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Reversed-phase ion-interaction chromatography of Cu(I)–cyanide complexes

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Abstract

It has been established that during the separation of Cu(I)–cyanide complexes, the cyanide:Cu(I) molar ratio, *R*, of the eluted complex remained constant irrespective of the *R* value injected onto the column, and there was considerable tailing of the unretained cyanide peak and fronting of the Cu(I)–cyanide peak in an eluent containing no cyanide. The addition of small amounts of cyanide (100 μM) to the eluent resulted in the elimination of these effects on peak shape and a significant increase in the retention of the Cu(I)–cyanide species. These results suggested that more than one Cu(I)–cyanide complex may be present in the Cu(I)–cyanide peak in an eluent containing no cyanide. Three different detection systems [Fourier transform Infrared (FTIR) and photodiode array spectrophotometry and a post-column reaction (PCR)], were used to determine changes that occurred to the Cu(I)–cyanide complexes during the separation with eluents containing from 0 to 100 μM cyanide. The FTIR approach was unsuccessful due to a lack of sensistivity. The UV spectrum of the Cu(I) peak in any one eluent remained constant, irrespective of the composition of the injected sample, but there were distinct changes in this spectrum among eluents. Similarly, the *R* value of the Cu(I) peak determined by PCR remained the same in any one eluent but ranged from about 2.5 to about 3.4 for these eluents. The *R* value was found to vary within the eluted Cu(I)–cyanide peak, especially in an eluent containing no added cyanide. These results show that more than one Cu(I)–cyanide complex is present in the eluted peak and that in the absence of cyanide in the eluent, the eluted peak consists of a mixture of the di- and tricyano complexes of Cu(I).

Keywords: Complex dissociation; Metal complexes; Cyanide complexes; Copper complexes

1. Introduction

The predominant method of gold extraction in the gold mining industry involves cyanidation of an ore under aerated conditions to form $Au(CN)_2^-$. Under such conditions, sulfides and base metals can form thiocyanate and metallo–cyanide complexes, resulting in the loss of cyanide from the extraction process. The most important of these base metals to the gold mining industry is copper, due to the presence of copper minerals in many gold deposits [1]. The resulting Cu(I)–cyanide complexes cause a significant positive interference in the standard titrimetric analysis method for free cyanide analysis, due to the partial dissociation of these complexes during the titration [2]. For some time, we have been studying the use of chromatographic methods as an alternative to the titration process.

The separation of metallo–cyanide species by ion chromatography has been the subject of a considerable number of publications over recent years [3], with the most common separation method being ion-interaction chromatography [4–15]. While these separations have been carried out on both reversed-phase silica [4–14] and polymeric columns [15], it has been shown that the silica columns provide

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greater selectivity with respect to these separations [15]. The aqueous eluents used generally contain a quaternary ammonium salt with various organic solvents and the metallo–cyanide complexes have generally been detected using a UV absorbance detector, although the use of a conductivity detector has also been reported [7,15].

As part of a project to further the application of ion chromatography in the gold mining industry, an ion-interaction method for the simultaneous determination of free cyanide and the metallo–cyanide complexes was developed [8]. Since cyanide is UV transparent, a post-column reaction (PCR) detection unit (comprising a PCR reactor and a spectrophotometric detector operated in the visible region) was inserted after the UV detector to enable the derivatisation and detection of free cyanide. The PCR used was a variation of the König reaction [16] and under the conditions used, the CN moeities in thiocyanate and the Cu(I)–cyanide complexes were also derivatised. Peaks for these species were therefore observed on both the UV detector (prior to derivatisation) and on the second detector (after derivatisation).

It was noted during the above work that peaks for both cyanide and Cu(I)–cyanide were observed in the PCR detector following the injection of a Cu(I)–cyanide standard and that the presence of Cu(I)–cyanide complexes in a cyanide sample would result in an increase in the observed cyanide concentration. This indicated that a partial dissociation of the Cu(I)–cyanide complexes was occurring on the column. It has also been shown by previous workers that the retention characteristics of the Cu(I)–cyanide complexes can be considerably altered by the addition of cyanide to the ion-interaction eluent [6,7,17], indicating that the above dissociation can be controlled.

Due to the importance of the Cu(I)–cyanide complexes in the gold mining industry, a series of studies investigating the ion-interaction chromatography of these complexes was performed. This paper examines the degree of the dissociation of these complexes which occurs during the separation process and the manner in which this dissociation effect can be controlled by the addition of cyanide to the eluent.

