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Anion-exchange chromatography of metal cyanide complexes with gradient separation and direct UV detection

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Abstract

In the regulatory analysis of water samples, cyanide content is usually expressed in various forms as free cyanide, total cyanide, weak-acid dissociable cyanide, available cyanide, and cyanide amenable to chlorination. Concentration of individual metal cyanide complex, not furnished in any of these methods, is useful in meaningful assessment of toxicity due to cyanide. In the present work, two macroporous anion-exchange columns, having high and intermediate hydrophobicity, were evaluated to achieve separation of cyano complexes of silver, iron, gold, copper, nickel, and cobalt. On the QS-A1 SC column, of high hydrophobicity, the monovalent cyano complexes of silver and gold eluted last while the multivalent cyano complexes, e.g. iron and copper, eluted early. It is suggested that the retention order on this column is due to relative hydrophobicity of the metal cyanide complex, and its affect on ion exchange. In contrast, on the QS-A2 SC column of intermediate hydrophobicity, with the exception of cyano complex with Fe, the separation of the cyano complexes of five other metals closely followed an anion-exchange mechanism. Under gradient conditions, the six metal cyanide complexes were well resolved on the QS-A2 SC column and the method with direct UV detection at 215 nm was accurate (spike recovery of 99.8–118.8%) and precise (RSD of 1.0–2.6%). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Metal complexes; Cyanides

1. Introduction

Cyanide content in water is of environmental concern because of its toxicity to aquatic, animal, and human life. The widespread use of cyanide compounds in some industrial processes has led to its entering the aquatic environment, either as free anion or as metal complexes. Various metal cyanide complexes are found in water. The stability of these complexes, and hence the associated toxicity, varies

among the various complexes. Weak and labile complexes such as $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$ can easily release cyanide and are considered more toxic, whereas stronger complexes such as $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Au}(\text{CN})_2]^-$ are considered less toxic [1]. The stability of metal cyanide complexes also has implications in their fate and transport in the geochemical environment, and in remediation and waste treatment.

The regulatory analysis of water samples for cyanide usually involves two steps [1,2]. In the first step, the sample is digested to convert all cyanide species into $\text{HCN}_{(\text{g})}$ which is trapped in a high pH solution. In the second step, cyanide is determined by pyridine barbituric acid chemistry with photo-

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metric detection [1,2] or by an amperometric method [3]. Cyanide content is expressed in various forms as free cyanide, total cyanide, weak-acid dissociable cyanide, and cyanide amenable to chlorination. Recently, in order to specifically determine available cyanide, a ligand-exchange based method was developed that would quantify free cyanide and cyano-complexes with only zinc, copper, cadmium, mercury, nickel, and silver [4]. The selectivity of ligands used was such that the method did not recover non-dissociable species (cyano complexes with iron, gold, and cobalt). Although these methods partially differentiate among the various cyanide species, they fail to furnish information on metal cyano complexes on an individual basis. A complete cyanide species mass balance is desirable to determine the extent of toxic and non-toxic metal cyanide species present in water samples.

Cyanide speciation has been accomplished using anion-exchange chromatography [5,6], ion-interaction chromatography [7] and capillary electrophoresis [8]. Metal cyanide complexes are anionic in nature but behave with hydrophobic character. In the anion-exchange chromatography, to achieve rapid and efficient separation of hydrophobic metal cyanide complexes, columns of low hydrophobicity are preferred. Drop et al. [5,6] employed gradient elution on Dionex's pellicular columns, AS5 of low hydrophobicity and AS11 of very low hydrophobicity, for the separation of $[\text{Ag}(\text{CN})_2]^-$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Au}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, and $[\text{Co}(\text{CN})_6]^{3-}$ complexes with subsequent UV detection at 215 nm. The method enabled detection of cyano complexes at mg/l levels without preconcentration and at $\mu\text{g/l}$ levels with preconcentration.

Separation of these metal cyanide complexes on macroporous anion-exchange columns has not been reported in the literature, and in order to further expand the choice of available columns, we thought it necessary to demonstrate separation of metal cyanide complexes on the macroporous columns. In the research work presented here, two macroporous columns of high and intermediate hydrophobicity were evaluated. An accurate and precise method was then developed using a column of intermediate hydrophobicity.

