Journal of Chromatography, 386 (1987) 173–183
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 968

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC SEPARATION AND QUANTITATION OF CYANIDE AS THE DICYANOBIS(1,10-PHENANTHROLINE)IRON(II) COMPLEX

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SUMMARY

The separation and quantitation of cyanide at trace levels by high-performance liquid chromatography as the dicyanobis(1,10-phenanthroline)iron(II) complex is described. Cyanide is determined in the 10–200 ppm range using photometric detection at 548 nm and down to 0.10 ppm using photometric detection at 262 nm or with electrochemical detection. The effect of various experimental variables on the quantitative formation of the dicyano complex is described.

INTRODUCTION

Numerous methods have been proposed for the determination of cyanide at trace levels. Spectrophotometric methods are most commonly used but are subject to numerous interferences[1]. Ion chromatography has been used to separate cyanide from most common anions but the small acid dissociation constant for hydrogen cyanide severely limits the sensitivity although Rocklin and Johnson[2] reported a sensitive electrochemical detector developed by Pihlar and Kosta[3,4] could be used to determine cyanide after separation by ion chromatography. They reported a detection limit of 2 ppb* for cyanide using a 100-μl injection loop.

The separation and quantitative determination of the cyanide ion by high-performance liquid chromatography (HPLC) as the dicyanobis(1,10-phenanthroline)iron(II) complex is described. Schilt reported the synthesis and characterization[5,6], as well as the use of this complex as the basis of a spectrophotometric method for the determination of cyanide ion[7]. Others have studied the equilibrium[8,9] and the kinetics[10–13] for the reaction of the cyanide ion with the tris(1,10-phenanthroline)-iron(II) cation (ferroin). The inert nature of this complex and its intense absorption bands in both the visible and UV regions of the spectrum suggested it could be separated by HPLC and determined at trace concentration levels using photometric detection. The dicyano complex has also been proposed for use as an oxidation–reduction indicator with a formal oxidation–reduction potential in 2 *M* sulfuric acid

* Throughout the article the American billion (10^9) is meant.

0021-9673/87/$03.50

of 0.806 V[14]. The electrochemical detection of this species thus appeared feasible.

An objective of the present investigation was to develop a chromatographic separation of the cyanide complex from reaction products and the reagents used to prepare the complex where the cyanide complex could be determined directly without the extraction step into chloroform necessary in the procedure developed by Schilt. This was accomplished and it is shown that linear calibration plots for cyanide can be obtained in the range from 10 to 200 ppm based on photometric detection of the cyanide complex at 548 nm and down to approximately 0.1 ppm cyanide using UV or electrochemical detection. The chromatographic behavior of the dicyanobis(1,10-phenanthroline)iron(II) complex on a variety of columns, the detection of the complex based on its absorbance in the visible or UV region, and the electrochemical detection of the dicyano complex were studied.

EXPERIMENTAL

Apparatus

The HPLC system consisted of a Waters Assoc. 6000A pump and a U6K injector. A Spectromonitor I variable-wavelength photometric detector equipped with an 8-μl flow-through cell was used to monitor the elution in the visible and ultraviolet. A glassy carbon electrochemical transducer (Bioanalytical Systems) was used in series with the photometric detector together with a PAR 174 polarographic analyzer for the electrochemical studies. Hamilton microsyringes were used to inject the samples. Visible and UV spectra of the complex were obtained on a Perkin Elmer 576 spectrophotometer and the IR spectrum on a Beckman IR-10.

Chemicals

All chemicals used were ACS reagent grade. The methanol and acetonitrile used in the mobile phases were HPLC grade ("Omnisolve grade", Taylor Chemical, St. Louis, MO, U.S.A.). All water employed in the mobile phases and preparation of solutions was freshly distilled using an all glass still. Solid dicyanobis(1,10-phenanthroline)iron(II) was prepared by a minor modification of a method proposed by Schilt[5,6]. The IR spectrum was obtained in a potassium bromide pellet and showed the characteristic cyanide stretching frequencies at 2065 cm^{-1} and 2077 cm^{-1}. The visible absorption in chloroform and acetonitrile were identical to those given by Schilt[5].

