Determination of metallo-cyanides by capillary electrophoresis after concentration on supported liquid membranes

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Abstract

A method for the determination of traces of metallo-cyanide complexes by capillary zone electrophoresis is described. The suitability of preconcentration procedures based on supported liquid membranes in a flow system is investigated. Methyltrioctylammonium chloride in dibutyl ether is used as the active component of the membrane liquid. Due to ion-pairing mechanisms enrichment factors ranging from 50 to 600 can be achieved for cyanide complexes of Fe(II), Fe(III), Ni, Co, Pd, Pt, Cr, Au and Ag. The final capillary electrophoretic separation of the metallo-cyanides is performed off-line with a phosphate–triethanolamine buffer at pH 8.5 as the carrier electrolyte. Its separation selectivity and compatibility with the preconcentration procedure are optimized by addition of hexamethonium bromide, sodium perchlorate and sodium cyanide. Detection limits in the low nmol range can be achieved by direct UV detection at 214 nm. An approach for the analysis of free and labile cyanide is discussed which involves the conversion of these species into the nickel cyanide complex. Applications in the fields of environmental monitoring and industrial process control are possible.

Keywords: Membranes; Sample preparation; Metallo-cyanides

1. Introduction

The recovery of gold from its ores generally involves a leaching process with cyanide resulting in the formation of gold cyanide as well as a range of other metallo-cyanides from the crude ore. Monitoring of the different cyanide species at various stages of the process and in waste solutions is essential for maintaining the optimal conditions for the leaching procedure and for environmental protection.

Several spectroscopic methods have been used for gold recovery process monitoring for many years.

Their main disadvantages, such as the inability to differentiate between oxidation states [e.g., Fe(II) and Fe(III) cyanides] or between free and bound cyanide have led to the development of several more selective methods based on modern separation techniques. In particular, reversed-phase ion interaction chromatography allows a speciation analysis of both industrial process solutions and environmental samples [1].

Recently it has been demonstrated that capillary zone electrophoresis (CZE) with its high separation efficiency is a promising alternative to liquid chromatography for the separation of metallo-cyanide complexes [2]. Direct UV detection at 214 nm yielded detection limits in the range between 100 and 1 ppm. It has been emphasized that some environmental applications may require the use of pre-

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concentration procedures in order to achieve adequate sensitivity [2], but up to now satisfactory enrichment techniques prior to capillary electrophoresis of traces of metallo-cyanides are still missing.

Sample preparation procedures based on the use of supported liquid membranes (SLMs) have attained considerable importance during the last few years due to the ease of operation, low consumption of organic solvents and higher donor/acceptor volume ratio than in classical liquid–liquid extraction. The term "supported liquid membrane" refers to an organic liquid phase that is held in the pores of a thin porous support (usually a PTFE membrane). This organic layer is interposed between two aqueous solutions, one of them being the sample solution (donor solution) and the other the acceptor solution. The enrichment process is based on a diffusive transport of the analytes across this liquid membrane from a relatively large volume of sample into a much smaller volume of acceptor solution. The various mechanisms that can be applied for this preconcentration have been discussed briefly by Jönsson et al. [3,4]. The transfer of ionic analytes from the sample to the membrane can be enhanced by the presence of ion-pairing reagents in the membrane phase. This approach looks very promising for metallo-cyanides, which are well known to form strong ion pairs with hydrophobic ammonium compounds. The chemical composition of the aqueous acceptor phase must be chosen in a way to convert the analyte of interest into a non-extractable form so that a quantitative transfer from the organic membrane into the acceptor phase is possible.

Recently, SLM systems containing primary, secondary, tertiary and quaternary amines have been investigated for extraction of dicyanoaurate from alkaline process solutions in a flow-injection manifold [5]. Applications to the preconcentration of different metallo-cyanides in combination with an efficient separation technique have not yet been reported. The aim of the work presented in this paper was the development of appropriate conditions for an SLM extraction step compatible with CZE in order to achieve sufficiently low detection limits for the analysis of cyanide species in waste solutions or environmental samples.

2. Experimental

2.1. Instrumentation

The CZE instrument employed was a Quanta 4000 (Waters, Milford, MA, USA) interfaced to a Hewlett–Packard 3359 data acquisition system. Separations were carried out in fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) of 60 cm length and 75 μm inner diameter with a detection window 8 cm from the end of the capillary. Injection was performed hydrostatically by elevating the sample at 10 cm for 10 s. Direct UV detection at 214 or 254 nm was used.

