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Spectrophotometric Determination of Hexacyanoferrate(III) by Use of Coagulated Material Prepared from Finely Divided Anion and Cation Exchange Resins

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A simple and sensitive method for the determination of hexacyanoferrate(III) is described. This method is based on the preconcentration of hexacyanoferrate(III) ion on the coagulated material prepared from finely divided anion and cation exchange resins. The mixed resin is collected on a filter paper, forming a disk of thin layer. The hexacyanoferrate(III) fixed on the resin is converted to Turnbull's Blue by treating with iron(II) ammonium sulfate solution. The colored compound in the resin phase is determined by a densitometer equipped with a linearizer. The working range is 0.4—3.0 μmol dm^{-3} hexacyanoferrate(III). Among cations likely to be present, only copper(II) interferes, however, the interference is removed by the addition of EDTA. Hexacyanoferrate(II) ion shows the same coloration as hexacyanoferrate(III), and the total amount is determined when both ions are present.

Mutual coagulation takes place when a suspension of finely divided anion and cation exchanger is mixed with each other.$^{1)}$ The resulting coagulated material is bulky and easily separated from the solution by filtration. By use of a cylindrical filter holder, a disk of thin layer of the mixed resin is prepared on a filter paper. Metal complexes with negative and/or positive charge are much more effectively fixed on the mixed resin than simple ions. When a colored complex is retained on the resin, the resulting thin layer is directly subjected to spectrophotometric analysis. In this manner, chromium(VI) was determined as the diphenylcarbazide compound,$^{2)}$ and phosphate as the Molybdenum Blue complex,$^{3)}$ both in ppb range.

The determination of hexacyanoferrate(III) is important in environmental analysis. Yogo *et al.*$^{4)}$ reported a method in which hexacyanoferrate(II) and (III) were converted to the 1,10-phenanthroline complex and determined spectrophotometrically, in which, after adding mercury(II) heating was required for accelerating the ligand exchange reaction. In the present report, hexacyanoferrate(III) is selectively concentrated on the mixed resin and determined as Turnbull's Blue.

Experimental

Reagents. All chemicals used were of analytical reagent grade.

Standard hexacyanoferrate(III), 10^{-2} mol dm^{-3} solution was prepared by dissolving potassium salt in water.

Standard hexacyanoferrate(II), 10^{-2} mol dm^{-3} solution was also made by dissolving potassium hexacyanoferrate(II) trihydrate in water containing 0.05% of sodium carbonate.

Iron(II) ammonium sulfate, 0.5 mol dm^{-3} solution was prepared by dissolving Mohr's salt in water containing 0.06 mol dm^{-3} hydrochloric acid.

Sodium chloride, 1 mol dm^{-3} solution was used to adjust the ionic strength of sample solutions.

Ion exchange resin suspension. The ion exchangers used were macroreticular type Amberlyst 15 and A-27 (both Rohm and Haas Co.) in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively. The cation exchange resin suspension (CRS) and the anion exchange resin suspension (ARS) were prepared according to the method already reported.$^{1)}$ The ion exchange capacities of CRS and ARS were determined by conductometric titration with the sodium hydroxide and silver nitrate solutions, respectively. The exchange capacities were 9.73 μequiv. ml^{-1} for CRS and 2.43 μequiv. mol^{-1} for ARS. When one part of CRS was mixed with two parts of ARS, both resins were almost completely coagulated.$^{1)}$

Apparatus. A Shimadzu Chromatoscanner CS-920 was used for absorption measurement. A Shimadzu UV-visible recording spectrophotometer, type UV-240, was used for measuring absorption spectra. A Toyo KG-25 filter holder was used for the preparation of thin layer of the mixed resin by filtration. Filter papers of No. 5A (Toyo Roshi) were used.

All experiments were carried out at room temperature.