2. Experimental

2.1. Anion exchange chromatography with gradient separation

Lachat's IC+ System on QC8000 (Lachat Instruments, Milwaukee, WI, USA) was used. The system was equipped with an XYZ autosampler, a low-pressure gradient mixing system with LabGrad software, a peristaltic pump for drawing the sample, an electronically actuated six-port injection valve with a 100- μl loop, a DVW-10L UV detector, and an OmnionIC data station. Of the two macroporous columns evaluated, the QS-A1 SC column has high hydrophobicity and the QS-A2 SC column has intermediate hydrophobicity (columns obtained from Transgenomic, San Jose, CA, USA). Both columns are packed with resin made of 55% cross-linked polystyrene-divinylbenzene co-polymer with 80- \AA porosity. The QS-A2 SC resin is more hydrophilic since it is first sulfonated and then functionalized with a quaternary amine. The QS-A1 SC resin, with functional groups from several quaternary amines, is more hydrophobic since the resin is not initially sulfonated.

As explained in the Results and discussion section, the gradient method was optimized using the QS-A2 SC column. The chromatographic run time was kept longer than the gradient duration time. Upon completing a gradient run, the gradient was kept on hold, with eluent composition maintained at initial conditions, until a sample was injected, at which time the hold was released and the gradient program advanced to the next event line.

2.2. Reagents, standards, and synthetic wastewater sample

Eluent constituents, NaOH, NaClO_4 , and methanol, of ACS reagent grade were used. The eluent composition was based on the earlier studies reported by Drop et al. [5,6], and no further studies were conducted to choose an alternative eluent composition. Although carbonate does not interfere in chromatographic separation, it could adhere to the anion-exchange resin of the columns. The retained carbonate may eventually lead to unstable baseline and

shortened retention times [5,6]. To minimize this effect, eluent containing NaOH was prepared fresh daily and its exposure to ambient air was minimized during the operation. Eluent concentrations were; A, 20 mM NaOH+150 mM NaCN+10% MeOH; B, 20 mM NaOH+250 mM NaClO₄+10% MeOH; and C, 20 mM NaOH+10% MeOH.

Synthetic standards for the metal cyanide complexes were prepared using ACS reagent grade chemicals. A 10 mM NaOH solution was used in preparing all standards in order to match the matrix of the standards to that of the alkaline preserved samples. Also, the high pH acted as a safety measure to prevent formation of gaseous HCN, a highly toxic species, in the event of decomposition of the metal cyanide standards. Stock solutions, expressed as 1000 mg metal cyanide complex/l, of cobalt cyanide, gold cyanide, iron cyanide, nickel cyanide and silver cyanide were prepared by dissolving appropriate amounts of K₃Co(CN)₆, KAu(CN)₂, K₄Fe(CN)₆·3H₂O, K₂Ni(CN)₄, and KAg(CN)₂, respectively, in 10 mM NaOH solution. To prepare stock solutions of copper cyanide solution, appropriate amounts of CuCN and 0.6922 g of NaCN were dissolved in 10 mM NaOH solution and final volume made to 1 l with the NaOH solution [5,6]. The stock solutions for cobalt cyanide, gold cyanide, and iron cyanide are relatively stable up to 1 month, whereas those for copper cyanide, nickel cyanide, and silver cyanide are not stable and hence were prepared daily. Once prepared, all stock solutions were stored in amber color bottles to prevent photodecomposition of the complexes.

The substitute wastewater sample was prepared as described in the ASTM Standard D5905-96 [9].

