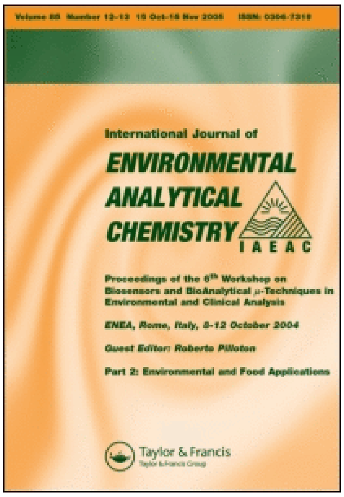

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Ion Chromatography of Cyanide and Metal cyanide Complexes: A Review

E. O. Otu[a]; J. J. Byerley[b]; C. W. Robinson[b]
[a] Division of Natural Sciences, Purchase College, State University of New York, Purchase, NY, USA [b] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

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ION CHROMATOGRAPHY OF CYANIDE AND METAL CYANIDE COMPLEXES: A REVIEW

E. O. OTU*[1], J. J. BYERLEY[2] and C. W. ROBINSON[2]

[1]*Division of Natural Sciences, Purchase College, State University of New York, Purchase, NY 10577 USA;* [2]*Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

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Ion chromatography (IC) for the separation and determination of the cyanide ion and metal cyanide complexes is reviewed. The United States Environmental Protection Agency (USEPA) classifies cyanides as hazardous substances, hazardous waste constituents and priority toxic pollutants. IC is a reliable analytical technique that is not affected by the high salt concentration typical of process and environmental samples. The technique of IC is routinely used for the analysis of wastewater, soils and sediments, plating solutions and hydrometallurgical effluent for cyanides and other ions. IC provides knowledge of all cyanide species, free and complexed (to metal) and conveniently provides speciation information for different oxidation states, for example, iron II and III, and gold I and III cyanide complexes. This obviates the necessity for distillation to convert metal cyanide species to hydrogen cyanide for determination of total cyanide. Detection limit ranging down to 1 µg/L CN^- and 5 µg/L $Au(CN)_2^-$, without preconcentration, have been reported.

KEY WORDS: Cyanide, metal cyanide complexes, separation, determination, environment, ion chromatography.

INTRODUCTION

Many industrial processes such as metal plating, case hardening of steel and precious metals extraction use cyanides. Metal cyanides, for example, sodium, copper, zinc and potassium cyanide are used for electroplating certain metals and are vital to other industrial manufacturing operations. Hydrogen cyanide is used in the production of polyacrylonitrile plastics. Sodium cyanide is used in the hydrometallurgical extraction of gold from ores (cyanidation process). The cyanidation process also results in the formation of a wide range of other metal cyanide complexes, some of which are more stable and in higher concentration than gold cyanide.

When a polyacrylonitrile plastic is exposed to intense heat, it decomposes yielding deadly hydrogen cyanide[1]. The primary effluents from cyanidation processes are toxic to humans and aquatic life and are known to cause considerable damage to the environment if discharged in an untreated state. The USEPA stipulates a 3.5 µg/L level in water to protect freshwater and marine aquatic life and wildlife. The allowable daily intake for man is 8.4 mg/day. World Health Organization standard for drinking water is 50 µg/L and the National Institute for Occupational Safety and Health (NIOSH) stipulates a level of 5 mg/m^3 for hydrogen cyanide. Possible routes of contamination are inhalation, ingestion and skin absorption. Therefore, strict control and monitoring of cyanide levels in the environment is necessary. The need for rapid determination of cyanide(s) in air and wastewaters is thus of major interest for both process and environmental control.

A review of sampling and analytical methods for the analysis of cyanide and its salts in various matrices (including water, air, and human fluids-blood and urine) was published in 1976 by NIOSH[2]. These methods include colorimetry, tritrimetry, gas chromatography and atomic absorption and infrared absorption spectrophotometry. Ion chromatographic techniques are increasingly being applied to the analysis of a large range of constituents in different complex media[3]. The principal motivation for the use of ion chromatography is its ability to eliminate interferences, and the accurate evaluation of cyanide metal complexes concentrations (in high matrix background) compared to other analytical methods such as atomic absorption spectrophotometry[4,5].