2. Experimental

2.1. Instrumentation

The instrument has been previously described in detail [8] and consisted of a Waters (Milford, MA, USA) M510 isocratic HPLC pump, a Waters 717 auto-sampler, a Waters M486 variable-wavelength absorbance detector and a PCR detection system. The PCR system consisted of two Eldex pumps, two stitched open tubular reactors, a Waters column heater to maintain the reactors at a constant temperature (usually 40°C) and a photometric detector operated at 515 nm. The first reactor was a coil 1.4 m in length with an I.D. of 0.025 mm and the second reactor consisted of three 5 m coils with an I.D. of 0.025 mm, connected in series. The reaction coils were prepared using the method described by Lillig and Engelhardt [18]. The PCR detector was a Waters M484 variable-wavelength absorbance detector operating at 515 nm.

The photodiode array (PDA) investigation used a Waters 996 PDA detector. Data were acquired and processed with a Waters Millenium data system. A Bruker IFS-66 FTIR instrument fitted with a demountable micro FTIR flow cell (Spectra-Tech, Stamford, CT, USA) with CaF_2 windows and 25–50 mm Pb spacers was used for the FTIR investigation.

2.2. Preparation of the eluents

All the reagents used in this work were obtained from Aldrich (Castle Hill, Australia), unless otherwise stated. The eluents were prepared with Grade 1 water from a Milli-Q system (Millipore, MA, USA), acetonitrile (Waters, Lane Cove, Australia), a salt of tetrabutylammonium hydroxide (TBAOH) and a NaCN stock solution. A NaOH solution was used to adjust the apparent pH of these eluents to 7.95±0.05. All eluents were filtered (0.45 μm) and degassed under vacuum in an ultrasonic bath prior to use.

The nature of the TBA^+ salt varied during these experiments. The eluents used during the PDA experiments were prepared from TBAOH (Aldrich) and H_3PO_4, with a TBA^+ concentration of 5 m*M*. The eluents used for the PCR study were prepared with a proprietary reagent, LowUVPICA (Waters)

containing a TBA^+ concentration of 5 m*M*. The acetonitrile concentration in the eluents was 20% for the PDA experiments and 25% for the PCR experiments.

2.3. Preparation of the post-column reaction reagents

The two PCR reagents were prepared as follows and kept in the dark at less than 4°C. Both reagents were filtered (0.45 μm) under vacuum prior to use each day.

2.3.1. Reagent 1

N-Chlorosuccinimide (0.1%, w/v) was added to a succinate buffer (0.1 *M*, pH 5.6) containing succinimide (2% w/v).

2.3.2. Reagent 2

This reagent contained the sodium salts of isonicotinic acid (INA, 0.3 *M*), barbituric acid (BA, 4 m*M*) and EDTA (10 m*M*) and was prepared by dissolving the INA and BA in excess NaOH prior to the addition of Na_2EDTA. The final reagent pH was 7.8.

2.4. Standards

Cyanide standards were prepared from a 0.1 *M* stock solution of NaCN in 0.1 *M* NaOH. A Cu(I)–cyanide stock solution (10 m*M*) was prepared from CuCN and NaCN in a 10 m*M* NaOH solution, such that the CN:Cu mole ratio of this stock solution was 3.0. These solutions were kept alkaline to improve their stability. The Cu(I)–cyanide standards used for analysis were prepared from the stock solutions of Cu(I)–cyanide and NaCN.

Thiocyanate standards were prepared from a 0.1 *M* stock solution of KSCN. Both the NaCN and KSCN 0.1 *M* stock solutions were standardised potentiometrically with a standardised $AgNO_3$ solution. The copper concentration in the 10 m*M* Cu(I)–cyanide stock solution was checked using atomic absorption spectrometry, while the cyanide concentration was checked by total cyanide distillation. Both the copper and cyanide concentrations were within 1% of expected values.

2.5. Operation of the instrument

All separations were performed on a 150×3.9 mm I.D. Waters Nova-Pak C_{18} analytical column fitted with a Waters guard column. The eluents were pumped through the column at a constant flow rate of 1.0 ml/min. An injection volume of 10 μl was used throughout this work. The UV absorbing metallo–cyanide complexes were detected immediately after elution from the column with a variable-wavelength detector set at an appropriate wavelength between 205 and 245 nm. The wavelength was changed to adjust the sensitivity of the detector with respect to the Cu(I)–cyanide peak.