The preconcentration device is depicted schematically in Fig. 1. Its membrane unit consisted of two polyethylene blocks (70 m long, 40 mm wide and 10 mm thick), each with a flat rectangular groove (40 mm long, 2 mm wide and 0.25 mm deep) forming a flow channel for the donor phase or acceptor phase with a volume of 20 μl. A PTFE membrane filter TE 35 (Schleicher & Schuell, Dassel, Germany) of 0.2 μm pore size with a polyethylene backing was immersed into a 10 mM solution of methyltrioctylammonium chloride in dibutyl ether and sonicated for 3 min. Afterwards, the membrane was placed between the two polyethylene blocks and the device was screwed together. The sample (donor phase) was delivered to the donor phase compartment by an Ismatec MP 25 GS4 peristaltic pump (Ismatec, Zurich, Switzerland). The acceptor phase was held
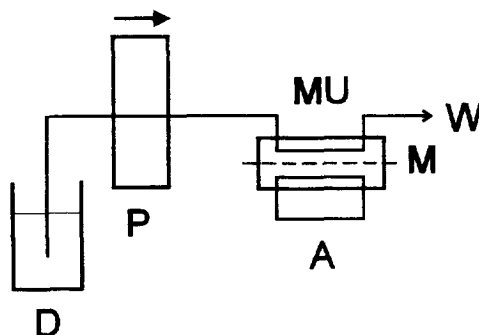

Fig. 1. Instrumentation for preconcentration of metallo-cyanides. D=donor solution (sample), P=peristaltic pump, MU= membrane unit, M=supported liquid membrane, A=acceptor solution, W=waste.

static. Metal-free tubing and fittings were used to avoid contamination resulting from the dissolution of metal parts by free cyanide present in the sample.

2.2. Chemicals

Carrier electrolytes consisted of a phosphate–triethanolamine buffer at pH 8.5 (prepared from 5 mM disodium hydrogenphosphate and 5 mM triethanolamine) containing varying amounts of hexamethonium bromide (Fluka, Buchs, Switzerland), sodium cyanide and sodium perchlorate.

$K_4Fe(CN)_6 \cdot 3H_2O$ and $K_3Fe(CN)_6$, were obtained from Merck, $KAg(CN)_2$ and $KAu(CN)_2$ from Fluka. Cyano complexes of Ni(II) and Cu(I) were formed by mixing solutions of nickel and copper sulfate with a fourfold excess of a sodium cyanide solution. $Na_3Co(CN)_6$ was prepared from solid CoF_3 which was dissolved directly in a stochiometric amount of a sodium cyanide solution. A solution of $Pt(CN)_4^{2-}$ was obtained from H_2PtCl_6 (Sigma, Vienna, Austria) after addition of a two-fold excess of sodium cyanide. The kinetics of this reaction are very slow and a total transformation was accomplished only after several days. $Na_2Pd(CN)_4$ was prepared form $PdCl_2$, which was dissolved in a stochiometric amount of 1 M HCl to form the water-soluble chloro-complex and neutralized with 1 M NaOH; afterwards, a stochiometric amount of sodium cyanide was added. $Na_3Cr(CN)_6$ was prepared from solid chromium(III) chloride by addition of a three-fold excess of a sodium cyanide solution; the mixture was treated in an ultrasonic bath for 15 min and stirred overnight.

All solutions were prepared from analytical-reagent grade chemicals except for methyltrioctylammonium chloride and dibutyl ether (synthesis grade). Doubly distilled water was used throughout this work.

2.3. Preconcentration and separation procedure

20–100 ml of sample solution were pumped through the membrane unit at a flow-rate between 0.1 and 1.0 ml/min, while the acceptor phase compartment was filled with 20 μl of a 10 mM sodium perchlora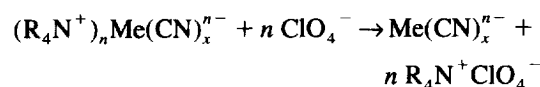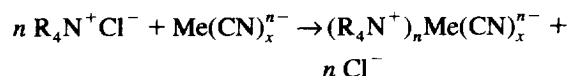te solution. The membrane could be used for at least 20 preconcentration runs, if it was rinsed with the ion-pairing solution in dibutyl ether for 10 min between runs. This was done by pumping the solution through the donor side of the cell. After the preconcentration step the acceptor solution was injected into the CZE instrument without any further treatment.

Each day the fused-silica separation capillary was conditioned by subsequent rinsing with sodium hydroxide, water and carrier electrolyte for 10 min. In addition, before each electrophoretic run a three minute rinsing step with carrier electrolyte was included. Carrier electrolytes containing free cyanide had to be replaced every hour since free cyanide slowly evaporated as hydrogen cyanide.

3. Results and discussion

3.1. Optimization of the preconcentration procedure

A new mechanism for the enrichment of the metallo-cyanides is used in the current study as schematically shown by the following equations:

$$n\,R_4N^+Cl^- + Me(CN)_x^{n-} \rightarrow (R_4N^+)_nMe(CN)_x^{n-} + n\,Cl^-$$

$$(R_4N^+)_nMe(CN)_x^{n-} + n\,ClO_4^- \rightarrow Me(CN)_x^{n-} + n\,R_4N^+ClO_4^-$$

Metallo-cyanides in the donor phase form an ion pair with R_4NCl by replacing easily dissociable chloride ions and subsequently diffuse through the membrane. In the stripping step a suitable anion in the acceptor phase forms a more stable ion-pair with methyltrioctylammonium ion than the metallo-cyanides. The metallo-cyanides are thus liberated and accumulate in the acceptor compartment of the membrane unit. Perchlorate was selected as the reagent in the acceptor phase, as it was suitable for the preconcentration step as well as the CE separation of metallo-cyanides.