The total cyanide concentration in a sample can be broadly (or loosely) divided into free cyanide (which includes CN^-, HCN and cyanide complexes of Ag, Cd, Cu, Ni and Zn that can readily dissociate in weak acid solution, i.e., labile) and complexed cyanide (which includes cyanide complexes of Au, Co, Fe, Hg, Pd and Pt that have high formation constants). Titrimetric, colorimetric and ion selective electrode methods require cyanide concentration greater than 1 mg/L, 20 μg/L and between 0.05 to 10 mg/L, respectively[6], and are reliable in the absence of interfering substances like sulphide, thiocyanate and metal cyanides in the free cyanide group. Real samples are not free of interfering substances, which makes IC the method of choice.

The role of ion chromatography (IC) in chemical analysis continues to develop and expand. Separations of the various components of a mixture to be analyzed is generally fast, quantitative and useful for very low levels of ions, for example, 5 μg/L for $Au(CN)_2^-$ with a sample size of 150 μL[4]. Currently, competing alternatives for determining low concentrations of anions do not provide the same reliability, especially at the high concentrations of concommitant ions that is typical of most process and environmental samples. IC has proven to be versatile, selective and sensitive for the determination of a wide variety of ions in diverse environments as evidenced by the numerous publications in the literature. Simultaneous analysis of several ions in one injection makes IC a frequent method of choice for the analysis of environmental samples.

Cyanide can generally be determined by a variety of wet chemical methods such as atomic absorption spectrophotometry (AAS), various electrochemical methods[6], but problems with interference, the sometimes long experimental manipulations and the presence of metal complexes often complicate these procedures. A number of works exist in the literature[e.g.,7–9] that describe indirect use of AAS to determine cyanide. One approach involves precipitation of the cyanide by adding excess metal ion followed by determination of either the metal in the precipitate (after dissolving in a suitable solvent) or of excess metal (in the filtrate). Although this strategy minimizes interferences, the added precipitation and filtration steps make the method slow and takes away the advantage of the high sensitivity obtainable with AAS. IC with indirect conductivity[10–16], UV/VIS[4,17–19] or electrochemical[5,20,21] detection are methods that can be used to determine low levels of cyanide(s). Ion chromatography has proven to be a powerful technique for the routine separation and detection of metal cyanide complexes(e.g., 4,5,17).

Speciation and quantitation of metal cyanide species of the same metal would be useful in environmental and toxicological studies. IC is a multi-element analytical technique which is also capable of differentiating between cyanide complexes, oxidation states of a metal and separation of interferences, making in an excellent choice for the analysis of complex samples.

IC modes for cyanide determination

IC as applied to the separation and detection of cyanides fits two modes of chromatography, ion exchange and ion-pairing or ion-interaction. Ion exchange chromatography (IEC) is a reversible adsorption process based upon the differential affinity of ions for the stationary phase. At any specified volumetric flow rate of the eluent, type of stationary phase and the volume, void fraction and particle size of the stationary (solid) phase, the rate of migration of each species of ion through the column is dependent on the type and concentration of ions in the eluent.

Traditionally, IEC has been used for the separation of ionic substances, mostly inorganic ions. One major strategy that has been applied to these separations is based on the addition of an hydrophobic ion of opposite charge to the target analyte ion. A patented form (Dionex Corp.) of this mode of separation called mobile phase ion chromatography (MPIC), is in fact very similar to what is commonly called ion pair chromatography. The packing material of the column employs resins, PS/DVB or a silica-bonded phase, with essentially no fixed ion exchange capacity. Ion exchange sites are dynamically (sometimes permanently) formed as the eluent flows through the column and this mode of operation has been found to increase the retention of ionic species, improve selectivity, and to often increase resolution[22-27].

