

Metal Ion Promoted Ligand-Exchange of Cyanide Ion in Potassium Hexacyanoferrate(II) by Aromatic Nitroso Compound: Part III—Spectrophotometric Determination of Ag(I) Using Nitroso-R-salt

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Ag(I) promoted abstraction of CN^- from potassium hexacyanoferrate(II) in the presence of excess nitroso-R-salt has been utilised for the spectrophotometric determination of Ag(I) in the concentration ranges 0.05-0.5 $\mu\text{g/ml}$ at pH 4.0 and 60°C and 0.5-11.0 $\mu\text{g/ml}$ at pH 6.6-7.0 and 85°C.

In continuation of our earlier spectrophotometric determinations of Ag(I) and Hg(II) in microgram level by kinetic method using 2,2'-bipyridyl and 1,10-phenanthroline¹⁻⁴, sodium 1-nitroso-2-hydroxynaphthalene 3,6-disulphonate (nitroso-R-salt)^{5,6} and nitrosobenzene⁷⁻⁹, we report herein the use of nitroso-R-salt for Ag(I) promoted ligand-exchange of CN^- in potassium hexacyanoferrate(II) for the determination of Ag(I) in sub-micro gram level (0.05-11.00 $\mu\text{g/ml}$).

Solutions of $\text{K}_4\text{Fe}(\text{CN})_6$, nitroso-R-salt and AgNO_3 (all AR grade) in doubly distilled water were used throughout. Acetate buffer (0.01 mol dm^{-3}) and ammonium acetate (0.01 mol dm^{-3}) were used for maintaining the pH at 4.0 and 6.6-7.0 respectively. Absorbance was measured using a Spectronic-21 UV visible spectrophotometer and pH using a Perkin-Elmer Metrion V pH meter.

Determination of Ag(I)

For the determination of Ag(I) in the concentration range 0.05-0.5 $\mu\text{g/ml}$, thermally equilibrated solutions (60° ± 0.5) of AgNO_3 (0.1-1 ml; $10^{-4} \text{ mol dm}^{-3}$), $\text{K}_4\text{Fe}(\text{CN})_6$ (1,3,5 ml; $10^{-3} \text{ mol dm}^{-3}$), nitroso-R-salt (4 ml; $10^{-2} \text{ mol dm}^{-3}$) and the acetate buffer solution (pH 4.0) were mixed and the volume made upto 20 ml. The solution was transferred to the cuvette of the spectrophotometer maintained at the same temperature and absorbance measured at 720 nm, the λ_{max} of the product. Similarly the absorbances of the blank solutions without Ag(I) were also determined and subtracted from the above values to give the net

absorbances due to Ag(I) promoted abstraction of CN^- .

For the determination of Ag(I) in the concentration range 0.5-11.0 $\mu\text{g/ml}$, AgNO_3 (0.1-2.0 ml; $10^{-3} \text{ mol dm}^{-3}$) were mixed with aliquots of $\text{K}_4\text{Fe}(\text{CN})_6$ ($10^{-3} \text{ mol dm}^{-3}$), nitroso-R-salt (4 ml; $10^{-2} \text{ mol dm}^{-3}$) and ammonium acetate buffer ($10^{-2} \text{ mol dm}^{-3}$) to maintain the pH at 6.6-7.0 and the volume made upto 20 ml. The solution was heated for 15 min at 85°C, cooled in freezing mixture bath and absorbance measured at 720 nm. Under these conditions the reaction was complete and the absorbance remained constant. Simultaneously blanks were also treated similarly and their absorbances subtracted to get net absorbance due to Ag(I).

For studying the effect of various common cations and anions $\text{K}_4\text{Fe}(\text{CN})_6$ (5 ml; $10^{-3} \text{ mol dm}^{-3}$), NRS (4 ml; $10^{-2} \text{ mol dm}^{-3}$), AgNO_3 (2 ml; $10^{-3} \text{ mol dm}^{-3}$) and water soluble sulphates and nitrates were mixed, volume made upto 20 ml and heated at 85°C for 15 min in the case of pH 6.6-7.0 and absorbance measured at 720 nm. Similar procedure was employed at pH 4.0 using AgNO_3 (1 ml; $10^{-4} \text{ mol dm}^{-3}$) and the solution heated at 60°C for 10 min and blanks were treated under identical conditions.