The PCR comprised three reactions and two reagent additions. The first reagent contained a chlorinating reagent (N-chlorosuccinimide) to enable formation of CNCl. A pyridine derivative (isonicotinic acid) in the second reagent combined with the CNCl to form an aldehyde. An in situ condensation reaction then occurred between the aldehyde and barbituric acid to form an intermediate polymethine dye product with a λ_{max} of 515 nm. This polymethine dye will further react with barbituric acid at a considerably slower rate to form a second polymethine dye with a λ_{max} of 600 nm. A large excess of isonicotinic acid was used since it has been shown that this stabilises the intermediate polymethine dye [19]. The flow-rates of the first and second PCR reagent pumps were approximately 0.1 and 0.2 ml/min, respectively. The derivatised cyanide and Cu(I)–cyanide peaks were detected after the PCR unit with a second variable wavelength detector operated at 515 nm.

3. Results and discussion

3.1. Chromatographic behaviour of the Cu(I)–cyanide complexes

When a series of Cu(I)–cyanide standards with a constant copper concentration and increasing CN:Cu mole ratios, *R*, were analysed in an eluent containing no added cyanide, one peak was observed with the UV detector and two peaks were observed with the PCR detector, as shown in Fig. 1. The peak labelled

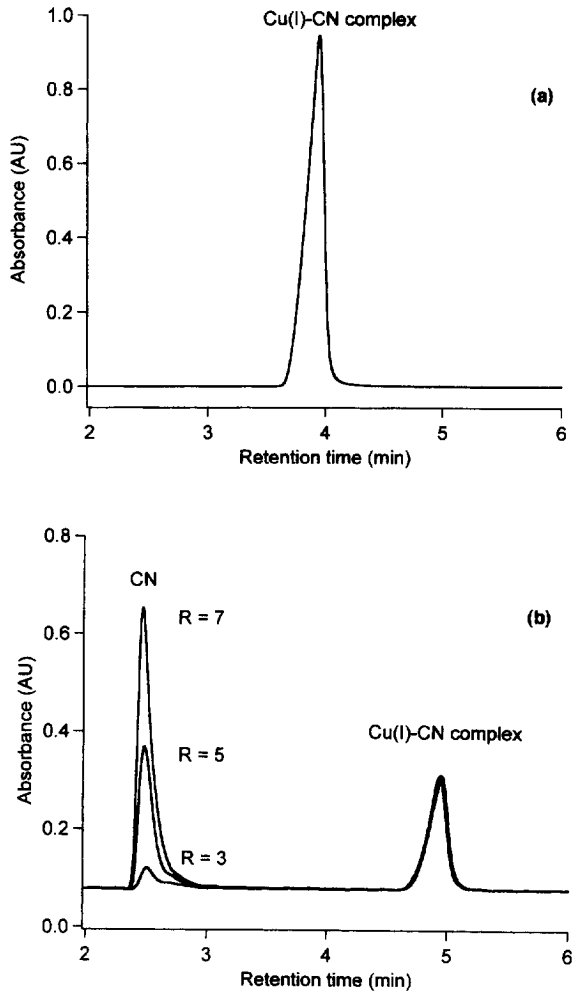

Fig. 1. UV (a) and PCR (b) detector chromatograms of Cu(I)–cyanide standards with CN:Cu(I) mole ratios (R) of 3, 5 and 7. The total [Cu] of each standard was 1.0 mM. Eluent: 25% acetonitrile, 5 mM Low UV PIC A.

as Cu(I)–CN complex in both the UV and PCR detector chromatograms was due to the eluted Cu(I)–cyanide species and its retention time and peak area did not change with the value of R injected, provided the injected amount of copper was constant. The cyanide peak in the PCR chromatogram (which corresponded to the void peak in the UV detector chromatogram) increased almost proportionally with R. Close examination of the shapes of the peaks obtained on the PCR detector in Fig. 1b reveal that the cyanide peak showed considerable tailing, whilst the Cu(I)–cyanide peak exhibited considerable fronting (this was also evident on the UV detector, Fig. 1a). When the value of R was maintained at 3.0 and the concentration of copper in the sample was varied, the peak for Cu(I)–cyanide showed increased fronting at higher copper concentrations (Fig. 2).

