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The Color Reaction between Chromium(III) Ion and Potassium Ferrocyanide*

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The observation of the orange-coloring reaction between potassium ferrocyanide and the chromium(III) ion on filter paper and its application in the paper chromatographical analysis of the chromium(III) ion has been reported on previously by the present authors. The color reaction has now been observed in an aqueous solution as well and studied in relation to the reaction temperature, the reaction time, the characteristic absorption, the species of chromium(III) salts, the chromium(III) ion concentration, the pH level, and the presence of an acetic acid buffer, by measuring the absorption spectra of the reaction solutions. The recommended conditions for getting a satisfactory color reaction and a suitable wavelength for the measurement of this color reaction have been presented.

In continuation of previous work[1] on the color reaction of potassium ferrocyanide with chromium(III) ions on filter paper, the present paper will report on the coloration which takes place in an aqueous solution.

When Cr^{3+} and $K_4[Fe(CN)_6]$ were mixed together in an aqueous solution, the color of the solution gradually changed to reddish orange and its intensity reached near the maximum within 1.5—3 hr. at room temperature; on the other hand, the reaction proceeded more quickly at a higher temperature, a satisfactory coloration being obtained in 15 min. at 50°C.

With regard to the reaction solution described above, the absorption spectra at various Cr^{3+} concentrations for visible light and the variation in the spectra during the reaction were measured. It was thus found that the maximum variation in color intensity was observed at a wavelength between 410 and 420 mμ. It was also found that, in the case of a reaction for 15 min. at 50°C, a strictly linear relationship held between the extinction at 415 mμ and the Cr^{3+} concentration.

The major part of the experiments in this work was done with chrome alum as the representative source salt of Cr^{3+}, and the chromium(III) ion will be referred as having a more general significance in the statement of the experimental results, because of the preliminary experimental proof of the agreement in extinction at 415 mμ of the reaction solutions derived from different chromium(III) salts, such as chromic chloride and chrome alum.

In the course of studying the relation between the pH value and the coloration, interference with the coloration by the acetic acid - sodium acetate buffer was found.

The coloration caused by the present reaction is thought to be due to the formation of a complex anion containing chromium; attempts to isolate such a complex in a crystalline form are now in progress.

Experimental

The Absorption Spectra of Reaction Solutions at Various Cr^{3+} Concentrations.—Solutions of chromium(III) ions from $KCr(SO_4)_2 \cdot 12H_2O$ and potassium ferrocyanide solutions were mixed together in the various ratios shown in Fig. 1, and the absorption spectrum of each solution was measured after 3-hr.'s reaction at room temperature (Fig. 1). The extinction was found to vary widely in accordance with the Cr^{3+} concentration in the wavelength range between 410 and 420 mμ.

The Relation between the Color Intensity and the Reaction Time.—With the Cr^{3+} and $K_4[Fe(CN)_6] \cdot 3H_2O$ used in the final concentrations of 40 μg./cc. and 10 mg./cc. respectively, the absorption spectra were measured after reaction at room temperature for the times of 0, 20, 40, 60, 100, 140 and 180 min. (Fig. 2). In this experiment, the color intensity almost attained its maximum within 100 min. after mixing.

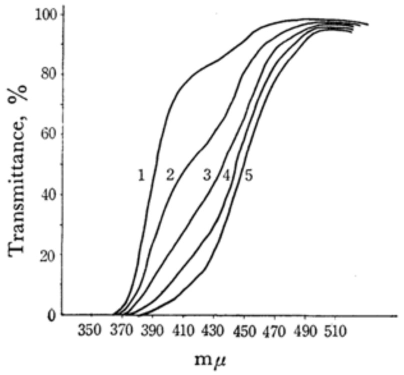

Fig. 1. Absorption curves of the reaction solutions at varying Cr^{3+} concentrations observed after 3-hr.'s reaction at room temperature.
Concentration of $K_4[Fe(CN)_6] \cdot 3H_2O$ after mixing is 10 mg./cc. in each case.

Curve No.	1	2	3	4	5
Cr^{3+} concn. after mixing, μg./cc.	0	10	20	30	40

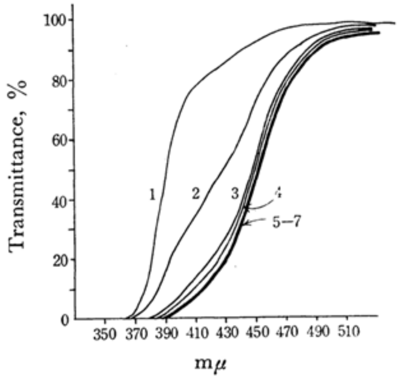

Fig. 2. Absorption curves at varying times after mixing.
Concentrations of Cr^{3+} and $K_4[Fe(CN)_6] \cdot 3H_2O$ after mixing are 40 μg./cc. and 10 mg./cc. respectively.