Excellent linear correlation exists between absorbance and Ag(I) concentration in the range 0.05-0.5 $\mu\text{g/ml}$ (Fig. 1), the optimum $\text{K}_4\text{Fe}(\text{CN})_6$ concentration is in the range $1.5-2.5 \times 10^{-4} \text{ mol dm}^{-3}$, so that the blanks were not too high. The calibration graphs and the results of linear regression analysis with standard

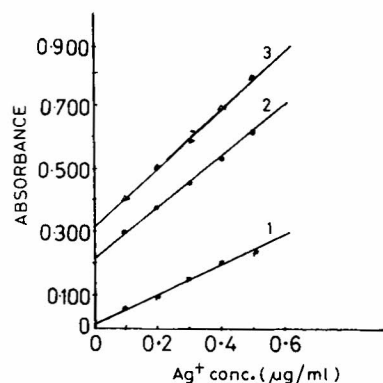


Fig. 1—Absorbance of $\text{Fe}(\text{NRS})_3^{1-}$ versus $[\text{Ag}^+]$ ($\mu\text{g/ml}$) at 60°C ± 0.5 after 10 min at pH 4.0; concentrations of $\text{K}_4\text{Fe}(\text{CN})_6$: 1, 0.5; 2, 1.5; 3, 2.5 ($10^{-4} \text{ mol dm}^{-3}$) Linear regression equations:

$$A = 0.258 \pm 0.009 \times 10^5 [\text{Ag}^+] + 0.018 \pm 0.013;$$

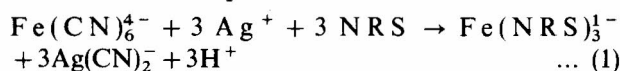
$$A = 0.443 \pm 0.009 \times 10^5 [\text{Ag}^+] + 0.210 \pm 0.001;$$

$$A = 0.509 \pm 0.005 \times 10^5 [\text{Ag}^+] + 0.110 \pm 0.014;$$

(Origin for 1 at 0.200 absorbance)

deviation of slope and intercept at 99.5% confidence level are given in the figures.

The green product formed in the reaction was predominantly $\text{Fe}(\text{NRS})_3^{1-}$ as found for the reaction of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{Hg}(\text{II})$ in the presence of nitroso-R-salt⁵. The formation of $\text{Fe}(\text{NRS})_3^{1-}$ was further confirmed by comparison of the spectrum with that of $\text{Fe}(\text{NRS})_3^{1-}$ formed by the interaction of ammonium ferrous sulphate with nitroso-R-salt. Mol ratio method gave break at $[\text{AgNO}_3]/[\text{Fe}(\text{CN})_6^{4-}]$ ratio > 2.5 , in accordance with stoichiometric Eq.(1). This is in conformity with the abstraction of CN^- in the presence of other ligands like 2,2'-bipyridyl⁴ and nitrosobenzene⁷ reported earlier.



This was also verified from the spectrophotometric titration of Ag^+ (20 ml; $1.5 \times 10^{-4} \text{ mol dm}^{-3}$) with $\text{K}_4\text{Fe}(\text{CN})_6$ (0.1 to 0.5 ml; $10^{-3} \text{ mol dm}^{-3}$), the absorbance being measured after heating the reactants in the presence of excess nitroso-R-salt at 85°C for 15 min. This gave a slope of $1.75 \pm 0.05 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{Fe}(\text{CN})_6^{4-}$. Similarly $\text{K}_4\text{Fe}(\text{CN})_6$ (1 ml; $10^{-3} \text{ mol dm}^{-3}$) heated with excess AgNO_3 (4 ml; $10^{-3} \text{ mol dm}^{-3}$) and excess nitroso-R-

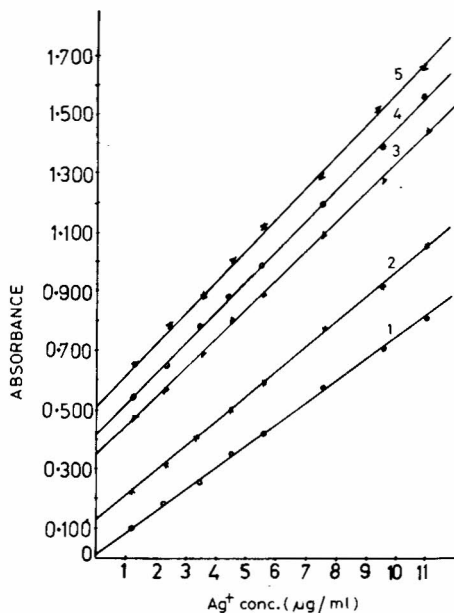


Fig. 2—Absorbance of $\text{Fe}(\text{NRS})_3^{1-}$ versus $[\text{Ag}^+]$ ($\mu\text{g}/\text{ml}$) at $85^\circ\text{C} \pm 0.5$ after 15 min at pH 6.6-7.0; Concentrations of $\text{K}_4\text{Fe}(\text{CN})_6$: 1, 0.5; 2, 2.5; 3, 5.0; 4, 7.5; 5, 10.0 ($10^{-4} \text{ mol dm}^{-3}$) Linear regression equations:

$$A = 0.801 \pm 0.012 \times 10^4 [\text{Ag}^+] + 0.029 \pm 0.002;$$

$$A = 0.918 \pm 0.023 \times 10^4 [\text{Ag}^+] + 0.133 \pm 0.013;$$

$$A = 1.182 \pm 0.078 \times 10^4 [\text{Ag}^+] + 0.141 \pm 0.025;$$

$$A = 1.187 \pm 0.066 \times 10^4 [\text{Ag}^+] + 0.117 \pm 0.022;$$

$$A = 1.187 \pm 0.042 \times 10^4 [\text{Ag}^+] + 0.113 \pm 0.030;$$

(Origin for I, II and III at 0.200, 0.300 and 0.400 absorbance respectively)