Procedure. An aliquot of sample solution containing more than 20 nmol of hexacyanoferrate(III) is placed in a 100-ml beaker. A 5-ml portion of 1 mol dm^{-3} of sodium chloride is added for controlling the ionic strength and the volume is adjusted to 50 ml with water. A 3-ml portion of CRS and 6 ml of ARS are added. The mixture is stirred for 5 min by means of a magnetic stirrer. The resulting coagulated resins are collected on the filter paper by suction with a running water. A disk of thin layer of the mixed resin of 17 mm in diameter and about 0.3 mm in thickness is prepared. It is then dipped into the iron(II) ammonium sulfate solution for 1 h to develop the coloration. The wet filter paper holding the colored resin is placed on a white plastic plate fixed on the scanning board in the apparatus. The center of the disk of thin layer is exposed by a light beam, the section area is 1.44 mm^2. The board is periodically moved from side to side in a range of 24 mm wide, so that the absorbance of the thin layer is determined against the filter paper substrate. The absorbance is measured at 630 nm and the value is printed out automatically.

Another disk of resin is prepared without addition of hexacyanoferrate(III). The absorbance corresponding to the reagent blank including the resin matrices is also measured. The net absorbance of the complex in the resin phase is obtained as the difference.

Results and Discussion

Preparation of Thin Layer. During the course of stirring, hexacyanoferrate(III) ion is fixed on the anion

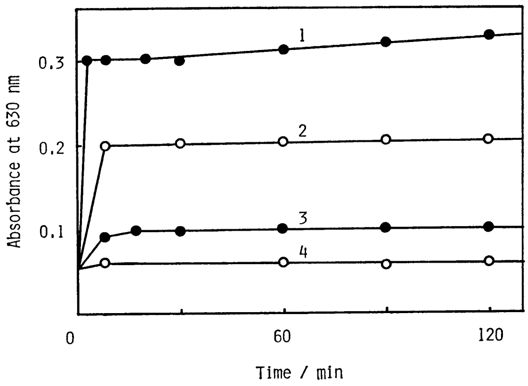

Fig. 1. Rate of color development at various concentrations of hexacyanoferrate(III).
(1): 2.0 μM, (2): 1.2 μM, (3): 0.4 μM, (4): blank. Sample volume: 50 ml.

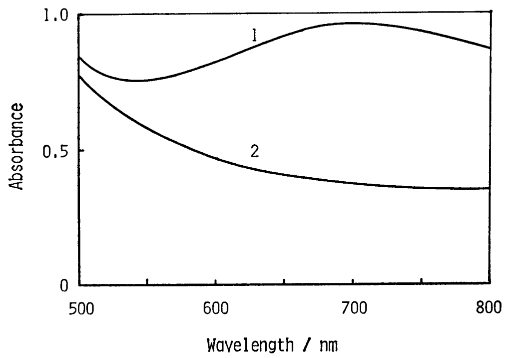

Fig. 2. Absorption spectra of the Turnbull's Blue on the thin layer of mixed resin prepared from 50 ml of solution.
(1): 2.0 μM of hexacyanoferrate(III), (2): blank, reference: wet filter paper.

exchanger and the latter is simultaneously combined with the cation exchanger, forming a coagulated material. The homogeneous dispersion of the mixed resin in the sample solution is essential for preparing the thin layer with a smooth surface. The degree of dispersion depends on the ionic strength of the sample solution. The finely dispersed mixed resin was obtained from the solution containing sodium chloride in 0.1—0.3 mol dm^{-3}. The average rate of filtration was about 30 ml min^{-1}. When sodium chloride was added too much, a long time was required for collecting the coagulated material.

Color Development. The color producing reagent used was 0.5 mol dm^{-3} of iron(II) ammonium sulfate. With decreasing concentration of the reagent, a longer dipping time was needed for the coloration of Turnbull's Blue. The dependence of coloration on the soaking time was examined with varying concentrations of hexacyanoferrate(III). A rapid coloration was found at the higher hexacyanoferrate(III) concentration, while at the lower concentration more than 20 min were necessary for obtaining a constant coloration (Fig. 1). The blue coloration was stable at least for 1.5 h in the iron(II) salt solution.

Absorption Measurement. The absorbance of Turnbull's Blue in the resin phase was determined by the densitometer at 630 nm, that is the upper limit of measurable wavelength of the apparatus. Since the complex has an absorption maximum at around 700 nm, higher sensitivity would be obtainable, if the measurement at the maximum wavelength is possible (Fig. 2).

