ESTIMATION OF POTASSIUM DICHROMATE OR CHROMATE AND HYDROGEN PEROXIDE IN THE PRESENCE OF EACH OTHER

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Hydrogen peroxide can be determined in the presence of potassium dichromate concentrations not exceeding 700 μM or potassium chromate concentrations not exceeding 1400 μM, by its reaction with potassium ferricyanide in 1N KOH solutions. The decrease in potassium ferricyanide concentration is measured spectrophotometrically at 418 mμ. An extinction coefficient value of 959 cm^{-1} mole^{-1} was determined for ferricyanide in 1N KOH at room temp (29°C). Potassium dichromate can be determined directly in the presence of hydrogen peroxide in alkaline solution by its absorption at 373 mμ. The extinction coefficient value for potassium chromate above pH 9 is 4690 cm^{-1} mole^{-1} and the value calculated for dichromate concentrations is 9380 cm^{-1} mole^{-1}.

The usual methods for the determination of hydrogen peroxide are not directly applicable to alkaline solutions containing potassium dichromate or chromate. Such mixtures can be separated by the use of ion exchange resins and the hydrogen peroxide then estimated.[1] A spectrophotometric method for estimation of hydrogen peroxide based on the reaction:

$$H_2O_2 + 2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$
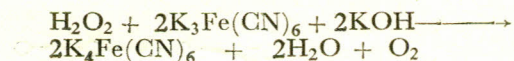
has recently been developed by the authors.[2] It is applicable to the direct determination of hydrogen peroxide in basic solutions containing potassium dichromate or chromate. The change in potassium ferricyanide concentration is measured at 418 mμ spectrophotometrically. Ferrocyanide ion does not absorb at this wavelength.

Experimental and Results

Chemicals.—Potassium dichromate and chromate (E. Merck) of analytical purity were dried at 130°C for a few hours and cooled in a desiccator.

Potassium ferricyanide (A. R.) was dried at 60°C for 20 hr and cooled in a desiccator.

Potassium ferrocyanide (A. R.) was dehydrated by heating at 110°C for 24 hr and cooled in a desiccator.

Hydrogen peroxide 50% solution was used as received from the Food Machinery and Chemical Corporation, U. S. A.

Distilled water was redistilled from alkaline KMnO$_4$ in a stream of oxygen.

Standard KOH solutions were either from British Drug Houses or were prepared from A. R. potassium hydroxide.

The solutions of potassium ferricyanide (325 μM) and potassium dichromate (600 μM) in 0.001N and 1N KOH showed no change in optical density at the absorption maximum of ferricyanide ion (418 mμ) after many hours standing. Thus ferricyanide ion is quite stable in alkaline dichromate solutions. Potassium dichromate has an appreciable absorption at 418 mμ, and it was compensated in blanks.

No absorption at 418 mμ appeared for ferricyanide ion after many hours in 0.001N and 1N KOH solutions containing potassium ferrocyanide (700 μM) and potassium dichromate (260 μM) indicating that potassium ferrocyanide is not oxidized by dichromate in alkaline solutions.

Hydrogen peroxide decomposes catalytically in alkaline solutions. The rate of decomposition increases with the concentration of alkali. Hydrogen peroxide at a concentration of 4336 μM in 0.1N KOH and at concentration of 1657 in 1N KOH decomposed at room temperature (27-30°C) by about 43% in 44 hr and 59% in 16 hr, respectively. The presence of 230 μM of potassium dichormate did not affect the decomposition rate of hydrogen peroxide in 1N KOH solution.

The rate of reaction of hydrogen peroxide with potassium ferricyanide in 0.1N KOH solution is retarded by the presence of potassium dichromate. A mixture containing 62 μM dichromate, 400 μM hydrogen peroxide and about 1000 μM potassium ferricyanide in 0.1N KOH took about 140 min. for complete disappearance of hydrogen peroxide through its reaction with potassium ferricyanide. In the absence of potas-

sium dichromate the reaction time is about 13 min. In 1N KOH solutions the retarding effect of dichromate on the reaction rate of hydrogen peroxide and potassium ferricyanide is nearly absent. The time required for completion of reaction in 1N KOH in absence or presence of dichromate is about 5 min.

The absorption of potassium ferricyanide at 418 mµ n 1N KOH is lower than in 0.1N KOH or water solutions. The extinction coefficients at room temperature (29°C) are:

ε for 0.1N KOH and water solutions[2]
$$= 1012 \text{ cm}^{-1} \text{ mole}^{-1}$$
ε for 1N KOH solution $= 959 \text{ cm}^{-1} \text{ mole}^{-1}$

Potassium dichromate at high concentration suppresses and shifts the absorption maximum of ferricyanide ion bathochromically. However, these effects are not observable for mixtures, containing potassium ferricyanide at a concentration of 829 µM and potassium dichromate at concentrations of 1625 µM and less. Potassium dichromate at high concentrations interferes with the estimation of hydrogen peroxide and the interference disappears only at a concentration of about 700 µM or so of dichromate.