Cyanide solutions

Stock cyanide solutions (500–1000 ppm cyanide) were prepared by dissolving sodium cyanide in water and used with procedure A in the initial studies based on photometric detection in the visible at 548 nm. A stock cyanide (102.7 ppm cyanide) solution was prepared by dissolving 0.0643 g of potassium cyanide in 250 ml of freshly distilled water sparged with helium to remove any dissolved oxygen to prepare the calibration curves using UV and electrochemical detection. A 5-ppm working solution was prepared shortly before use in the calibration plots by dilution of this solution with freshly distilled water sparged with helium. A stock ferroin reagent solution was prepared by dissolving 3.1659 g of 1,10-phenanthroline monohydrate and 1.9519 g of ferrous ammonium sulfate hexahydrate in 1 l of water giving a

solution 0.005 *M* in ferroin and also 0.001 *M* in 1,10-phenanthroline. Stock solutions of hydroxylammonium sulfate (2 and 10%) and a 1 *M* stock solution of disodium hydrogen phosphate were also prepared by dissolving the reagents in HPLC grade water sparged with helium to remove oxygen. Solutions of the dicyanobis(1,10-phenanthroline)iron(II) complex were prepared by dissolving the pure solid in acetonitrile.

Procedure A (10–200 ppm cyanide)

A 5-ml or smaller aliquot containing not more than 200 μg of cyanide is placed in a 10-ml volumetric flask. Then 0.10 ml of 10% solution of the hydroxylamine solution, 1.00 ml of the 0.005 *M* ferroin solution, and 1.00 ml of the phosphate buffer solution are added. The volume is adjusted to exactly 10.00 ml with water and the samples placed in a boiling water bath for 10 min. The samples are cooled to room temperature and 50–150 μl portions chromatographed (150 μl for cyanide concentrations less than 3 ppm in the final solution).

Procedure B (0.10–10 ppm cyanide)

A mixed reagent solution is prepared by mixing 50 ml each of the 0.005 *M* ferroin solution, the 1.00 *M* buffer solution and the 2% solution of hydroxylamine. The pH of this solution is adjusted to 9.50 and the solution sparged with helium to remove any air. This solution should be kept no more than three days. Exactly 3.00 ml of this solution is added to a 10.00-ml volumetric flask containing the cyanide sample (50 μg of cyanide or less in a volume of 5.00 ml or less). The pH of this solution should be between 9.3 and 9.7 and is adjusted to within this pH range if it is not. The volume of the solutions are then heated for 8.00 min in a boiling water bath. The solutions are then cooled to room temperature and 25-μl samples chromatographed.

Preparation of mobile phases

Mobile phases were prepared by volume by mixing the required volumes of methanol or acetonitrile with freshly distilled water and adding perchloric acid or lithium perchlorate. The mobile phase used with procedure A was methanol–water (65:35, v/v) and 0.003 *M* in perchloric acid. The mobile phase used with procedure B was acetonitrile–water (27.8:72.2, v/v) and 0.0015 *M* in perchloric acid. The mobile phases were sparged with helium to remove any dissolved air immediately before use.

Chromatographic parameters

A flow-rate of 1.00 ml/min was used for quantitative studies in the visible with procedure A and 2.00 ml/min for studies using the UV or electrochemical detectors. A wavelength of 548 nm was used for quantitative studies in the visible (procedure A) and of 262 nm for detection in the UV (procedure B). The effluent from the photometric detector was fed into the electrochemical cell. The nominal voltage applied to the electrochemical cell for maximum response for the dicyano complex was 0.8 V *versus* the Ag/AgCl reference electrode supplied with the electrochemical transducer (Bioanalytical Systems). The outputs from both the photometric and electrochemical detectors were monitored on strip chart recorders. A 10-mV recorder was used with the photometric detector as recommended. A variable-voltage recorder usually operated at 1 V was used with the PAR 174. All data are reported based on

a sensitivity setting of 0.05 μA on the PAR 174 and 1.0 V on the recorder. The photometric data are all reported for a sensitivity setting of 0.02 a.u.f.s. to permit comparisons. The actual data were obtained at the sensitivity giving the proper sized peaks on the chart. The range conversion error was negligible compared with other experimental errors. Unless otherwise indicated, the strip chart recorders were operated at 20 cm/h (photometric detection) and 0.2 in./min (electrochemical detection).