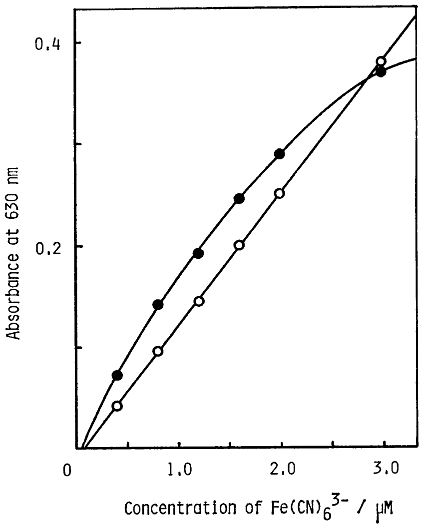

Fig. 3. Calibration curve.
○: Linearizer on, ●: linearizer off. Sample volume: 50 ml.

Collection of Hexacyanoferrate(III). A trace amount of hexacyanoferrate(III) was effectively fixed on the mixed resin by stirring the sample mixture for 5 min, even in the presence of 0.3 mol dm^{-3} of sodium chloride. The recovery was considered to be quantitative, since the hexacyanoferrate(III) was not found in the filtrate. A 100-nmol portion of hexacyanoferrate(III) was quantitatively collected from 50—200 ml of sample solution.

Effect of pH. The pH of test solution was adjusted with the addition of hydrochloric acid or sodium hydroxide solution. A constant absorbance was obtained for the given amount of hexacyanoferrate(III) in the pH range of 1—12.

Calibration Curve. The calibration curve deviated from the linearity. By use of the linearizer a good linearity was obtained, however, the line did not go through the origin (Fig. 3). The relative standard deviation was 2.4% (n=6) for 1.2 μmol dm^{-3} of hexacyanoferrate(III).

Effect of Foreign Ions. Among the diverse ions studied, copper(II) interfered with the determination of 1 μmol dm^{-3} of hexacyanoferrate(III) even in the same concentration level (Table 1). When the concentration of foreign ions was 100 times hexacyanoferrate(III), copper(II), mercury(II), and zinc(II) gave negative error, while silver(I) a positive one. The interference from copper(II) was successfully eliminated by EDTA. The addition of EDTA was also effective for masking zinc(II), manganese(II), and lead(II) even in 1000 times concentration of hexacyanoferrate(III).

Effect of Hexacyanoferrate(II). As well known, hexacyanoferrate(II) combines with iron(III) to form

TABLE 1. EFFCT OF FOREIGN IONS ON THE DETERMINATION OF HEXACYANOFERRATE(III)[a)]

Ion	Concentration/M			
	10^{-6}	10^{-5}	10^{-4}	10^{-3}
	Relative error/%			
Ca(II), Mg(II), Cd(II), Ni(II), Co(II), Fe(II), Fe(III), Cr(III), Al(III)				none[b)]
Zn(II)		none	−7	−10 (none)[c)]
Cu(II)	−8	−56	−93 (none)	−88 (−24)
Mn(II)			none	−14 (none)
Pb(II)			none	−17 (none)
Hg(II)		none	−9 (−8)	−64 (−75)
Ag(I)		none	+11	>+100

a) $Fe(CN)_6^{3-}$: 10^{-6} M. b) None: within 5% error. c) ( ): In the presence of EDTA.

the familiar Prussian Blue. The spectrophotometric determination of hexacyanoferrate(II) as the Prussian Bule was reported.[5,6)] Galik and Vopravilova extracted the Prussian Blue into chloroform in the presence of a quaternary ammonium ion.[6)]

Hexacyanoferrate(II) was found to be fixed on the mixed resin and showed a blue coloration as well as hexacyanoferrate(III); namely, the Prussian Blue and Turnbull's Blue are the same compound.[7)] In the presence of hexacyanoferrate(II) and (III), the sum of them was determined (Table 2).

TABLE 2. DETERMINATION OF HEXACYANOFERRATE(II) AND (III)

$Fe(CN)_6^{3-}$ taken (nmol)	$Fe(CN)_6^{4-}$ taken (nmol)	Total taken (nmol)	Total found (nmol)	Relative error / %
0	50	50	51.0	+2.0
0	80	80	80.7	+0.9
0	100	100	99.7	−0.3
50	30	80	78.7	−1.6
50	50	100	99.7	−0.3

Sample volume: 50 ml.

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