Estimation of Hydrogen Peroxide in Presence of Potassium Dichromate.—Various standard solutions of hydrogen peroxide, potassium dichromate and 5N KOH were used in the analyses. To perform the analysis, an aliquot of alkali was added to an aliquot of potassium dichromate. A known volume of hydrogen peroxide solution was added to the stirred mixtures. A known volume of potassium ferricyanide solution was then added. The mixture was diluted to a definite volume with distilled water. The final solution had 1N KOH strength, and ferricyanide concentration was more than double the concentration of H_2O_2 expected. The mixture was allowed to stand for 15 min. The blanks of potassium ferricyanide at an alkali strength of 1N KOH, with and without potassium dichromate were prepared. The blank of potassium ferricyanide without dichromate was compared with 1N KOH and the final solution with the blank of ferricyanide with dichromate at 418 mµ in 1-cm silica cells. The difference between the optical density measured for the blank of ferricyanide without dichromate, and for the final solution provides a direct measure of the ferricyanide reduced by H_2O_2. The difference divided by 2 × ε (ε = 959 cm⁻¹ mole⁻¹) gave the value for the concentration of H_2O_2 in final solution. In some experiments, the order of mixing of solutions was changed to alkali, dichromate, ferricyanide and then hydrogen peroxide. No effect on the results was observed. The results

of a series of analyses are summarized in table I. The standard deviation of the analyses is ±4.2%.

Absorption Spectrum of Potassium Dichromate.— In acidic solutions potassium dichromate has an absorption peak at 350 mµ [3-7] and another peak has been reported at 440 mµ by Nozaki and Ueno,[6] and at 450 mµ by Cardone and Compton,[3] and by Farhataziz and Dyne.[7] The absorption is dependent upon the acid concentration of the solution. The absorption spectrum of dichromate changes as pH is raised to higher values (Fig. 1)*.

TABLE 1.—A COMPARISON OF THE CONCENTRATIONS OF HYDROGEN PEROXIDE EXPECTED IN ITS MIXTURES WITH POTASSIUM DICHROMATE AT A CONCENTRATION OF 709 µM WITH THOSE CALCULATED ON THE BASIS OF POTASSIUM FERRICYANIDE REDUCED IN 1N KOH SOLUTIONS.

(H_2O_2) expected µM   551 415 346 281 277 156 140   77 39

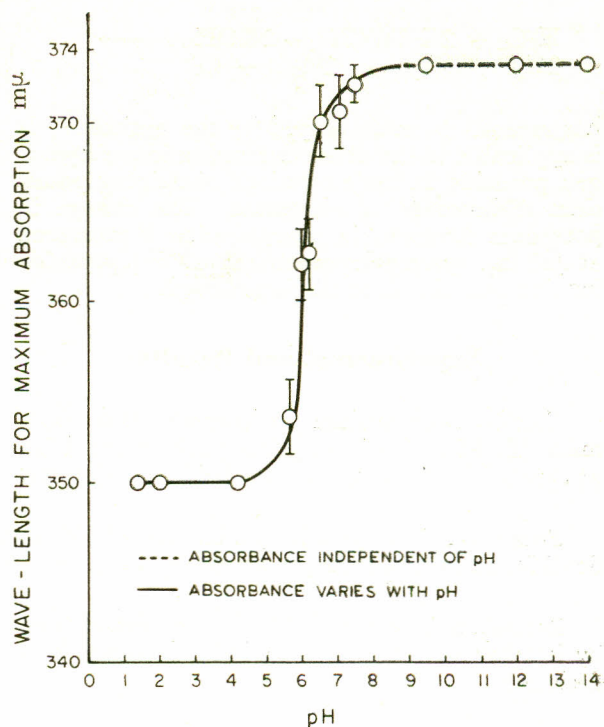(H_2O_2) measured µM   547 412 347 285 273 152 147   78 35

Fig. 1.—The pH dependence of wavelength for maximum absorption by potassium dichromate solutions

*The changes in pH were affected only by changing the concentration of potassium hydroxide.

