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Colorimetric Determination of Hydrogen Peroxide

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DURING a study of the effect of humidity on the production of ozone from air by the action of the silent electric discharge, qualitative tests revealed the formation of hydrogen peroxide. Attempts at quantitative estimation by means of the commonly employed volumetric methods and by those few colorimetric procedures (3, 4) reported in the literature were not entirely satisfactory. It was therefore necessary to develop a method which would be sensitive to very small amounts of peroxide. This procedure, in compari-
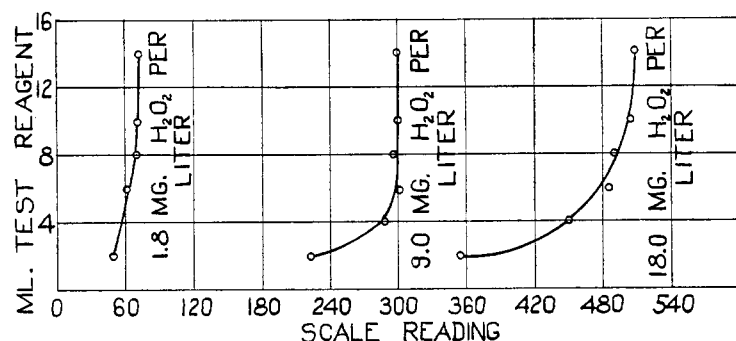

FIGURE 1. EFFECT OF VARYING QUANTITIES OF TEST REAGENT ON COLOR INTENSITY

K. & S. colorimeter, filter 40, cell depth 40 mm.

son with other methods based on the same chemical reaction, has the advantage of yielding a straight-line calibration curve over the concentration range specified.
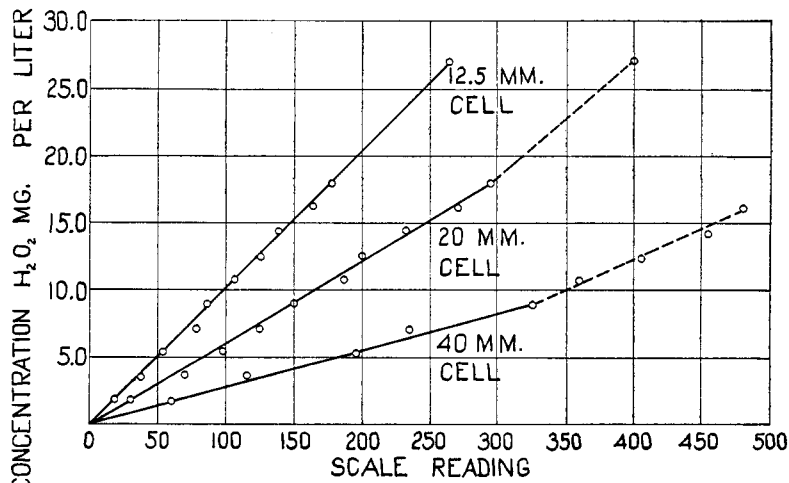
Principle of Method

The method is based on photoelectric measurement of the color intensities of hydrogen peroxide solutions treated with titanium sulfate reagent. The yellow color produced in the reaction was first observed by Schonn (5) and according to Treadwell and Hall (6) is due to the formation of pertitanic acid. The reaction equation is usually written

$$Ti^{++++} + H_2O_2 + 2H_2O = H_2TiO_4 + 4H^+$$

although some chemists prefer to write the formula of pertitanic acid as $TiO_2.H_2O_2$, showing a true peroxide structure. It was Jackson (2) who pointed out the quantitative possibilities. Richardson (4) and Knecht (3) developed methods in which colors were compared visually. More recently Allsop (1) reported on a photoelectric method which is discussed in greater detail below.

Reagents and Solutions

All reagents were of the purest grade obtainable.

The titanium sulfate test reagent was prepared by digesting 1 gram of anhydrous titanium dioxide (Schering-Kahlbaum) with 100 ml. of sulfuric acid (specific gravity 1.84) for 15 to 16 hours on a sand bath at a temperature of 150° C.

The solution was cooled, diluted with 4 parts (by volume) of distilled water, and filtered through an asbestos mat prior to use. Preliminary experiments in which varying quantities of reagent, ranging from 2 to 50 ml., were diluted to 100 ml. with distilled water indicated no color or turbidity to be present.

A standard hydrogen peroxide solution was made by diluting 20 ml. of 30 per cent hydrogen peroxide solution to 1 liter with distilled water and standardized by titration with permanganate.

Apparatus

The photoelectric colorimeter was a Klett-Summerson Model 900-3 in which was used a KS-40 filter (transmission limits 380 to 430 millimicrons). An unusual feature of this instrument is the scale on which readings are made. This scale is logarithmic and has been designed so that under certain specified conditions the scale readings are a measure of and are proportional to the optical density of the colored solution as determined by the photoelectric cell. Since the optical density is theoretically proportional to the concentration of the colored substance, the scale readings are likewise proportional to the concentration under the specified conditions.

Optimum Quantity of Test Reagent for Maximum Color Development

To ascertain whether the intensity of color is a function of the quantity of titanium sulfate used, varying quantities of the test reagent were added to known quantities of hydrogen peroxide solution contained in a series of 100-ml. Nessler tubes. All solutions were then diluted to 100-ml. volume with distilled water and the intensity of color was measured by transferring to the solution cell of the colorimeter. In all, three such experiments were made in which concentrations of 18, 9, and 1.8 mg. of hydrogen peroxide per liter were used. Cell depth was 40 mm. Results are shown graphically in Figure 1.

It is evident that 1 volume of titanium sulfate reagent per 10 volumes of peroxide solution is required for maximum color development. As far as could be ascertained, the color is developed instantly and remains stable for at least 6 hours. In view of this finding, 10 ml. of reagent were used in all subsequent experiments.