3. Results and discussion

3.1. Selection of column for method optimization

Two macroporous columns were evaluated to achieve gradient separation of the metal cyanide complexes. Eluent composition included perchlorate, the anion of strong eluting power, and it enabled elution of metal cyanide complexes from the column. Synthetic standards of individual cyanide complex

were injected to identify the peaks. As mentioned in the Experimental section, the resin in QS-A1 SC column is very hydrophobic, and it exhibited unique elution sequence for the metal cyanide complexes (Fig. 1, Table 1). With anion-exchange chromatography, one would expect increasing retention times of anionic complexes with increasing valence of the cyano metal complex, but it was hardly the case with the elution sequence on this column. The monovalent complexes eluted last while the tetravalent complex of cyanide with Fe(II) eluted first with the di- and trivalent complexes eluted in between. This unique selectivity seemed to follow hard–soft acid–base theory since cyanide complexes of the soft, polarizable metals, Ag and Au, eluted last, while those of metals with intermediate hardness, Fe, Cu, and Co, eluted early. The Au–CN complex was very tightly held, with a retention time of 19.7 min (Fig. 1b) on the QS-A1 SC resin. It was not possible to accomplish separation, even under gradient conditions, that would have a relatively short run time and adequately separate early eluting peaks for complexes with Fe, Cu, and Co.

Experiments were then performed on the QS-A2 SC column, which had intermediate hydrophobicity, due to initial sulfonation of its resin. Unlike the QS-A1 SC column, elution sequence of cyanide complexes on the QS-A2 SC column, with the exception of the tetravalent cyano complex of Fe(II) that eluted early, closely followed a typical anion-exchange pattern (Table 1, Fig. 2), similar to that reported by Drop et al. [5,6]. It is possible that due to steric hindrances on the macroporous resin, the large molecule of tetravalent [Fe(CN)₆]⁴⁻ ion eluted off the column with slight retention. In the eluent optimization experiments with this column, 10% methanol was maintained in the three eluents, to minimize surface interactions of the complexes. The solvent would be beneficial in preventing fouling of the column due to repeated injections of wastewater samples containing unknown organics.

3.2. Optimized method on column with low to medium hydrophobicity

Optimum concentration for sodium perchlorate was 250 mM (eluent B) since it provided adequate