RESULTS

Absorption spectra of dicyanobis(1,10-phenanthroline)iron(II)

The absorption spectra of the solid complex in anhydrous chloroform and acetonitrile were essentially identical with the major peak in the visible at 600 nm and a shoulder at 525 nm. Two peaks were observed in the UV region at 228 and 262 nm. On the addition of even a small amount of water to the violet acetonitrile solution the color immediately changed to rose and the wavelength of the largest absorption band decreased. The absorption spectra in chloroform was identical to that given by Schilt[5]. As reported by Schilt[5] the complex is weakly basic and the absorption maximum shifts to shorter wavelengths on protonation. The wavelength maxima observed by the present authors for several different acetonitrile concentrations in water decreased from 600 nm in 98% acetonitrile to 548 nm in 50% acetonitrile. In 0.003 *M* perchloric acid, the wavelength maxima increased from 455 nm in 98% acetonitrile to 548 nm in 50% acetonitrile.

The wavelength of the absorption maximum of the cyanide complex in 95% acetonitrile decreased nearly linearly from 575 to 438 nm as the perchloric acid concentration was increased from $4 \cdot 10^{-6}$ to $4 \cdot 10^{-2}$. It is clear that the extent of protonation is much greater for a given acid concentration at high acetonitrile concentrations. For mobile phases containing less than 70% acetonitrile, however, the absorption maxima were close to 448 nm and this wavelength was used for the quantitative studies. The molar absorptivities for the cyanide complex in 65% acetonitrile which was 0.006 *M* in perchloric acid were 5400 l mol^{-1} cm^{-1} at 548 nm and 21 000 l mol^{-1} cm^{-1} at 262 nm. These were the wavelengths used to monitor the elution of the complex in the chromatographic studies in the visible and UV. An increase in sensitivity of about 3.9 would thus be expected if the species could be monitored in the UV as compared to the visible (all other conditions remaining the same).

Chromatographic behavior of cyanide complex

The retention of the cyanide complex and the tris(1,10-phenanthroline)iron(II) cation was determined on a number of different columns and with various mobile phases. Preliminary studies were carried out on a μBondapak CN column previously used for the separation of tris(1,10-phenanthroline)iron(II) and other metal complexes[15]. Solutions of the pure complexes were injected and the elution of the peaks monitored at 512 and 548 nm. Separate peaks for the cyanide complex and the cationic iron(II) complex were observed with the elution volume of the cyanide complex increasing at both high and low concentrations of the organic component of the mobile but essentially independent of the perchlorate ion concentration. The retention of the cationic iron(II) complex decreased with increasing perchlorate ion concentration as previously reported[15,16]. Lithium perchlorate was used to adjust the

pairing ion concentration and the mobile phase was nearly neutral. Although good separations of the two species were obtained with various combinations of solvent and perchlorate ion concentration, column performance gradually changed due to retention of neutral 1,10-phenanthroline on the column. This problem was eliminated by using dilute perchloric acid as a source of the pairing ion and to convert any 1,10-phenanthroline to its protonated form.

Only one peak was observed for the cyanide complex regardless of the form in which it was injected. Injection of violet solutions of the complex in acetonitrile or chloroform gave peaks with the same retention times as for the rose colored solutions of the complex in aqueous solutions. Maximum response for the complex was observed at 548 nm in the visible and at 262 nm in the UV. Peak heights observed for the cyanide and the cationic iron(II) complexes monitored at different wavelengths were consistent with the known absorption of the two complexes with absorption maxima of 548 and 512 nm, respectively. Similar results were obtained on a 10-μm Whatman PAC column (300 × 3.9 mm I.D.) and on a 5-μm IBM cyano column (250 × 4.5 mm I.D.) with greater retention and broader peaks observed with the latter. Very little retention of the cyanide complex was observed on a Hamilton PRP-1 column previously found useful for the separation of cationic metal–1,10-