The above behaviour can be attributed to the on-column dissociation of the Cu(I)–cyanide complexes. Vibrational spectrophotometric studies have shown that three monomeric Cu(I)–cyanide complexes, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ exist in aqueous solution [20]. Radiochemical studies have shown that the cyanide ligands are kinetically very labile [21]. The concentrations of the three complexes are governed by the equilibria shown in Table 1. These equilibria depend on the value of R and are also pH dependent over the approximate pH range of 7–11 (since the pK_a for HCN is 9.2 [22]). The changes in the concentrations of the three complexes and uncomplexed cyanide when the R value is varied can be calculated using equilibrium calculations. Fig. 3 shows these changes when R is varied from 2.6 to 5.0 at pH 8 with a total copper concentration of 1.0 mM. This pH value was used for these calculations as this was the eluent pH. It is apparent from Fig. 3 that the tricyano complex is predominant when R exceeds 3, with the average number of complexed CN ligands increasing only slowly when R exceeds 3.8. Most of the uncomplexed cyanide occurs as

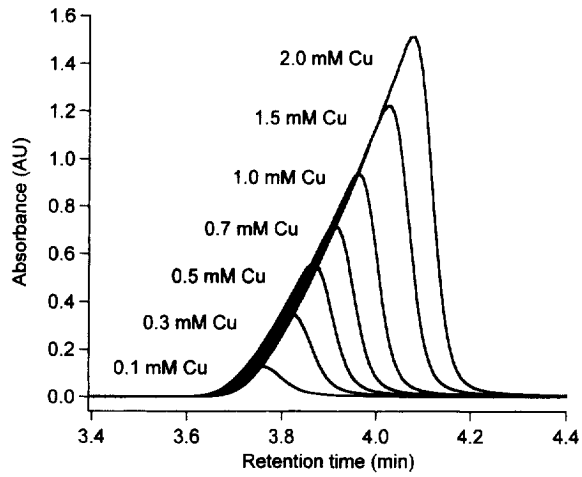

Fig. 2. UV detector chromatograms of Cu(I)–cyanide standards (all R=3) with total [Cu] varying from 0.1 to 2.0 mM. Eluent as for Fig. 1.

Table 1
Step-wise (log K) and overall (log β) stability constants of Cu(I)–cyanide complexes

Equilibria	Stability constant	1987 IUPAC review [22][a]	Literature range
$Cu^+ + 2CN^- \leftrightharpoons Cu(CN)_2^-$	Log β_2	21.7	16–24
$Cu(CN)_2^- + CN^- \leftrightharpoons Cu(CN)_3^{2-}$	Log K_3	5.3	4.5–5.4
$Cu(CN)_3^{2-} + CN^- \leftrightharpoons Cu(CN)_4^{3-}$	Log K_4	1.5	0.8–2.4

[a] These constants were selected in this review as being the most accurate.

HCN at pH 8. There is an almost linear increase of the HCN concentration when the CN:Cu mole ratio exceeds 3.8.

It should be noted that Fig. 3 is only a guide to the equilibrium conditions occurring in the eluent at pH 8. This is because the acetonitrile present in the eluent will perturb the equilibria in two ways. The first perturbation will occur by changing the activities of the various ions and stabilisation of Cu(I) in aqueous solution. Acetonitrile is a well known ligand with a reported stability constant of $10^{4.35}$ for $Cu(CH_3CN)_2^+$ [23].

To account for the observed chromatographic behaviour we consider as an example a sample having an R value of 3.0, which contains an equilibrium mixture composed mostly of the di- and tricyano–Cu(I) complexes, with small concentrations of cyanide and the tetracyano–Cu(I) complex. For a sample containing a total copper concentration of 1 mM, the concentrations of the di-, tri- and tetracyano–Cu(I) complexes were calculated to be 0.069, 0.929 and 0.002 mM, respectively, with a total complexed cyanide concentration of 2.933 mM, giving by difference that the uncomplexed cyanide concentration was 0.067 mM. These calculations were performed with the same constants and conditions as used for Fig. 3.

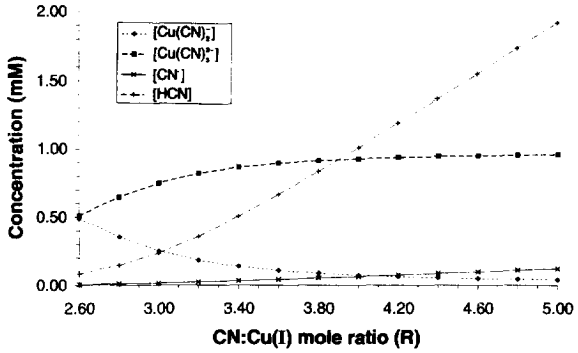

Fig. 3. Plots of calculated equilibrium concentrations of $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and uncomplexed cyanide (both HCN and CN^-) for varying R values. The concentration of the tetracyano complex has been omitted from this figure as it was very low. The constants (obtained from Ref. [22]) and parameters used for these calculations were: pK_a HCN=9.2; log β_2, β_3 and β_4=21.7, 27.0 and 28.5, respectively. pH=8; total [Cu]=1 mM; [CN]:[Cu] ratio varied from 2.6 to 5.0.

