the rate of further liberation of iodine from the potassium iodide increases markedly with increase of acidity, and that even a small amount of acid causes a comparatively large increase in the magnitude of the "blank" reading. In experiment A (no acid) a decrease instead of an increase in the extinction reading of the test solution was eventually recorded. This decrease became noticeable after the solution had stood for half an hour, and is typical of other similar experiments carried out by the recommended method.

Discussion

This method has been developed mainly for the determination of very small concentrations of hydrogen peroxide in pure water and in neutral salt solutions. The presence of large amounts of fluoride, chloride and bromide ions were shown to have no measurable influence on the absorption of the periodide solution.

The degree of accuracy that may be expected is shown by the position of the points from which the calibration graph was obtained; this graph is reproduced in Fig. 3 as curve

G. Curve H in the same figure is the corresponding graph obtained using a Spekker photoelectric absorptiometer with a mercury-arc source and the filters already mentioned. With monochromatic radiation of 353 mμ., unit extinction per cm. is obtained with 12·4 μg. of hydrogen peroxide per 10 ml. of final solution. The corresponding figure with the recommended filter system is 15·4 μg.

As a matter of interest, and as it might possibly be of use at higher concentrations of hydrogen peroxide, the titanium method was given a trial. The conditions specified by Allsopp[2] were followed, except that monochromatic radiation at 410 mμ. (the absorption maximum of the peroxidised titanium system) was used. The calibration graph is shown as curve J in Fig. 3, and the accuracy is again very good. However, it is well known that

TABLE I

EXTINCTION READINGS AT 353 Mμ.

Experiment A	Time, min.		5	10	15	32	60	90	115
	$E_{1\,cm.}$	Test*	0·725	0·725	0·721	0·725	0·717	0·695	0·685
		Blank	0·010	0·010	0·010	0·010	0·010	0·010	0·010
Experiment B	Time, min.		3	5	18	48	130		
	$E_{1\,cm.}$	Test*	0·720	0·720	0·730	0·740	0·750		
		Blank	0·030	0·028	0·035	0·050	0·063		
Experiment C	Time, min.		3	5	12	32	70	140	
	$E_{1\,cm.}$	Test*	0·738	0·748	0·750	0·765	0·789	0·858	
		Blank	0·036	0·037	0·040	0·050	0·070	0·105	
Experiment D	Time, min.		4	5	19	49	69	119	
	$E_{1\,cm.}$	Test*	0·750	0·750	0·780	0·828	0·859	0·898	
		Blank	0·050	0·050	0·063	0·081	0·089	0·145	
Experiment E	Time, min.		3	6	18	48	73		
	$E_{1\,cm.}$	Test*	0·778	0·802	0·866	0·933	1·040		
		Blank	0·103	0·109	0·130	0·198	0·236		

* The values of E recorded for the tests have not been corrected for their corresponding blanks.

many anions, particularly fluorides, have a profound effect on the formation of the peroxidised titanium complex, and the authors consider it safer to use the more sensitive periodide method wherever practicable. The range of the periodide method may be extended by volumetric dilution of the sample. Conversely, its sensitivity may be increased to a limited extent by the use of cells of greater optical depth, provided that their working capacity does not exceed 10 ml.

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