The identity (charge) of the ion exchange sites and the capacity of the system can readily be modified as necessary to meet new analytical conditions. Different identity is achieved by using different pairing agents and the capacity is changed by using different concentration levels. Thus, ion pair chromatography confers a much greater degree of flexibility than does conventional fixed site ion exchange chromatography[28]. However, because of this great degree of flexibility, optimization of a particular analysis of interest is more difficult than in fixed site ion exchange chromatography. The nature of the interaction between the analyte ion, the hydrophobic ion and the stationary phase has been widely studied and several models have been proposed to account for the retention of the analyte ions[28-33].

In this review, the ion exchange and ion pair modes of chromatography for separation of cyanides are discussed. The aim is not to compare the two modes, so we have not presented the results from either mode in separate sections.

APPLICATIONS

Direct determination of cyanide. The electrochemical activity of cyanide with a silver electrode has formed the basis of its direct and sensitive detection at parts per billion levels. Rocklin and Johnson[5] employing amperometric and conductivity detection in tandem used ion exchange chromatography to simultaneously determine "'free" and "labile" cyanide, sulphide and halide ions. The electrochemical detector was placed between the separator column and the suppressor column while the conductivity detector (which relies on removal of most of the ions in the eluent by the suppressor) was placed after the suppressor. Cyanide was detected by the electrochemical detector. They used a Dionex AS4 column with an eluent composed of 1.0 mM Na_2CO_3, 10 mM Na_2HBO_3, and 14.7 mM ethylenediamine at pH 11.0 and achieved a detection limit of 2 μg/L for CN^- with a 100 μL sample injection size. Under the chromatographic conditions used by them, the cyanide complexes of cadmium and zinc dissociated completely (i.e., were labile) and were determined as free cyanide. The cyanide complexes of nickel and copper dissociated slowly causing peak tailing. The cyanide complexes of gold, iron and cobalt did not dissociate at all and were retained on the column, under the chromatographic conditions.

Pohlandt[20] determined total cyanide with amperometric detection after photochemical irradiation in the presence of 3% v/v hypophosphorous acid which was added to dissociate the metal cyanide complexes. The eluent was the same as that used by Rocklin and Johnson[5]. Irradiation in the presence of phosphoric acid was not as effective. The presence of hypophosphoric acid without irradiation liberated some cyanide from weak metal complexes. Light emitted in the near UV region was more effective in dissociating the metal complexes. Hexacyanocobaltate(III) did not successfully dissociate when present as the sole cyanidic species, but 95% total cyanide yield was obtained from a solution containing it in the case of a mixed-metal cyanide complex solution. The method suffers from the accumulation of mercury on the column packing: the mercury recombines with cyanide ion on subsequent injections, resulting in loss of sensitivity for CN^-. The source of the mercury was from $Hg(CN)_4^{2-}$ in the sample. Also, irradiation may yield cyanate, nitrate and/or nitrite which will reduce the total cyanide unless acidic reducing conditions are strictly maintained.

Koch[34] used a Dionex AS2 column to develop a method applicable to the analysis of cyanide in air/dust. Samples were collected on dry laboratory tissues and ultrasonically extracted with the eluent. The eluent was similar to that of Rocklin and Johnson[5] except that it also contained 5 mM NaOH. Using amperometric detection, a detection limit of 1 μg/L for CN^- was achieved without interference from sulphide. Bond *et al.*[35] simultaneously determined CN^- and S^{2-} using an eluent containing 5 mM OH^- at pH 11.7 and amperometric detection. The pH was chosen to ensure that HCN in solution existed as CN^- for detection. They noted that a dropping mercury or Hg-plated solid electrode detector provided the optimum response compared to a gold electrode. The dropping mercury electrode proved more reliable on a daily basis than the Hg-plated solid electrode detector. However, the latter gave a better detection limit than the former, 150 μg/L and 250 μg/L, respectively.