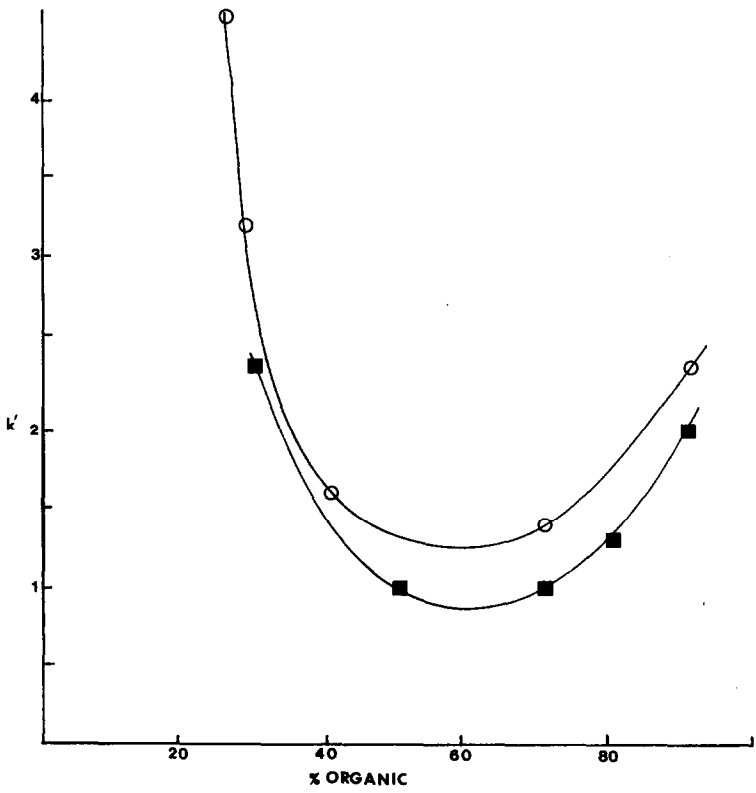

Fig. 1. Retention as function of acetonitrile or methanol concentrations at constant $[HClO_4] = 0.003\ M$ Acetonitrile, O; methanol, ■.

phenanthroline complexes[16]; or on a 5-μm IBM amino column (250 × 4.5 mm I.D.). Very similar plots of capacity factor (k') *versus* acetonitrile percentage (mobile phase 0.003 M in perchloric acid) were obtained on Whatman SCX and SAX (cation and anion) exchange columns (both with 10-μm diameter particles and 250 × 4.5 mm I.D.) with k' decreasing from about 4 at 20% acetonitrile to a minimum near 2 at 50% and then increasing at higher acetonitrile concentrations. Clearly retention involved a neutral species throughout the range of solvent compositions.

The sharpest peaks and best separations of the dicyano- and tris(1,10-phenanthroline)iron(II) complexes were obtained using perchlorate as the pairing ion on the 10-μm Waters μBondapak C_{18} column and it was used in all subsequent work. Retention data for the cyanide complex are given in Fig. 1 for both methanol–water and acetonitrile–water mobile phases also 0.003 M in perchloric acid.

Separation of dicyano- and tris(1,10-phenanthroline)iron(II)

Retention data for the dicyanobis(1,10-phenanthroline)- [$Fe(phen)(CN)_2$] and the tris(1,10-phenanthroline)iron(II) [$Fe(phen)_3^{2+}$] complexes on the μBondapak C_{18} column for acetonitrile–water–0.003 M perchloric acid are given in Fig. 2. It is apparent that the order and extent of separation can be controlled by either varying the acetonitrile–water ratio keeping the perchloric acid concentration constant or by varying the acid concentration keeping the acetonitrile–water ratio constant. This is shown in Fig. 3 for the case where the acid concentration was held constant ([$HClO_4$]