FIGURE 2. CONFORMITY TO BEER'S LAW

TABLE I. ACCURACY OF METHOD

(12.5-mm. cell)

Scale Reading Divisions	Concentration of H₂O₂ Mg./100 ml.		Deviation Mg./100 ml.
	Actual	Calculated	
18	0.18	0.18	0.00
38	0.36	0.39	+0.03
54	0.54	0.55	+0.01
78	0.72	0.80	+0.08
86	0.90	0.88	−0.02
106	1.08	1.08	0.00
125	1.26	1.27	+0.01
139	1.44	1.42	−0.02
164	1.62	1.67	+0.05
177	1.80	1.80	0.00
263	2.70	2.68	−0.02
		Av.	±0.03

Conformity to Beer's Law

A series of solutions, containing from 1.8 to 27 mg. of hydrogen peroxide per liter, was prepared by placing the appropriate quantity of peroxide in 100-ml. Nessler tubes, adding 10 ml. of titanium sulfate reagent to each tube, and diluting to the mark with distilled water. After thorough mixing the solutions were transferred to the colorimeter cell. Color intensity was measured using three different cell depths: 40, 20, and 12.5 mm.

That Beer's law is followed by the color system is evident from the fact that a straight line is obtained when the scale readings are plotted against the hydrogen peroxide concentration (Figure 2). The deviation from the straight-line relationship for the higher color intensities (scale readings above 300) observed in the cases of the 20- and 40-mm. cell depths is probably due to the fact that a relatively wide band-pass filter was used. The use of a smaller cell, 12.5 mm., eliminates this deviation and increases the effective range of the method. In view of this, in order to obtain conformity to Beer's law throughout any given range of concentrations, it is necessary that the cell depth be adjusted to the colorimetric system.
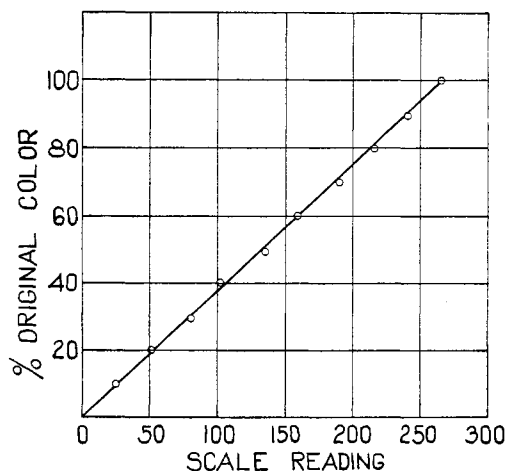

FIGURE 3. EFFECT OF DILUTION ON COLOR INTENSITY

Figure 3 shows the results of tests made to determine whether relatively dark solutions could be diluted and still have the resultant color system conform to Beer's law. It is obvious that this can be done.

Allsop (1) reported on a photoelectric method which, although similar in some respects to the one described herein, does not give a linear calibration curve over the entire concentration range nor does it cover the same range of concentra-
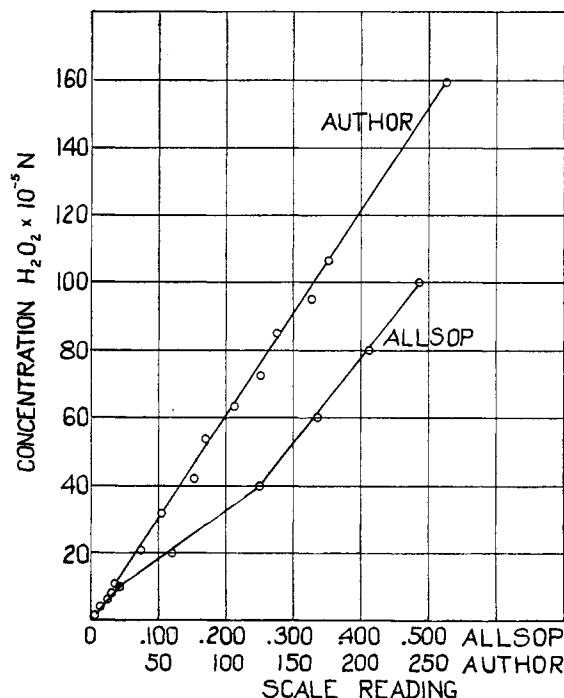

FIGURE 4. COMPARISON OF ALLSOP'S AND AUTHOR'S DATA

tions. Using a Hilger absorptiometer equipped with a 4-cm. cell and a blue filter giving maximum transmission at 470 millimicrons, he measured the optical densities of solutions containing varying amounts of hydrogen peroxide treated with titanium sulfate. For purposes of comparison, his data are shown graphically in Figure 4, together with the results obtained by the author. The difference in the linear character of the two curves is obvious.

The accuracy with which hydrogen peroxide can be determined with this method is shown in Table I. With the 12.5-mm. cell it is possible to determine hydrogen peroxide in concentrations ranging from approximately 0.2 to 3.0 mg. per 100 ml. with an average deviation of ±0.03 mg. per 100 ml.

Summary and Conclusions

A rapid and accurate colorimetric method for the determination of hydrogen peroxide is described. Beer's law is valid for measurements at 380 to 430 millimicrons. However, in order to obtain conformity to Beer's law throughout any given range of concentration, it is necessary that the cell depth be adjusted to the colorimetric system. A 12.5-mm. cell increases the effective range of the method, permitting determination of hydrogen peroxide concentrations ranging from approximately 0.2 to 3.0 mg. per 100 ml. of solution with an average deviation of 0.03. Relatively dark solutions can be diluted without invalidating Beer's law. For maximum color development 1 volume of test reagent per 10 of solution is required.

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