The first effect expected to occur following sample injection would result from the changed solution matrix of the sample due to dispersion in the eluent. The two most significant changes in the solution matrix are the low pH of the eluent (pH 8) and the presence of acetonitrile in the eluent. The eluent pH would result in a decrease of the total complexed cyanide concentration as shown in Fig. 4. The effect of acetonitrile has been discussed above.

We turn now to the role played by the retention differences between the cyano species and the subsequent perturbations of the composition of the equilibrium mixture traversing the column. The most pronounced retention difference occurs between the uncomplexed cyanide, which is unretained, and the

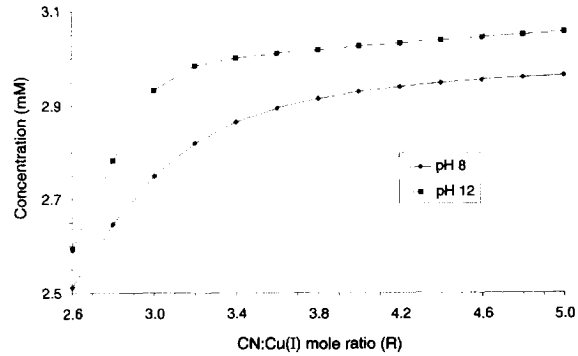

Fig. 4. Plots of calculated total complexed cyanide for varying R values at pH 8 and 12. The constants and parameters used for these calculations were the same as those used for Fig. 3.

Cu(I) cyanide complexes, which are retained. Due to the kinetic lability of the cyanide ligands, as the cyanide is separated from the Cu(I) cyanide complexes, the tetra- and tricyano complexes will undergo dissociation to produce cyanide and the tri- and dicyano complexes. This process will continue until a kinetically stable mixture results and this mixture will be represented in the eluted Cu(I) peak.

Fronting of the Cu(I) peak can be expected due to increased dissociation at low copper concentrations, leading to increased proportions (relative to the main body of the peak) of the dicyano species in the lower concentration regions. The dicyano species is eluted more rapidly than the tricyano species, so that the eluted band of Cu(I)–cyanide complexes comprises a faster moving, low concentration band relatively rich in the dicyano species (which reaches the detector first), followed by a slower moving, higher concentration band relatively rich in the tricyano species (which reaches the detector last). A fronted peak shape results (Fig. 1) and this fronting becomes more pronounced as the total amount of Cu injected is increased (Fig. 2). This mechanism is identical to that used to explain the fronted peaks observed for ion-exclusion chromatography of carboxylic acids when water is used as eluent [24]. The same explanation can be proposed to account for the observed tailing on the cyanide peak (Fig. 1b).

Some insight into the validity of the above mechanism can be gained when small amounts of cyanide are added to the eluent. The concentration-dependent dissociation should be reduced, leading to improved peak shape for the Cu(I)–cyanide and cyanide peaks, and the equilibrium position of the eluting band of mixed Cu(I)–cyanide complexes should be shifted towards higher levels of the tricyano complex, leading to increased retention. Both of these trends were evident as can be seen from Fig. 5 and from the data shown in Table 2 (which for comparison also includes data for thiocyanate). An eluent containing 150 μ*M* NaCN produced an almost Gaussian Cu(I)–cyanide peak (Fig. 5), having a significantly longer retention time than that obtained using an eluent without cyanide (Table 2). In contrast, there was very little change to either the retention time for the closely eluted species, SCN^-, also shown in Table 2. An unavoidable side-effect resulting from the addition of NaCN to the eluent was an increase in the baseline absorbance of the PCR detector and a consequent decrease in the signal-to-noise ratio due to pump pulsations, as shown in Table 2.