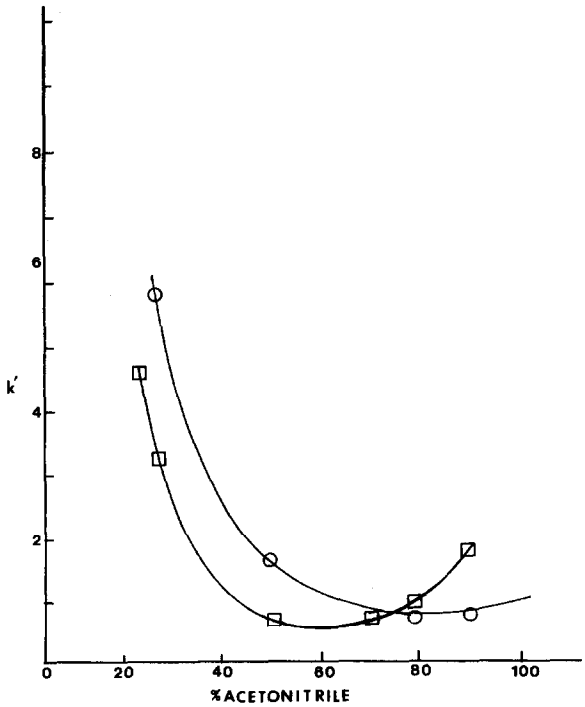

Fig. 2. Retention of $Fe(phen)(CN)_2$ (□) and $Fe(phen)_3^{2+}$ (○) as function of acetonitrile concentration at constant [$HClO_4$] = 0.003 M.

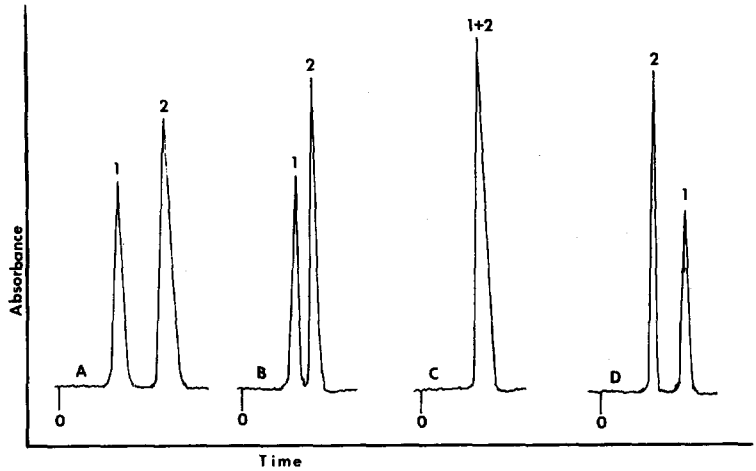

Fig. 3. Elution of $Fe(phen)_3^{2+}$ (1) and $Fe(phen)_2(CN)_2$ (2) at constant $[HClO_4]$ = 0.003 *M* at various acetonitrile concentrations. Acetonitrile–water (A, 90:1; B, 80:1; C, 70:1; D, 50:1).

= 0.003 *M*). Similar behaviour was observed when the acetonitrile concentration was held constant at 88% and the perchloric acid concentration varied from 0.001 to 0.01 *M*.

Quantitative determination of cyanide

Preliminary quantitative studies were performed on solutions prepared by procedure A. The mobile phase was methanol–water (65:35, v/v) and was 0.003 *M* (0.006 in some studies) in perchloric acid. The peaks for the dicyano- and the tris(1,10-phenanthroline)iron(II) complexes were well separated under these conditions. A linear calibration plot, $y = 31.88x - 90.12$ was obtained for the injection of 50 μl of a series of solutions containing 10–50 ppm cyanide with a correlation coefficient of 0.9977. The peak height, *y*, is in mm and the cyanide concentration in ppm (μg CN/ml). Extrapolation of the curve intercepted the concentration axis at 2.8 ppm. A plot of data for 150-μl injections in the range 1–10 ppm cyanide was not linear but curved toward the *y*-axis and leveled off at approximately 1 ppm cyanide. It was initially thought this might be due to small amounts of the cyanide complex in the reagents but it was later found to be caused by another species eluting under the cyanide peak which adsorbed in the visible region of the spectrum. It became clear that the sensitivity of the proposed HPLC method based on monitoring the elution of the peaks in the visible region was limited to approximately the same range as reported by Schilt[7] for the spectrophotometric method although the extraction step could be eliminated. The non-linear calibration plot for cyanide concentrations less than 3 ppm obtained using detection in the visible suggests UV or electrochemical detection be employed for cyanide at these levels or below.