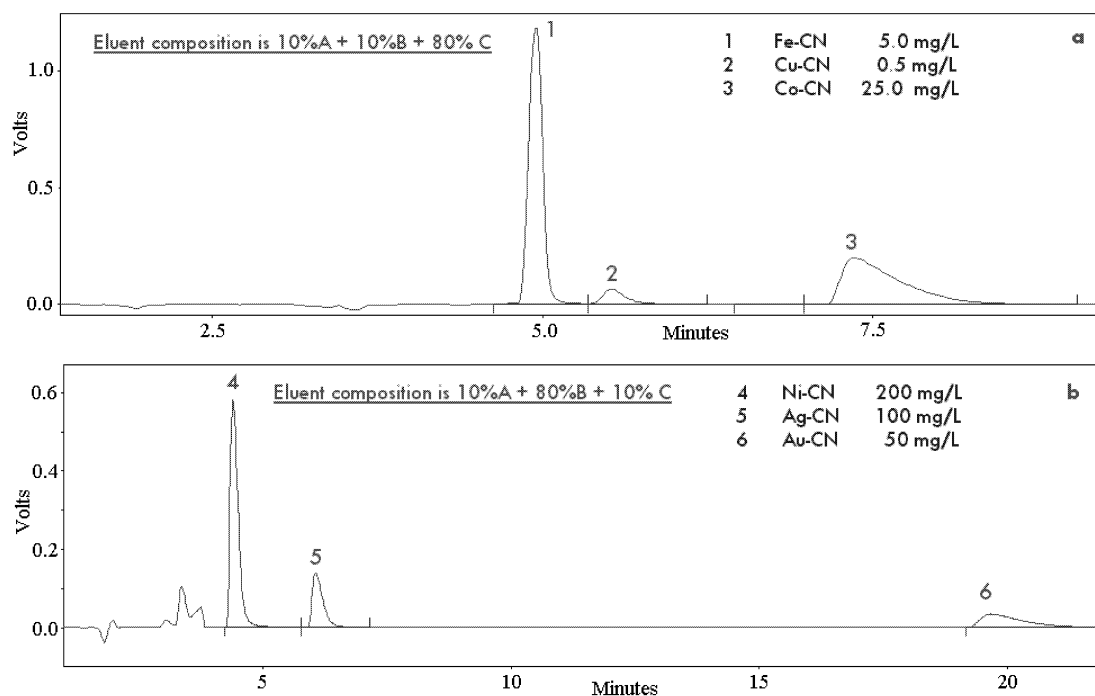


Fig. 1. Separation of metal cyanide complexes on column having high hydrophobicity, QS-A1G (50×4.6 mm) and QS-A1 SC (250×4.6 mm) using (a) eluent composition of 10:10:80 for early eluting peaks, and (b) eluent composition of 10:80:10 for late eluting peaks. Eluent concentrations were: A, 20 mM NaOH+150 mM NaCN; B, 20 mM NaOH+100 mM NaClO₄; and C, 20 mM NaOH. Sample loop, 100 μl.

separation of early eluting peaks and a run time of 28 min. Various experiments were conducted to optimize the gradient profile. As presented in Fig. 2, the six metal cyanide complexes were nicely resolved. A 100-μl sample loop provided adequate sensitivity for the metal cyanide complexes. It has been reported that under the alkaline conditions of the analysis, [Fe(CN)₆]³⁻ is reduced to [Fe(CN)₆]⁴⁻, yielding a

single analyte peak and any unreduced [Fe(CN)₆]³⁻ will exhibit a tailing on the [Fe(CN)₆]⁴⁻ peak [5,6]. This finding was confirmed under the present chromatographic conditions by injecting a 5-mg/l standard of ferri-CN complex, [Fe(CN)₆]³⁻. The elution time was 5.9 min for the [Fe(CN)₆]³⁻ peak compared with 5.4 min for the [Fe(CN)₆]⁴⁻ peak. The chromatograms obtained showed that, in certain

Table 1
Elution sequence of metal cyanide complexes on various columns

| Column | Hydrophobicity | Retention times for metal cyanide complexes |
|-----------------|----------------|---|
| Dionex, AS-5 | Low | [Ag(CN) ₂] ⁻ < [Au(CN) ₂] ⁻ < [Cu(CN) ₃] ²⁻ < [Ni(CN) ₄] ²⁻ < [Fe(CN) ₆] ⁴⁻ < [Co(CN) ₆] ³⁻ |
| Dionex, AS-11 | Very low | [Ag(CN) ₂] ⁻ < [Au(CN) ₂] ⁻ < [Cu(CN) ₃] ²⁻ < [Ni(CN) ₄] ²⁻ < [Fe(CN) ₆] ⁴⁻ < [Co(CN) ₆] ³⁻ |
| Lachat QS-A1 SC | High | [Fe(CN) ₆] ⁴⁻ < [Cu(CN) ₃] ²⁻ < [Co(CN) ₆] ³⁻ < [Ni(CN) ₄] ²⁻ < [Ag(CN) ₂] ⁻ < [Au(CN) ₂] ⁻ |
| Lachat QS-A2 | Low to medium | [Ag(CN) ₂] ⁻ < [Fe(CN) ₆] ⁴⁻ < [Au(CN) ₂] ⁻ < [Cu(CN) ₃] ²⁻ < [Ni(CN) ₄] ²⁻ < [Co(CN) ₆] ³⁻ |