Wilson *et al.*[36] and Nadkarni and Brewer[37] used a Dionex AS3 column, an eluent consisting of 1.0 mM Na_2CO_3, and 10 mM NaH_2BO_3, 14.7 mM ethylenediamine and amperometry and reported a limit of detection of 20 μg/L for CN^- in aluminium processing wastewater, after converting the CN^- and cyanide complexes to HCN by refluxing in mineral acid in the presence of Mg^{2+}.

Mehra and Franhenberger[38] reported simultaneous determination of CN^-, Cl^-, Br^-, and I^- in lake water and soil using a Vydac 302 IC column, 5 mM potassium hydrogen phthalate (pH 4.3) eluent and amperometric detection. The detection limit was in the 0.2 to 12 μg/L range with 95–105% recovery. Jandik[39] determined cyanide in soil samples with a Waters IC-Pak anion column, 5.0 mM KOH eluent, amperometric detection and achieved a limit of detection of 100 mg/L. In another study of river and soil water, Jandik *et al.*[40] also used amperometry and a Waters IC-Pak anion column, and two eluents; 2 mM potassium hydrogen phthalate (KHP), 5 mM KOH or 5 mM phosphate buffer as eluent and obtained a detection limit of 2 μg/L.

Wang *et al.*[41] used an XAD-1 anion exchange resin and Dionex AS1 column, utilizing 1×10^{-5} mM KHP (pH 4.1, 6.25 and 7.1 adjusted with sodium tetraborate) and 3 mM $NaHCO_3$ plus 2.4 mM Na_2CO_3 and 10 mM NaOH, respectively for the two columns, as eluents with the columns. Sulfide interference on the determination of cyanide was observed for the XAD-1 column and attributed to the low pH of the eluent. The authors neither reported limits of detection nor compared such for the two columns. They mentioned that the drawback of their ion-selective electrode for detecting cyanide was the electrodes' slow response time in the flow system.

Suzuki *et al.*[42] used a 2 mM acetic acid-sodium acetate (pH 6.4) eluent, with detection by potentiometry and reported a detection limit of 52 µg/L for CN^-. Franks and Pullen[43] determined cyanide using a column containing Permutit Zeo-Karb 225 (Cd form) and 2.5 mM cadmium acetate as eluent with potentiometric detection. Girard[21] used Aminex A25 column, 0.20 M $NaNO_3$ as eluent with controlled-potential coulometry.

Waters Corporation in their chromatography cookbook[44] describes a flow injection analysis of cyanide using 0.4% chloramine-T (N-chloro-p-sulfonate sodium salt) as eluent, a pyridine barbituric acid reagent as a post-column reagent and UV detection at 570 nm. The method is subject to both thiocyanate and sulphide interferences and they reported a detection limit of 1 µg/L with 100 µL sample size.

Imanari *et al.*[45] determined cyanide, hexacyanoferrate (II&III) using TSK (Toyo Soda Tokyo, Japan) GEL IEX 520 QAE, a silica type pellicular ion exchanger column. They used post-column derivatization with 0.05 M $Fe(ClO_4)_3$ and 0.8 M $HClO_4$ as reagents and UV detection at 340 nm. Absorbance at this wavelength is about 60–70% of that at λ_{max} (= 305 nm) but was used to circumvent interferences. The eluent was 0.1 M $NaNO_3$ or 0.05 M acetate buffer containing 0.05 M $NaNO_3$ at pH 5.48. Detection limits were 0.16, 0.19 and 39.2 µg/L for cyanoferate II, III and cyanide, respectively.

Golombek and Schwedt[46] used a Hamilton PRP-X 100 strongly basic anion exchange resin, an eluent containing 70 mg/L 2,4-dihydroxybenzoic acid at pH 10.1 (adjusted with KOH) and indirect UV (λ = 312 nm). Jandik *et al.*[47] used a Waters IC Pak A column, 5 mM KOH eluent, amperometry at Ag electrode and indirect conductivity to determine cyanide in river, stream, pond and lake waters.