Use of UV and electrochemical detection

The use of UV or electrochemical detection of the peak due to the dicyano complex requires the separation of this peak from all other species that absorb or show an electrochemical response. This required the use of a weaker mobile phase

and it was found that an acetonitrile–water (27.8:72.2, v/v) mobile phase which was 0.0015 *M* in perchloric acid was suitable. The elution of the dicyano complex for a solution containing 0.257 ppm cyanide prepared by procedure B and monitored using both UV and electrochemical detectors in series is shown in Fig. 4. Retention volumes of 10.2 ml and 15.6 ml for the dicyano- (peak B) and tris(1,10-phenanthroline)iron(II) (peak Fe, Fig. 4A) complexes were obtained. The column volume, V_M, was 2.65 ml. The peak for the dicyano complex is well separated from the much larger peak due to the excess iron(II) phenanthroline and early eluting peaks due to $H(phen)^+$, hydroxylamine, and other reaction products or impurity peaks. Peaks A, B and D gave maximum responses with both the UV and electrochemical detectors at exactly the same time. Peak Fe in Fig. 4A due to the elution of $Fe(phen)_3^{2+}$ is not seen on the electrochemical detector at 0.8 V but is observed if the applied voltage is increased to 1.2 V. The small peak labeled C in Fig. 4 has not been identified.

Quantitative studies based on UV detection

A series of solutions containing 0–2.565 ppm cyanide were prepared using procedure B (Experimental section) and 25-μl portions of these solutions injected. The UV and electrochemical detectors were in series. Chromatograms were obtained on these solution the same day as prepared and over a period of three days. No significant change was observed with time.

Calibration plots of the height of the cyanide peak (V_r = 10.2 ml) monitored at 262 nm *versus* the ppm cyanide were linear at cyanide concentrations greater than about 0.5 ppm but curved toward the y axis at lower concentrations. A small peak at the same elution volume as the cyanide (V_r) was always observed in the blank samples. This was initially believed to be caused by cyanide in the reagents but subsequent work with electrochemical detection suggest it is due to another species which elutes with nearly the same retention volume.

The data (excluding the blank) fit the linear equation, $y = 192.1x + 10.7$, with a correlation coefficient of 0.9971. The peak height, y, is in mm and the cyanide concentration in ppm.

Calibration plots with the electrochemical detector

Calibration data obtained with the electrochemical detector were obtained at the same time as the UV data with the UV and electrochemical detectors in series thus any errors in sample injection affect both equally. The data fit the linear equation, $y = 523x - 19.4$, with a correlation coefficient of 0.9987. Excluding the data for 0 ppm cyanide, the remaining data fit the equation, $y = 525x - 23$. The standard deviation of the slope, σ_m, was 6.8 and the standard deviation of the intercept was 8.6. The intercept on the x axis corresponds to 0.043 ppm cyanide. A slightly higher slope of 534 with a correlation coefficient of 0.9995 was obtained if only the data from 0.513 to 2.565 ppm were plotted.

A series of blanks were prepared which gave no peak for cyanide with the electrochemical detector but a peak (average height 30 mm) with the UV detector. Small amounts of solution of the pure dicyano complex prepared from the pure solid and calculated to make the solutions approximately 0.1 ppm in cyanide were added to these solutions and 25-μl aliquots injected. The average peak height found with the electrochemical detector of 60 mm was consistent with the expected value based