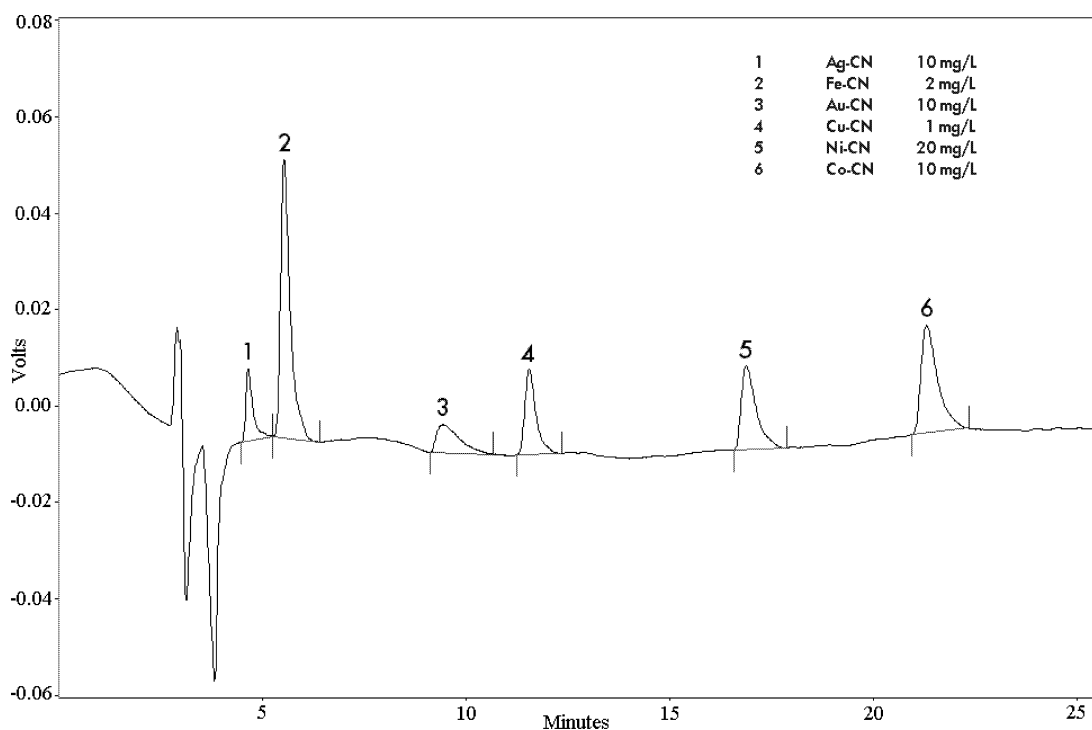


Fig. 2. Gradient separation of metal cyanide complexes on column of low to medium hydrophobicity. Eluent concentrations: A, 20 mM NaOH+150 mM NaCN+10% MeOH; B, 20 mM NaOH+250 mM NaClO₄+10% MeOH; and C, 20 mM NaOH+10% MeOH. In the gradient program, composition was maintained at 10:24:66 up to 2 min, then ramped up to 10:80:10 at 14 min and held up to 22 min and then back to 10:24:66 at 25 min. Eluent flow rate was 1.0 ml/min. Columns, QS-A2G (4.6×50 mm) Guard and QS-A2 SC (4.6×250 mm) Analytical; sample loop, 100 μ l.

instances, the $[\text{Fe}(\text{CN})_6]^{4-}$ showed a tailing peak due to the possible presence of unreduced $[\text{Fe}(\text{CN})_6]^{3-}$ peak.

As presented in Table 2, asymmetry values were ~ 2 for the metal cyanide complexes, with the exception of a value of 4.3 for the $[\text{Au}(\text{CN})_2]^-$ complex. The severe tailing on $[\text{Au}(\text{CN})_2]^-$ may have added to the uncertainty in determining peak area and the analytical results were accurate when calibration models were constructed using peak height as an attribute for $[\text{Au}(\text{CN})_2]^-$. The analytical results were accurate with area as the attribute for the other five metal cyanide complexes. The linear calibration range for $[\text{Au}(\text{CN})_2]^-$ was 20, and it was 100 for all other five metal cyanide complexes (Table 2). The method was precise with RSD in the range of 1.0% for $[\text{Ni}(\text{CN})_4]^{2-}$ to 2.6% for $[\text{Co}(\text{CN})_6]^{3-}$. The method detection limit values, calculated at signal-to-noise ratio of 3, ranged from

0.07 mg/l for $[\text{Fe}(\text{CN})_6]^{4-}$ to 0.83 mg/l for $[\text{Co}(\text{CN})_6]^{3-}$.

3.3. Potential application of the method for wastewater analyses

To assess the applicability of the method for wastewater analysis, a synthetic wastewater sample [9] was analyzed by the optimized method followed by duplicate analyses of wastewater sample spiked with a mixed standard (Fig. 3) containing $[\text{Ag}(\text{CN})_2]^-$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Au}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, and $[\text{Co}(\text{CN})_6]^{3-}$ at 5, 1, 5, 0.5, 10, and 5 mg/l, respectively. Spike recovery values in the range of 99.8% for $[\text{Ag}(\text{CN})_2]^-$ to 118.8% for $[\text{Cu}(\text{CN})_3]^{2-}$ were obtained. For duplicate analyses of the spiked sample, replicate difference values ranged from 1.7% for $[\text{Fe}(\text{CN})_6]^{4-}$ to 8.2% for $[\text{Au}(\text{CN})_2]^-$.