Using an eluent composed of 1.0 mM boric acid, 0.3 mM phthalate (pH 11.9) and 10% acetonitrile, Behrend *et al.*[48] determined cyanide in industrial wastewaters and effluents by conductivity detection. Toida *et al.*[49] determined cyanide in blood, serum and plasma by fluorescence detection at 583 and 607 nm after dual post-column reaction with chloramine-T then pyridine and barbituric acid. The column was a TSK Gel LS-222 and the eluent was 0.1 M acetate buffer plus 0.2 M perchlorate.

Indirect determination of cyanide. For an ion to be detected by conductivity its pK_a should be less than 7. The low dissociation constant of HCN (pK_a = 9.3) precludes the use of conductivity for direct detection of cyanide. However various workers[10–16] have employed different indirect methods. DuVal *et al.*[10] utilized the reaction of cyanide and iodine ($I_2 + HCN \leftrightarrow H^+ + I^- + ICN$ $K_{eq} = 0.73$; buffered pH = 4.75) and subsequent quantitation of the reaction product, iodide, after separation on an XAD-1 anion resin column using unsuppressed conductivity (the so called single-column IC) to measure I^-. They removed excess I_2 by adsorbing it on a glass precolumn containing unfunctionalized XAD-4 resin which was intermittently taken off-line, cleaned with 0.05 M nitric acid in acetone mixture followed by water and then placed back in-line. Use of glass for the precolumn allowed visible observation of the build-up of iodine (yellow coloration) which made it easier to know when to regenerate it. The precolumn was connected to the injection valve and preceded the sample loop. It was slowly loaded with 2–3 mL of the reaction solution. The eluent was 0.2 mM sodium or potassium hydrogen phthalate at pH 6.25 pumped at a flow rate 1.5 mL/min. The method was found to be sensitive for CN^- because of the higher sensitivity of detecting iodide than cyanide directly; the detection limit reported for cyanide was 400 µg/L for 100 µL sample size. The drawback with this method is that all species oxidizable by iodine, such as thiosulfate and thiocyanate, commonly found in cyanidic effluents and cobalt and mercury are potential interferences.

Hisayuki[11] patented an indirect method of determining cyanide ion using IC. He reacted CN^- and AgI in a precolumn to form I^-. Nonomura[12,13] used a Dionex anion exchange (AS4) column, and an eluent of 2.2 mM Na_2CO_3 to detect cyanide (free and metal cyanide complexes) in natural and wastewaters after oxidation to cyanate (pK_a = 3.66) by hypochlorite. The oxidation reaction of CN^- (metal bound) to CNO^- was not able to dissociate the strong cyanide complexes of Fe, Au and Co, even at an elevated temperature (80°C). Interferences were from Cl^- at high concentrations (coming from the NaClO reactant) and from NO_2^- resulting from further oxidation of the CNO^-. Better resolution between Cl^- and CNO^- was obtained with a Dionex HPIC AS4A than AS4 column. Silinger[14] also used hypochlorite to oxidize free CN^- to CNO^- before chromatographic separation, achieving a detection limit of 1 μg/L CN^-. However, he did not optimize the method with respect to temperature, stability of cyanate ion formed, interferences and applicability to metal cyanide complexes as done in references 12 and 13.