Curve No.	1	2	3	4	5	6	7
Period of time after mixing, min.	0	20	40	60	100	140	180

Experiments at 50°C.—The reaction time could be shortened with the elevation of the reaction temperature until the temperature attained 50°C, at which point a satisfactory coloration was obtained in only 15 min. A temperature above 50°C, however, was not desirable because the reaction solution became turbid.

The Relation between the Extinction at 415 mμ and the Cr^{3+} Concentration.—The solutions of chromium(III) ions and potassium ferrocyanide were mixed together in the various ratios shown in Fig. 3 and allowed to react together for 15 min. at 50°C;

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* A part of this work was orally disclosed at the 11th Annual Meeting of the Japanese Society of Analytical Chemistry, Sapporo, July, 1962.

[1] Y. Matsumoto and M. Shirai, *Japan Analyst* (*Bunsekikagaku*), **12**, 608 (1963).

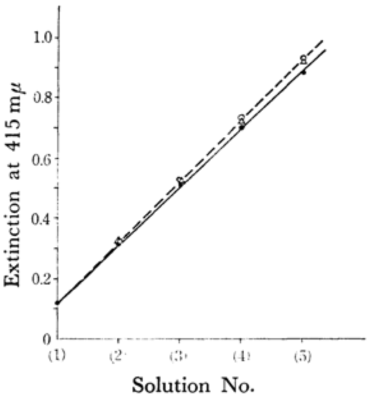

Fig. 3. Relation between color intensity and Cr^{3+} concentration after the reaction for 15 min. at 50°C.

(○) green } chromic chloride soln. (----)
(△) blue }
(●) chrome alum soln. (——)

Concentration of $K_4[Fe(CN)_6]\cdot 3H_2O$ after mixing is 5 mg./cc. in each case.

Solution No.	(1)	(2)	(3)	(4)	(5)
Cr^{3+} concn. after mixing, μg./cc.	0	10	20	30	40

then the extinction of each reaction solution was measured at 415 mμ (Fig. 3). The results showed a strictly linear relationship between the color intensity and the Cr^{3+} concentration.

A Comparison of the Different Chromium(III) Salts.—A chromic chloride solution in a green color and one in a blue color, considered to contain chiefly the species $[Cr(H_2O)_4Cl_2]^+$ and $[Cr(H_2O)_5Cl]^{2+}$ respectively, were prepared; then the chromium(III) concentration in each solution was determined by the titration method using potassium permanganate and iron(II) sulfate solutions. These chromic chloride solutions were treated with a potassium ferrocyanide solution, and the extinction was measured under the conditions stated in Fig. 3, and compared with the chrome alum solution, which corresponds to $[Cr(H_2O)_6]^{3+}$. The extinctions of the both chromic chloride solutions agreed exactly with each other, and agreed fairly well with that of the chrome alum solution at the same chromium(III) concentrations.

Restriction in pH Value.—This color reaction was not satisfactory at low pH levels, especially below 2, and not an orange but a light blue color was caused at pH levels below 1.5 due to the decomposition of potassium ferrocyanide.

The Effects of Using an Acetic Acid - Sodium Acetate Buffer.—An acetic acid - sodium acetate buffer was found to interfere considerably with this coloration. One evidence responsible for the interference was that the acetic acid itself, reacting with potassium ferrocyanide, gave rise to some coloration during the requisite time for the purposed reaction, which is 1.5—3 hr. in the case of room temperature. At 50°C, however, the purposed reaction proceeded so quickly that the coloration by the reaction between acetic acid and potassium ferrocyanide was found to be negligible. The other interfering factor of acetic acid was its reaction with chromium, which resulted in a considerable decrease in the color intensity of the reaction solution. Thus the presence of acetic acid as a buffering agent is undesirable for this color reaction.

Summary

The color reaction of potassium ferrocyanide with chromium(III) ions in an aqueous solution has been observed. The absorption spectra of the reaction solutions for visible light were measured, and the coloration in relation to the reaction temperature, the reaction time, the characteristic absorption, the species of chromium(III) salts, the Cr^{3+} concentration, the pH level, and the presence of an acetic acid buffer has been studied.

For getting a satisfactory color reaction and for measuring it, a reaction for 15 min. at 50°C and an extinction measurement at 415 mμ were found to be best.

Between the extinction and the Cr^{3+} concentration in the solution of a given chromium(III) salt, a strictly linear relationship held. The same concentration of Cr^{3+} ions from different chromium(III) salts, such as chrome alum and chromic chloride, proved to give almost the same extinction.

This color reaction was not satisfactory at low pH levels. An acetic acid buffer interfered strongly with the coloration.

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