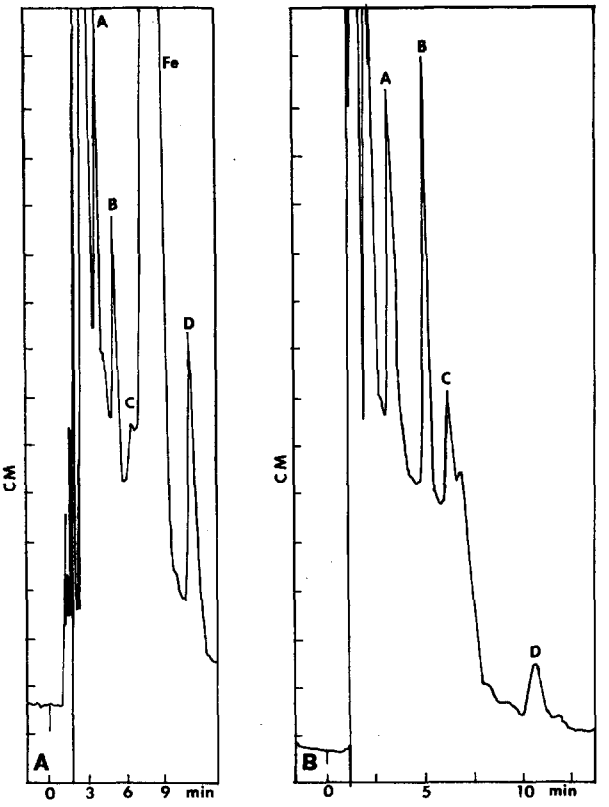

Fig. 4. Elution of $Fe(phen)_2(CN)_2$ prepared by procedure B. Mobile phase: acetonitrile–water (27.8:72.2, v/v) which was 0.0015 *M* in perchloric acid. Solution was 0.257 ppm in cyanide. (A) UV detection, 0.02 a.u.f.s., 262 nm, 2 ml/min, 10-mV recorder, 20 cm/h. (B) Electrochemical detection, 0.05 μA, 0.80 V applied, 1-V recorder, 0.2 in./min. See text for peak identification.

on the slope of the calibration plot. The height of the peaks based on UV detection increased from 30 mm in the blanks to approximately 50 in the spiked sample which was also consistent with the slope of the calibration plot for the UV data.

Both the electrochemical and the UV response decreased in a linear manner when successively smaller aliquots of the solution of the pure complex were injected and by increasing the sensitivity of the electrochemical detector to 0.01 μA cyanide concentrations corresponding to approximately 0.01 ppm could be easily detected with the electrochemical detector. At this level the UV response was obscured by noise. The detection limit of the proposed method thus appears to be limited by incomplete formation of the cyanide complex at concentration levels below about 0.05 ppm rather than the sensitivity of the detector. It is clear the small peaks observed in the blanks by UV are not due to the dicyano complex or an electrochemical response would certainly be seen.

Effect of experimental variables on complex formation

Although reproducible results could be obtained with procedure A for cyanide concentrations greater than 5 ppm, experimental conditions could not be controlled

accurately enough to obtain reproducible results using UV or electrochemical detection at the 0.05–2.5 ppm levels until procedure B was developed. The effect of various factors on the completeness of complex formation was studied in the development of procedure B. Factors which proved critical included the pH, hydroxylamine concentration, and age of the mixed reagent solution. The proper applied voltage was also a critical factor in obtaining the maximum electrochemical response.

The effect of the concentration of hydroxylamine in the final reaction solution was studied by preparing a series of solutions all 0.50 ppm in cyanide following procedure B except that the hydroxylamine concentration was varied and the solutions were heated 10 min in a boiling water bath. The maximum electrochemical response was found when the hydroxylamine concentration was 0.02% in the final reaction mixture. Larger amounts caused the electrochemical response to decrease but had less effect on the UV response. This may be due to an increase in the spurious peak observed in the UV eluting with the dicyano complex.

Occasionally low electrochemical responses were observed relative to the expected response based on the UV data. This was found to be caused by a small change in potential of the reference electrode. Increasing the applied potential slightly increased the electrochemical response to the expected value. A practical method of insuring that the applied potential was near optimum and that sufficient hydroxylamine was present was to observe the heights of the small electrochemical peaks eluting immediately before and after the dicyano complex and after the ferroin peak (peaks A, C, and D, respectively, in Fig. 4B). Reproducible results and maximum electrochemical response were consistently obtained when all three peaks were observed. Peak A was observed to increase in height with the hydroxylamine concentration in the reaction mixture and appears to be an iron(II)–1,10-phenanthroline–hydroxylamine complex. Peak D appears to be an iron complex. It appears as a small peak at the optimum applied potential for maximum response for the cyanide peak. It is not seen at lower potentials and becomes larger at higher applied potentials until it is obscured by a very large peak for $Fe(phen)_3^{2+}$ at a potential of approximately 1.2 V (about 0.4 V greater than the optimum potential for the dicyano complex).

The effect of time of heating on complex formation was studied and a maximum response was observed after heating 5 min with no change up to 10 min. An 8-min heating time is recommended in procedure B. The height of peak A (Fig. 4) decreases with length of heating and with prolonged heating finally disappears and the solutions fade. This is consistent with peak A being a hydroxylamine complex.