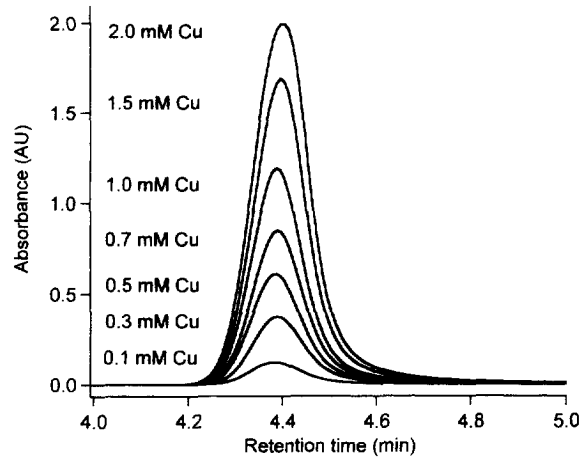

Fig. 5. UV detector chromatograms of the same Cu(I)–cyanide standards shown in Fig. 2, but with 150 μ*M* cyanide added to the eluent.

3.2. Elucidation of the nature of the eluted Cu(I)–cyano complexes using spectroscopic methods

In order to confirm the above mechanism and to determine quantitatively the composition of the eluted complexes under various eluent conditions, two alternative detection techniques were employed, namely Fourier transform infrared (FTIR) spectrometry, and photodiode array (PDA) detection. The vibrational spectrum of an aqueous solution of the Cu(I)–cyanide complexes can potentially provide characteristic information concerning the speciation of these complexes since the di-, tri- and tetracyano complexes have C–N stretching frequencies of 2125, 2094 and 2076 cm^{-1}, respectively [20]. However, it was found that the Cu(I)–cyanide complexes could not be detected by FTIR, even at concentrations 100-times greater than those expected to be eluted from the column. This was considered to be due to the high background IR absorbance of the eluent and the short residence time in the flow cell.

There have been several studies of the UV spectra of the Cu(I)–cyanide complexes which have shown that spectral changes occur as *R* is increased [25–29], although there is no clear discrimination be-

Table 2
Effect of eluent cyanide concentration on the chromatography of the Cu(I)–cyanide species

[NaCN] in eluent (μM)	Retention time (min)		Peak width (min)		Peak asymmetry		Resolution of Cu(I) and SCN^-	*S/N* ratio
	SCN^-	Cu(I)	SCN^-	Cu(I)	SCN^-	Cu(I)		
0	3.59	3.97	0.198	0.325	0.921	0.372	1.56	131
50	3.53	4.22	0.191	0.254	0.842	0.764	3.33	36
100	3.53	4.32	0.191	0.253	0.911	1.104	3.83	24
150	3.56	4.42	0.191	0.256	0.885	1.243	4.14	12

Peak width, peak asymmetry and resolution calculated at 10% peak height.

tween the three complexes. Unlike many other metal–ligand systems, it is not possible to obtain a spectrum of a solution of any of the pure Cu(I)–cyano complexes due to their instability in solution at low CN:Cu mole ratios, so that mathematical deconvolutions of the Cu(I)–cyanide spectra are required to calculate the spectra of the individual complexes [25,27–29]. It should therefore be possible to discriminate between spectrally different components in a single chromatographic peak using a PDA detector coupled with a computational package. Ten 0.5 mM Cu(I)–cyanide standards with R values ranging from 3 to 13 were analysed with the PDA detector in six eluents containing 0–200 μM NaCN. The spectrum of the eluted Cu(I)–cyanide peak was constant in the same eluent, but altered as the NaCN concentration in the eluent was increased. The largest spectral change occurred between the eluents containing no added cyanide and 10 μM NaCN, as shown in Fig. 6. The isosbestic points at 207 and 234 nm observed in Fig. 6 are similar to the reported values in spectrophotometric studies [29]. Whilst Fig. 6 provides strong evidence that cyanide added to the eluent results in the elution of different Cu(I)–cyanide complexes, it was not possible to obtain quantitative data regarding the nature of the eluted complexes. All further studies were therefore conducted using the PCR detection system.

3.3. Elucidation of the nature of the eluted Cu(I)–cyano complexes using PCR

In order to further explore the nature of the eluted complexes, modifications were made to the PCR conditions we have described earlier [8] to ensure that all cyanide entering the reactor, either as free or complexed cyanide, would be derivatised. In this way, quantitative measurements of the eluted cyanide species would be possible. The following modifications were made to the PCR reagents and conditions used in our previous studies:

1. The succinimide concentration in the N-chlorosuccinimide/succinimide reagent was increased to a 20-fold excess and the combined reagent was kept in the dark at less than 4°C. In addition, the reagent was buffered at pH 5.6 with a succinate buffer which served also to complex Cu(II) ions released during the derivatisation of Cu(I)–cyanide species. This was necessary since it has been previously noted that Cu(II) interferes in the