Dolzine *et al.*[15,16] analyzed air samples for cyanide. Airborne HCN was absorbed in an impinger containing 0.2 M NaOH, converting the HCN to NaCN. The latter was hydrolyzed at 110°C to sodium formate ($NaCN + 2H_2O \leftrightarrow NH_3 + HCOONa$) and the formate determined following ion chromatography on a Dionex anion exchange resin column (AS1) with suppressed conductivity detection. The eluent was 5 mM sodium borate and pumped at 2.3 mL/min and the sample loop size was 100 μL. The reaction kinetics were found to be dependent on time, temperature and alkali concentration. High alkalinity seriously affected the chromatography of formate; retention time increased (with poor peak shape) and other peaks which interfered with the formate peak appeared as well. This disadvantage was overcome by incorporating a clean-up step in which the sample solution was treated with a strong cationic resin, Amberlite IR-120, to remove Na^+ before injection into the IC. The reported yield following the clean-up was about 98% of that of a formate standard prepared in deionized water. However, analysis time was longer because extra peaks eluting at longer times were observed. Interferences were found from metals (copper, cadmium, iron, nickel, mercury and silver ions) capable of forming strong complexes with cyanide. In a 24 hour conversion study at 110°C all these metal ions resulted in a low yield of formate. When the conversion time was increased to 72 and 144 hours, at the same temperature, only solutions containing silver, mercury and copper did not yield quantitative result for formate. This method requires long man-hours.

In order to alleviate the limitation imposed by suppressed conductivity, i.e., only for ions with $pK_a < 7$, Pinschmidt[50] developed an analytical procedure for weak acid ions including CN^-. These weak acids produce an increase in resistivity which with the highly conductive eluent (2.5 mM NaOH/1 mM NaCl) gives rise to negative peaks that are in proportion to the concentrations of the species. The flow rate was 2.3 mL/min through a Dionex anion column and suppressor, and the sample size was 100 μL. The author did not report any detection limits.

In evaluating the use of IC in the steel industry to analyze free cyanide from coke oven or electroplating plants, Tusset and Hancart[51] did not achieve sufficient separation of the cyanide peak from other anions with a 1.42 mM sodium gluconate, 5.82 mM boric acid and 0.25% v/v glycerin eluent at pH 8.5 adjusted with NaOH. Cyanide was detected as an "inverse peak" using 5 mM KOH as eluent. They obtained a determination limit of 1000 μg/L and noted that oxidation of the cyanide improved sensitivity and produced a satisfactory detection limit in the range 30–100 μg/L with electrochemical detection. However, this system was still subject to interference by sulfide.

Okada and Kuwamoto[52] used non-suppressed indirect conductivity (resistivity) to determine cyanide and other anions using a TSK GEL-IC-Anion-PW column and 1 mM KOH eluent. They reported a detection limit of 100–200 μg/L. Iskandarani and Pietrzyk[28b] used a polystyrene divinylbenzene copolymer column, PRP-1 (Hamilton), but did not detect cyanide in the ion-pair mode with 0.5–1.0 mM tetrapentylammonium fluoride in 17.5 to 35% acetonitrile-water eluent with conductivity, UV or refractive index detection. Cyanide in the presence of other anions has been analyzed in pulping and bleaching liquors for environmental assessment using electrochemical and conductivity detection in tandem[53,54].

Tanaka *et al.*[55] used a Hitachi 2613 cation exchanger column, water as eluent and indirect coulometric detection. The hydrogen ion liberated from the resin by the counter-ions of cyanide and hexacyanoferrate (II and III) ions was detected with a flow coulometer. The number of coulombs arising from the reaction of the liberated H^+ ions with *p*-quinone at a Ag/AgI electrode was related to the anion (analyte) concentration. Yoshinori[56] also used a cation exchange resin, Diaion SK #1, controlled-potential coulometric detection and 0.5 M CH_3COONa (pH 9.4), 0.5 M Na_2SO_4 (pH 11.9) or 0.5 M $NaClO_4$ (pH 11.7) eluent to determine the same ions. Their non-linear calibration curve for cyanide ion was speculated to be due to the formation of more that two species in a possible reaction between cyanide ion and the Ag electrode.

Pohlandt[57] separated weak acid anions, including cyanide, from strong acid anions by ion-exclusion using dilute HCl solutions as eluents. Conductometric measurement of the separated species was made possible by precipitation-adsorption of the eluent anions on a Ag-loaded cation exchange column.