Table 1—Tolerance Limit of Various Ions $[\text{K}_4\text{Fe}(\text{CN})_6] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{NRS}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{AgNO}_3] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$; pH = 6.6-7.0; time = 15 min; temp = $85^\circ\text{C} \pm 0.5$

Ion	Concentration mol dm^{-3}	Relative error* %
Hg^{2+}	1×10^{-7}	(+) 4.80 ± 0.28
Pt^{4+}	1×10^{-7}	(+) 3.00 ± 0.42
Zn^{2+}	1×10^{-5}	(-) 5.20 ± 0.92
CO^{2+}	1×10^{-4}	(-) 3.80 ± 0.82
Cu^{2+}	1×10^{-4}	(-) 2.50 ± 0.73
Mn^{2+}	1×10^{-5}	(-) 4.00 ± 0.85
Pb^{2+}	1×10^{-4}	(-) 4.80 ± 0.73
Cd^{2+}	1×10^{-4}	(-) 8.20 ± 0.43
Cl^-	1×10^{-4}	(+) 0.52 ± 0.20
SO_4^{2-}	1×10^{-4}	(+) 0.60 ± 0.35
I^-	1×10^{-4}	(-) 5.30 ± 0.61
CN^-	1×10^{-7}	(-) 4.50 ± 0.50

* Average of at least three replicates.

salt gave an absorbance of $1.8 \pm 0.05 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. These are in agreement with the molar absorptivity of the $\text{Fe}(\text{NRS})_3^{1-}$ complex⁵.

At pH 4.0 as explained earlier⁴, $\text{Ag}(\text{I})$ concentration is constant over reasonable period of time and the reaction can be deemed catalytic abstraction of CN^- .

The rate of formation of $\text{Fe}(\text{NRS})_3^{1-}$ at pH 4.0 is given by Eq.(2).

$$\frac{d[\text{Fe}(\text{NRS})_3^{1-}]}{dt} = k_1 [\text{Fe}(\text{CN})_6^{4-}] + k_2 [\text{Ag}^+] [\text{Fe}(\text{CN})_6^{4-}] \quad \dots (2)$$

where, k_1 is the first order rate constant for the decomposition of $\text{Fe}(\text{CN})_6^{4-}$ at this pH, k_2 is the rate constant for the reaction between $\text{Ag}(\text{I})$ and $\text{Fe}(\text{CN})_6^{4-}$. Since a large excess of $\text{K}_4\text{Fe}(\text{CN})_6$ is used and the reaction is followed only for a short time; $[\text{K}_4\text{Fe}(\text{CN})_6]$ is practically constant and hence the rate of formation of $\text{Fe}(\text{NRS})_3^{1-}$ is linearly correlated with $[\text{Ag}(\text{I})]$. The time and concentration of $\text{Fe}(\text{CN})_6^{4-}$ are so chosen such that the absorbance due to catalysed path is larger than that due to the uncatalysed path. The slopes of absorbance versus $[\text{Ag}(\text{I})]$ plots increase with increase in $[\text{K}_4\text{Fe}(\text{CN})_6]$ suggesting a second order reaction between $\text{Ag}(\text{I})$ and $\text{Fe}(\text{CN})_6^{4-}$.

At pH 6.6-7.0, slope value increases with increase in $[\text{Fe}(\text{CN})_6^{4-}]$ from 0.5×10^{-4} to $5 \times 10^{-4} \text{ mol dm}^{-3}$ and remains constant beyond this value till $[\text{K}_4\text{Fe}(\text{CN})_6]$ is $10^{-2} \text{ mol dm}^{-3}$ (Fig. 2). The slopes are reproducible at all concentrations of $\text{K}_4\text{Fe}(\text{CN})_6$ and excellent linear correlation exists between $[\text{Ag}(\text{I})]$ and absorbance. The reason may be due to both incomplete reaction at lower $[\text{K}_4\text{Fe}(\text{CN})_6]$ and high absorbance of blanks at higher $[\text{K}_4\text{Fe}(\text{CN})_6]$.

This method was tested for different quantities of Ag^+ added from synthetically prepared AgNO_3 solutions in pH 6.6-7.0 and pH 4.0 and found to give

very good results, the relative per cent error being in the range 5.0 at 5×10^{-6} to 0.36 at $5.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Ag}^+$.

The effects of various interfering ions and their tolerance limits at pH 6.6-7.0 are given in Table I which also hold good for pH 4.0. Interference by Pt(IV) and Hg(II) at much lower concentration is due to their capacity to promote the abstraction of CN^- from $\text{Fe}(\text{CN})_6^{4-}$. Cd(II), Cu(II) and Mn(II) interfere at concentrations equivalent to that of Ag(I). Iodide and cyanide ions interfere more seriously than Cl^- and SO_4^{2-} .

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