Table 2
Summary of method performance

| Metal cyanide complex | Retention time (min) | Asymmetry ^a | Calibration range ^b (mg/l) | Precision ^c , RSD (%) | Spike recovery ^d (%) | Est. MDL ^e (mg/l) |
|--------------------------------------|----------------------|------------------------|---------------------------------------|----------------------------------|---------------------------------|------------------------------|
| [Ag(CN) ₂] ⁻ | 4.6 | 1.8 | 1–100 | 2.0 | 99.8 | 0.67 |
| [Fe(CN) ₆] ⁴⁻ | 5.4 ^f | 2.4 | 0.2–20 | 1.1 | 100.9 | 0.07 |
| [Au(CN) ₂] ⁻ | 9.4 | 4.3 | 5–100 | 1.5 | 102.0 | 0.47 |
| [Cu(CN) ₃] ²⁻ | 11.5 | 1.9 | 0.1–10 | 1.1 | 118.8 | 0.05 |
| [Ni(CN) ₄] ²⁻ | 16.8 | 2.5 | 2–200 | 1.0 | 102.1 | 0.63 |
| [Co(CN) ₆] ³⁻ | 21.3 | 2.4 | 1–100 | 2.6 | 100.0 | 0.83 |

^a Peak asymmetry values for the respective concentration values of metal cyanide complexes at 100, 20, 100, 10, 200, and 100 mg/l. Peak asymmetry values (A_s) were calculated as $A_s = W_{0.05}/2f$ where $W_{0.05}$ is the distance from the leading edge to the tailing edge of the peak measured at a point of 5% of the peak height from the baseline and f is the distance from the peak maximum to the leading edge of the peak.

^b Linear calibration curves with $R^2 > 0.998$. Concentration is expressed as mg of cyano metal complex/l.

^c Relative standard deviation (RSD) for replicate analysis ($n=5$) of a synthetic standard with respective concentration of metal cyanide complexes at 10, 2, 10, 1, 20, and 10 mg/l.

^d A synthetic wastewater sample was prepared as described in ASTM standard, and spiked with a mixed standard containing metal cyanide complexes at 5, 1, 5, 0.5, 10, and 5 mg/l, and analyzed using the gradient method. Percentage recovery value was calculated as, % recovery = $[(S-U)/(K)] \cdot 100$, where S and U are determined values in spiked and unspiked samples, and K is the known spike amount.

^e Est. MDL, estimated method detection limit at signal-to-noise ratio of greater than 3.

^f Peak for Fe(III)–CN complex, $[\text{Fe}(\text{CN})_6]^{3-}$ eluted at 5.9 min, and when present it showed as a tailing peak on the Fe(II)–CN complex $[\text{Fe}(\text{CN})_6]^{4-}$.