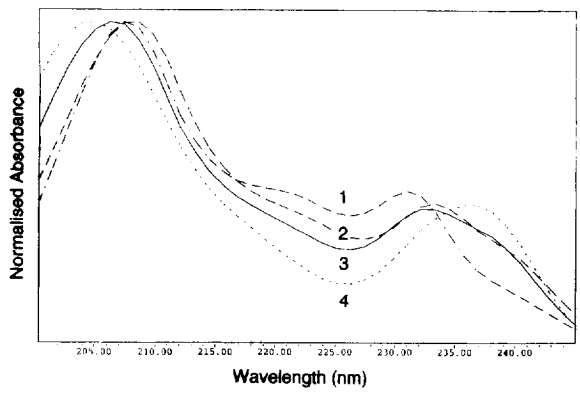

Fig. 6. Normalised UV spectra of Cu(I)–cyanide peak maxima in eluents containing various NaCN concentrations, obtained with the PDA detector. All the eluents were prepared with 20% acetonitrile, 5 mM TBAOH and buffered to pH 8 with H_3PO_4. The spectrum labelled (1) was obtained in an eluent containing no added NaCN. The spectra labelled (2) to (4) were obtained in eluents which contained 20, 40 and 200 μM NaCN, respectively. The spectra obtained for the eluents containing 10 and 80 μM NaCN were similar to the spectra obtained in eluents containing 20 and 40 μM NaCN, respectively, and have thus been omitted from this figure for the sake of clarity.

colour formation of a similar polymethine dye [30].
2. EDTA was added to the INA/BA reagent to further prevent interference by the liberated Cu(II) [30].
3. The concentrations of INA and BA in the combined INA/BA reagent were adjusted to 0.3 *M* and 4 m*M*, respectively, in order to improve reproducibility and cyanide response.
4. The lengths of the first and second reaction coils were increased to 1.4 and 15 m, respectively, and both reaction coils were maintained at 40°C.

A series of three 1 m*M* Cu(I)–cyanide standards with *R* values of 3, 5 and 7 were analysed in three eluents containing 25% acetonitrile, 5 m*M* PIC A and 100 μ*M*, 50 μ*M* or no added NaCN. The cyanide concentrations in the cyanide and Cu(I)–cyanide peaks were determined from cyanide calibration plots. The results are shown in Table 3. In the eluent without added NaCN, the mean cyanide concentration in the Cu(I)–cyanide peak was 2.53 and showed virtually no change with the *R* value of the injected standards (which is supported by the constancy of the Cu(I)–cyanide peak in Fig. 1b). When no cyanide was present in the eluent, the sum of the cyanide concentrations in the cyanide and Cu(I)–cyanide peaks was very similar to the total cyanide concentration in each of the standards. However, when cyanide was present in the eluent, increased complexation of the Cu(I) caused the observed levels of total cyanide in the two peaks to exceed that in the injected standards. The mean cyanide concentration in the Cu(I)–cyanide peak increased as cyanide was added to the eluent, reaching 3.35 m*M* for an eluent containing 100 μ*M* cyanide. For each concentration of cyanide in the eluent, the amount of cyanide in the Cu(I)–cyanide peak remained almost constant. Since each standard contained a total copper concentration of 1 m*M*, the average values of cyanide concentration in the Cu(I)–cyanide peak in Table 3 are also the average *R* values in the eluted Cu(I)–cyanide peak. The observed increase in *R* for the Cu(I)–cyanide peak with addition of cyanide to the eluent is in accordance with the retention model discussed earlier.

Two additional points should be noted. The calculated uncomplexed cyanide concentrations (both CN^- and HCN) for a Cu(I)–cyanide standard (1 m*M*, *R*=3) at pH 12 and pH 8 are 0.067 and 0.251 m*M*, respectively. The calculated total complexed cyanide concentrations at pH 12 and pH 8 for this standard are 2.933 and 2.749 m*M*, respectivly (Fig. 4). The observed cyanide peak for this standard in an eluent without added cyanide was 0.45 m*M*, while the observed *R* value of the eluted Cu(I) peak was 2.54 (Table 3). This difference between the calculated and observed results indicates that more dissociation occurred than was predicted by the change from pH 12 to 8. This is in accordance with the proposed on-column dissociation due to the retention differences between the uncomplexed cyanide and the Cu(I)–cyanide complexes. In addition to this, the equilibrium constants may have been significantly altered in the eluent due to the presence of acetonitrile for the reasons discussed earlier. This would have also contributed to the difference between the above calculated and observed results. It can also be noted that the change in speciation of the eluted Cu(I)–cyanide species occurring after cyanide addition to the eluent is in agreement with the calculated change in the average ligand number at low *R* values as shown in Fig. 4.