The mixed reagent solution used in procedure B is not stable at pH 9.50 and starts to darken in color soon after preparation. An increase in the heights of peaks C and D is observed and a slight increase in maximum electrochemical response for a given amount of cyanide is observed after the solution ages one to two days. After approximately three days the solution should be discarded or low and erratic results may be obtained.

Several studies of the effect of applied potential all showed no electrochemical response below an applied potential of approximately 0.6 V. A rapid increase in response occurred at applied potentials of 0.70 and reached a maximum at about 0.80 V then decreased slightly at higher potentials. A considerable time was required before the electrode gave reproducible results after each change in applied potential and the optimization procedure based on the relative heights of peaks A, B, C and

D (Fig. 4B) as described above proved more reliable than specifying a particular voltage in optimizing the electrochemical response. With the 27.8% acetonitrile mobile phase (0.0015 *M* in perchloric acid) an applied voltage of 0.80 V was generally close to optimum.

Effect of ferroin concentration on complex formation

The amount of ferroin in the mixed reagent was increased by factors of 2 and 3 with no detectable change in the peak height for the cyanide complex. It appears the low and erratic results obtained at cyanide levels less than 0.05 ppm are not simply an equilibrium problem. The rate of complex formation at very low cyanide concentrations may be the critical factor. This appears to be closely correlated with the age of the mixed ferroin reagent. Larger peaks were generally observed when the reagent aged for one or two days. A rapid reaction of cyanide with trace amounts of some reaction product can be postulated.

Interferences

Interference studies were carried out on several common anions and cations including thiocyanate, acetate, iron(III), copper(II), cobalt(II) and chromium(III) using spectrophotometric detection at 548 nm and procedure A. At the 7 ppm cyanide level no interference was observed for 100-ppm amounts of thiocyanate, acetate, and iron(II), respectively. No peak was observed in the presence of copper(II), cobalt(II) or chromium(III). The sulfide ion precipitated iron(II) sulfide and, as reported by Schilt[7], prevents any color reaction. Strong oxidizing anions such as the periodate ion would also be expected to interfer as noted by Schilt. Sodium sulfite was used successfully in some studies in place of hydroxylamine thus the sulfite ion does not interfere. Interferences would generally be expected to be a more severe problem at lower cyanide concentrations and with procedure B.

Any application of this method to real samples would clearly require a prior cleanup step to remove the sulfide ion and any cations expected to complex with 1,10-phenanthroline. Several possibilities including the formation of the dicyano complex on a cation-exchange pre-column partially loaded with ferroin (which could also serve to remove cationic interferences) are being investigated.

REFERENCES

1 N. J. Csikai and A. J. Barnard, Jr., *Anal. Chem.*, 55 (1983) 1677.
2 R. D. Rocklin and E. L. Johnson, *Anal. Chem.*, 55 (1983) 4.
3 B. Pihlar, L. Kosta and B. Hristovski, *Talanta*, 26 (1979) 805.
4 B. Pihlar and L. Kosta, *Anal. Chim. Acta*, 114 (1980) 275.
5 A. A. Schilt, *J. Am. Chem. Soc.*, 82 (1960) 3000.
6 A. A. Schilt, *J. Am. Chem. Soc.*, 79 (1957) 5421.
7 A. A. Schilt, *Anal Chem.*, 30 (1958) 1409.
8 R. Gillard and P. Williams, *Transition Metal Chem.*, 2 (1977) 247.
9 P. Williams, R. D. Gillard and L. A. P. Kane-Magure, *Transition Metal Chem.*, 2 (1977) 12.
10 V. Balazari, V. Carassiti and L. Moggi, *Inorg. Chem.*, 3 (1964) 1252.
11 J. Burgess, *Inorg. Chim. Acta*, 5 (1971) 133.
12 G. Nord, *Acta Chem. Scand.*, 27 (1973) 743.
13 F. M. Mikhail, P. Askalani, J. Burgess and R. Sherry, *Transition Metal Chem.*, 6 (1981) 51.
14 A. A. Schilt, *Analytical Applications of 1,10-Phenanthroline and Related Compounds*, Pergamon Press, Oxford, 1969, p. 124.
15 J. W. O'Laughlin and R. S. Hanson, *Anal. Chem.*, 52 (1980).
16 J. W. O'Laughlin, *Anal. Chem.*, 54 (1982) 178.