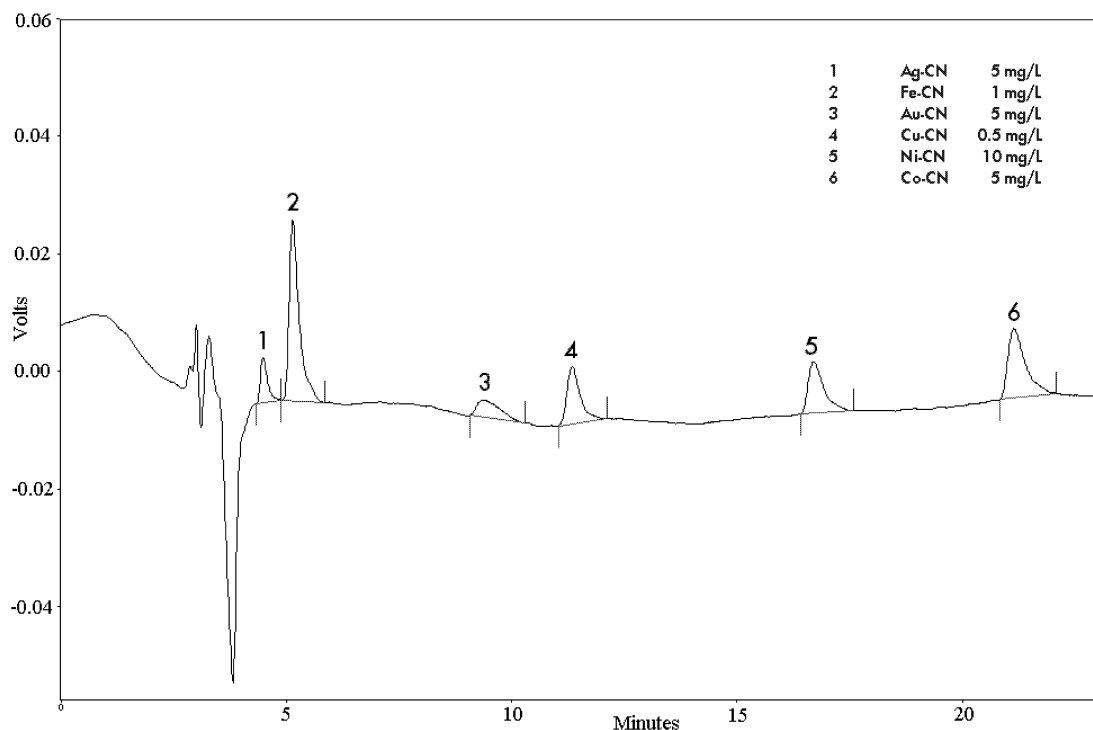


Fig. 3. A typical chromatogram showing separation of metal cyanide complexes spiked in a synthetic wastewater sample. For chromatographic conditions, see Fig. 2.

Table 3
Comparison of ranges in this study with reported studies

| Metal cyanide complex | Calibration range (mg/l), this study | Calibration range (mg/l), without preconcentration [5] | Calibration range (mg/l), with preconcentration [5] |
|---------------------------------|--------------------------------------|--|---|
| $[\text{Ag}(\text{CN})_2]^-$ | 1–100 | 1–100 | 0.01–0.125 |
| $[\text{Fe}(\text{CN})_6]^{4-}$ | 0.2–20 | 0.1–20 | 0.0005–0.02 |
| $[\text{Au}(\text{CN})_2]^-$ | 5–100 | 1–50 | 0.005–0.1 |
| $[\text{Cu}(\text{CN})_3]^{2-}$ | 0.1–10 | 0.05–2 | 0.0005–0.005 |
| $[\text{Ni}(\text{CN})_4]^{2-}$ | 2–200 | 1–200 | 0.05–0.1 |
| $[\text{Co}(\text{CN})_6]^{3-}$ | 1–100 | 1–100 | 0.001–0.2 |

Drop et al. [5,6] have conducted extensive research on applicability of the anion-exchange chromatographic method for determination of metal cyanide complexes in wastewater and calibration ranges from this study are compared with those published by Drop et al. [5] in Table 3. With the exception of $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Co}(\text{CN})_6]^{3-}$, the lower end of calibration was slightly higher than that published by Drop et al. [5]. Drop et al. [5] have also developed a preconcentration method (Table 3) to quantify as low as 0.5 $\mu\text{g/l}$ of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Cu}(\text{CN})_3]^{2-}$, and developing the preconcentration method would be the objective of our future studies.

4. Summary

Our research showed that separation of cyanide complexes on hydrophobic resin of the QS-A1 SC column did not follow a conventional anion-exchange mechanism. The mechanism could be explained by secondary retention mechanism due to adsorption of hydrophobic complexes. Cyano complexes of soft metal ions were held tightly by the hydrophobic resin while those of intermediate hardness were weakly retained. With the exception of cyanide complex with Fe, the separation of cyanide complexes of the other five metals closely followed anion-exchange mechanism on resin of low to

medium hydrophobicity of the QS-A2 SC column. The gradient method optimized with the QS-A2 SC column was accurate and precise.

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