A further prediction of the retention model was that in the absence of cyanide in the eluent, different

Table 3
Cyanide concentration in the cyanide and Cu(I)–cyanide peaks

[NaCN] in eluent (μ*M*)	*R*=3 [CN] (m*M*)			*R*=5 [CN] (m*M*)			*R*=7 [CN] (m*M*)			Cu(I) peak
	CN peak	Cu(I) peak	Total	CN peak	Cu(I) peak	Total	CN peak	Cu(I) peak	Total	Mean
0	0.45	2.54	2.99	2.45	2.51	4.96	4.45	2.54	6.99	2.53
50	0.14	3.06	3.20	2.37	2.98	5.35	4.35	3.06	7.41	3.03
100	0.00	3.41	3.41	2.05	3.30	5.35	4.14	3.35	7.49	3.35

Standards: 1 m*M* Cu(I)–cyanide with *R* values of 3, 5 and 7. Eluents contained 0–100 μ*M* NaCN. PCR detection wavelength was 515 nm.

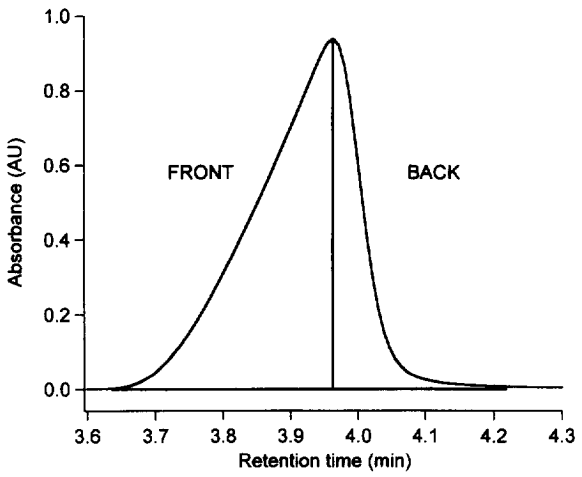

Fig. 7. UV detector chromatogram of 1.0 m*M* Cu(I)–cyanide standard ($R=3$), illustrating the FRONT and BACK portions of the Cu(I)–cyanide peak. Eluent as for Fig. 1.

R values should be observed in the front and back segments of the Cu(I)–cyanide peak. Further, this difference should be minimised when cyanide was added to the eluent. To investigate this hypothesis the Cu(I)–cyanide peaks in both the UV and PCR chromatograms for the 1 m*M* ($R=3$) standards obtained above were segmented at the peak maximum, as shown in Fig. 7. The cyanide and Cu(I)–cyanide concentrations in the front and back portions of each peak were then calculated from cyanide (PCR detector) and Cu(I)–cyanide (UV detector) calibration plots. The results are shown in Table 4, from which it is apparent that there was a significant change in the *R* value over the Cu(I)–cyanide peak in the first two eluents and that the peak was homogenous with 100 μ*M* NaCN in the eluent. These results provide quantitative evidence that the Cu(I)–cyanide complexes undergo partial dissociation during the chromatographic process in an eluent without added cyanide, leading to peak asymmetry.

Table 4
[CN]:[Cu] ratio in the front and back of the Cu(I)–cyanide peaks resulting from the injection of 1 m*M* Cu(I)–cyanide standard ($R=3$) in eluents containing 0–100 μ*M* NaCN

[NaCN] in eluent (μ*M*)	[CN]:[Cu] ratio	
	Front of Cu(I) peak	Back of Cu(I) peak
0	2.28	3.10
50	2.85	3.62
100	3.51	3.50

4. Conclusions

The partial dissociation of the Cu(I)–cyanide complexes on the HPLC column can be controlled by the addition of NaCN to the eluent, enabling manipulation of the retention time. While the PDA detector could detect differences in the eluted Cu(I)–cyanide species between the eluents, it was unable to discriminate between different complexes eluted within a peak. The PCR method was suitable for the determination of the change in the overall *R* value in the different eluents and also to gain some insight into the nature of the complexes existing within an eluted peak. These results show that the degree of dissociation of the Cu(I)–cyanide is reduced as the NaCN concentration in the eluent was increased and also confirm that the increase in the retention time caused by addition of cyanide to the eluent was due to the increase in the CN:Cu mole ratio of the eluted species.

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