A reversed phase HPLC method based on precolumn derivatization according to W. J. Koenig to produce a polymethine dye and spectroscopic or fluorometric detection has been used for micro-determination of cyanide[58]. The stationary phase was a Hypersil ODS or μ-Bondapak C_{18} column and the mobile phase a mixture of 50/50 (v/v) H_2O-MeOH and 0.010 M $NH_4H_2PO_4$ (pH = 4.7). Detection limits were 97 and 7 fmole for spectrophotometric and fluorometric detection, respectively. Fagan and Haddad[59] reported an ion-interaction method on a C_{18} column (mobile phase was 25% acetonitrile plus 5 mM Waters low UV-PIC A reagent) for the simultaneous determination of free cyanide (CN^-), thiocyanate and metal cyanide complexes in gold leach liquors. The free cyanide eluting in the column void volume was detected (VIS at 500 nm) after post-column reaction to form a polymethine dye. This method does not suffer from interference from most anions (up to 1000 mg/L). Pohlandt-Watson and Hemmings[60] quantitated total cyanide in wastewaters after converting CN^- into $Ag(CN)_2^-$ and chromatographing in the ion-interaction mode using a solvent composed of acetonitrile, tetrabutylammonium hydroxide and phosphate buffer as inorganic modifier with UV detection.

Metal cyanide complexes. The metal cyanide complexes have been determined either by ion exchange (IE)[4,61] or ion-pair/interaction[17-19,59,62-65] chromatography with UV or conductivity detection. The users of the latter mode of chromatography have argued that the high affinity of the metal cyanide complexes for IE resins is a disadvantage in that the type of eluents necessary to elute them are corrosive and toxic[17]. We have been able to achieve separation of some metal complexes using a Dionex HPIC AS5 anion exchange column by gradient elution[4]. Excellent separation of $Au(CN)_2^-$ from $Ag(CN)_2^-$, $Cu(CN)_4^{3-}$, $Ni(CN)_4^{2-}$, $Fe(CN)_6^{3-}$, and $Co(CN)_6^{3-}$ complexes was obtained by replacing 20 mM NaOH with 22 mM NH_4OH in an eluent composed of either of this and 15 mM NaCN plus 50–120 mM $NaClO_4$ at a flow rate of 1 mL/min. The detection limit for $Au(CN)_2^-$ was 5 μg/L with 150 μL sample size using UV detection at 215 nm.

Haddad and co-workers[17-19] have determined metal cyano complexes using ion-interaction (another name for ion pair chromatography) on Waters IC Nova Pak C_{18} and CN columns. In one study[17], these workers after preconcentrating 2 mL of sample solution containing 10 μg/L gold and 100 μg/L CN^- on a C_{18} pre-column achieved a detection limit of 0.43 μg/L for gold (not the complex, $Au(CN)_2^-$). The eluent was 68:32 5 mM tetrabutylammonium ion/methanol flowing at a rate of

1 mL/min. Detection was by UV at 215 nm. The preconcentration method was also used to determine the cyanide complexes of Pd(II) and Pt(II), $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, respectively. They observed that recoveries for preconcentration were strongly influenced by sample volume and slightly by flow rate. The amount of gold was adjusted to be the same in all the samples. As the sample volume increased, recovery decreased. This was attributed to either desorption of the pairing agent or competition for sites by the cyanide anion (CN^-), since the samples contained high concentrations of this ion.