The maximum at 350 mμ slowly shifts to higher wavelength with increasing pH and reaches 373 mμ at pH 8.5; after which an increase in pH has no effect on the wavelength for maximum absorption. Above pH 9 the absorbance is independent of pH. This behaviour of dichromate absorbance is due to the fact that with increasing pH dichromate is increasingly changed to chromate:

$$Cr_2O_7^{--} + H_2O \rightleftharpoons 2HCrO_4^-$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{--} + H_2O$$
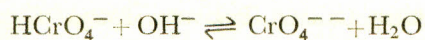
This is proved by the fact that absorption spectra as measured in 1-cm silica cell at room temperature (29°C) for dichromate at a concentration of 70 μM, and for chromate at a concentration of 140 μM in 0.1N KOH solutions are identical (Fig. 2). These spectra are identical to the spectrum of chromate as reported by Englis and Wollerman,[4] and Davies and Prue.[5]

The Beer-Lambert law is obeyed by dichromate solutions. The absorbance of dichromate solutions in 0.1N KOH in 1-cm silica cell at room temperature (29°C) is shown in Fig. 3. The extinction coefficient is 9380 cm-[1] mole-[1].

Hydrogen peroxide at a concentration of about 8000 μM in 0.1N KOH has no absorption at 373 mμ. Thus mixtures of H_2O_2 and dichromate at 373 mμ give optical densities only due to dichromate.

Estimation of Dichromate in Presence of Hydrogen Peroxide.—The various required volumes of a standard solution of hydrogen peroxide were added to an aliquot of 2N KOH. After shaking, the various volumes of a standard solution of potassium dichromate were added. The mixtures were then diluted with distilled water to such volumes so that final solutions had 1N KOH concentration. These mixtures were now compared in 1-cm silica cells versus a blank of 1N KOH at 373 mμ. From the optical densities dichromate concentrations were calculated. The whole experiment was repeated for measurements in 0.001N KOH. The results are summarized in Table 2.

The extinction coefficient for dichromate solution is the same both in 1N or 0.001N KOH.

Application of Method to Chromate and H_2O_2 Mixtures.—Above pH 9 chromate and dichromate have identical behaviour. The mixtures of chromate and H_2O_2 above pH 9 can be analyzed by the method described above. For H_2O_2 estimation, chromate concentration in final made up volume
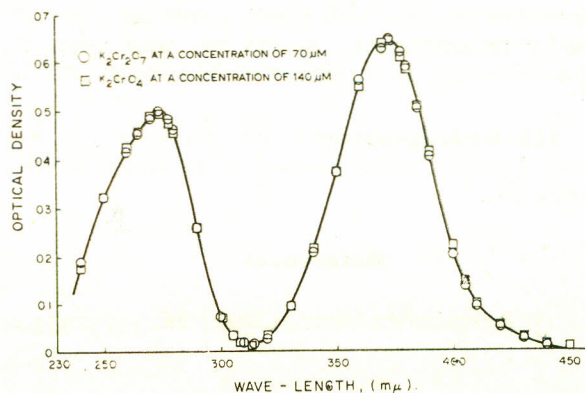

Fig. 2.—Absorption spectra of potassium dichromate and potassium chromate in 0.1N KOH solutions.
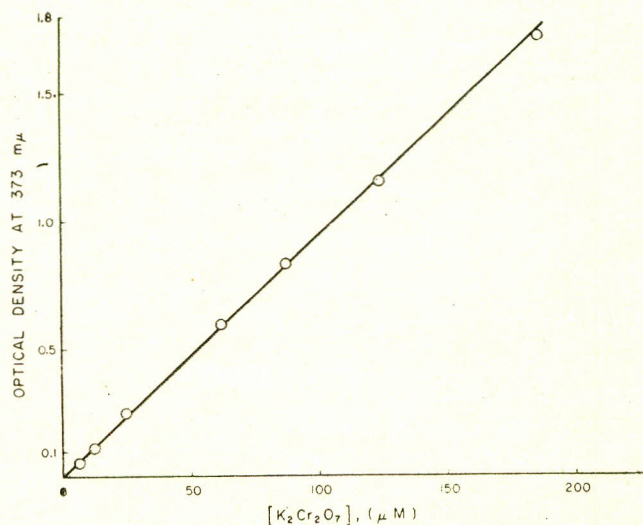

Fig. 3.—Conformity to Beer-Lambert Law by potassium dichromate in 0.1N KOH solution.

TABLE 2.—A COMPARISON OF THE CONCENTRATIONS OF POTASSIUM DICHROMATE EXPECTED IN ITS MIXTURES WITH HYDROGEN PEROXIDE AT A CONCENTRATION OF 1657 μM WITH THOSE CALCULATED ON THE BASIS OF OPTICAL DENSITIES MEASUREMENTS AT 373 mμ IN ALKALINE SOLUTIONS.

($K_2Cr_2O_7$) expected, μM	172	115	57.4	23
($K_2Cr_2O_7$) measured in 1N KOH, μM	172	116	57.7	22
($K_2Cr_2O_7$) measured in 0.001N KOH, μM	172	115	57.7	22.4

must be less than 1400 μM. The chromate concentration can be calculated from the optical density measurements at 373 mμ and using a value of extinction coefficient of 4690 mole^{-1} cm^{-1}.

References

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