In a recent study Haddad and Kalambaheti[64] reported a detection limit of 0.08–1.58 μg/L for the metal cyanide complexes of Co, Cr, Cu, Fe and Ni after preconcentrating 2 mL of solution containing these complexes. The mobile phase contained 5 mM tetrabutylammonium hydroxide plus 25:1:74 v/v/v methanol: tetrahydrofuran: 10 mM phosphate buffer at pH = 7.9. $Cu(CN)_4^{3-}$ and $Fe(CN)_6^{4-}$ complexes were not quantitatively recovered and this was attributed to dissociation/ligand exchange and poor binding, respectively. This method suffers from interferences from other anions. Giroux and Barkley[65] after evaluating various columns (silica, carbon and polymer-based), a series of ion-pairing agents (containing 1–4 carbon atoms in the tetraalkylammonium hydroxide group and 5–8 and 12 carbon atoms in the alkyltriethylammonium phosphate group) and organic modifiers concluded that silica-based C_{18} columns and a mobile phase containing tetrabutylammonium hydroxide and acetonitrile (pH = 8) gave better results in the analysis of metal cyanide complexes in a gold mine leach liquor. The pH was adjusted with NaH_2PO_4 which also acted as the inorganic modifier. That study found that the elution order of the metal cyanide complexes was dependent on the pH of the mobile phase as well as the column.

Haak[62] and Haak and Franklin[63] have used the patented MPIC method to study plating bath chemistry and determined the cyano complexes of $Au(CN)_2^-$, $Au(CN)_4^-$ and $Co(CN)_6^{3-}$ using suppressed conductivity detection. An appreciable concentration of $Au(CN)_4^-$ in the bath is indicative of poor performance of the bath. Ion chromatography conveniently provides(d) differentiation of these two oxidation states of gold. Cobalt salts are added to act as hardners in gold plating baths. The presence of free cyanide ion will complex cobalt and form the stable complex $Co(CN)_6^{3-}$ ($\log \beta = 64$) whose detection is necessary to monitor the product quality. The eluent used by these workers was composed of 2 mM TBAOH, 40% ACN and 1 mM Na_2CO_3, flowing at a rate of 1 mL/min and the column was a Dionex MPIC-NS1 protected with a guard column MPIC-NG1. They noted that placing an amperometric detector before the conductivity detector will detect CN^- as well. Other workers and instrument manufacturer's application notes have also indicated the determination of metal cyanide complexes in plating baths[13,66–70].

Grigorova *et al.*[71] determined seven metal cyanide complexes in metallurgical gold plant solutions and cyanide effluent. The mobile phase was 70:30 2.5 mM tetrabutylammonium hydrogen sulfate – methanol at a flow rate of 1 mL/min. They used a Waters C_{18} Nova Pak catridge column and UV detection at 210 nm. The metal cyanide complexes studied were those of Ag^+, Au^+, Cu^+, Ni^{2+}, Co^{3+}, Fe^{2+} and Fe^{3+}. It was found that the retention of the complexes was different in mixed solutions compared to solutions containing single complexes, poor resolution for nickel and iron (III), and tailing for copper complexes. They found a good agreement for total cyanide analysis between IC and acid reflux procedure, but cobalt was excluded in that experiment. Earlier report cited by the authors, as well as in earlier paragraphs of this review, indicate that low recoveries are obtained in the presence of $Co(CN)_6^{3-}$ complexes. Nonomura and Hobo[72] analysed metal cyanide complexes using a Dionex AS4A column and carbonate eluent. Their detection mode was by conductivity after oxidation of cyanide to cyanate with chloramine-T. Ion chromatography has been successfully used in carbon-in-pulp process solutions, for gold recovery[73], and alkaline solutions[74] using amperometry[66,74]. The detection mode employed for metal cyanide complexes determination includes conductivity[13,67,69,70], spectrophotometry[68,71,73].

CONCLUSION

What we have tried to do in this paper is provide a concise account for a reliable method to determine cyanide and metal cyanide complexes, in various samples of environmental interest. From the view point of environmental protection and control, and economics (in terms of precious metals mining), it is imperative that we are aware of the role ion chromatography has played and will continue to play in the determination of these species. As government regulatory agencies tighten their acceptable limits for discharge of waste process effluent, scientist are seeking for analytical methods to achieve values lower than the set limits. The ideal method or technique should achieve this value with minimal sample treatment. The application of ion chromatography eliminates matrix interference and yields low detection limits. This review had presented a myraid of methodologies that will be available for the monitoring of cyanide and metal cyanide complexes in any environment.

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