For high enrichment factors, several parameters of the SLM system must be optimized including the

concentration of the ion-pairing reagent in the organic phase, the reagent in the acceptor phase and the flow-rate of the sample solution. The concentration of the reagent in the organic membrane needs to be sufficiently high to ensure the linearity of the enrichment procedure over a wide concentration range. On the other hand, high concentrations of the membrane reagent in turn require high concentrations of the displacing reagent of the acceptor phase, which might lead to interferences in the subsequent electrophoretic separation. Investigations within a concentration range of 1 to 100 mM revealed that both methyltrioctylammonium chloride and sodium perchlorate yielded best results if used at a level of 10 mM. The use of higher concentrations could extend the linearity of the enrichment process, but high concentration of perchlorate would subsequently be necessary in the acceptor phase which would then become incompatible with the composition of electrolyte for CZE separation.

The optimization of the sample flow-rate was carried out between 0.1 and 1 ml/min. Since the available volume of the sample was not limited, it is better to aim at a high enrichment per unit time at some sacrifice of extraction efficiency [6]. Therefore, an increase of the donor flow-rate should lead to the highest enrichment factor. The results of the optimi-

zation study confirmed these assumptions and the highest enrichment was obtained at a flow-rate of 1 ml/min, as shown in Fig. 2. For all complexes studied, the plots of peak area versus enrichment time were linear for enrichment times in the range 15–120 min using a donor flow-rate of 1 ml/min.

3.2. Separation of metallo-cyanides by CZE

Some initial experiments were carried out with a carrier electrolyte containing 5 mM Na_2HPO_4, 5 mM triethanolamine and 0.8 mM hexamethonium bromide as reported previously [2]. In the analysis of samples containing the Cu(I)–cyanide complex it was necessary to add cyanide to the carrier electrolyte to avoid poor peak shape. Cu(I) forms cyano complexes with 2 to 4 cyanide ions, so that the actual composition of the copper complex during the separation process depends on the concentration of cyanide in the carrier electrolyte. Therefore, an increase in the concentration of cyanide in the carrier electrolyte increases the number of ligands of the migrating copper complex and hence its effective negative charge. This fact allows manipulation of the migration time of the copper cyano complex during optimization of the separation selectivity.

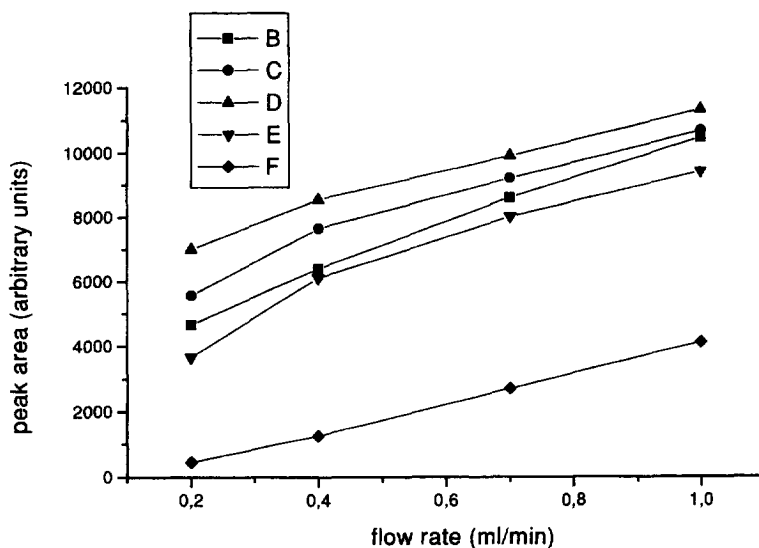Serious problems were encountered when injecting

Fig. 2. Dependence of the membrane preconcentration of metallo-cyanides upon flow-rate (preconcentration time: 1 h). $B = Co(CN)_6^{3-}$, $C = Pd(CN)_4^{2-}$, $D = Fe(CN)_6^{3-}$, $E = Au(CN)_2^{-}$, $F = Ag(CN)_2^{-}$.

the acceptor phase of the SLM preconcentration system. These interferences were caused by the perchlorate used in the acceptor phase at a concentration of 10 mM. Despite its low absorptivity at 214 nm, perchlorate caused a broad fronting peak in the region of the cyano complexes of Fe(III), Co(III), Ni(II) and Pd(II) and made quantification of these peaks impossible. Therefore, further investigations were directed to the use of perchlorate as an additive in the carrier electrolyte at concentrations of 1 to 20 mM. This modification of the carrier electrolyte led to two significant changes in the electropherogram. First, the interference of perchlorate present in the acceptor solution was completely removed; second, perchlorate in the carrier electrolyte caused changes in the separation selectivity for several metallo-cyanides. The latter results can be explained by the fact that perchlorate acts as a second ion-pairing reagent in addition to the hexamethonium ion already present in the electrolyte, thereby influencing the effective charge and the size of the analytes during the separation process. Fig. 3 shows the separation of ten metallo-cyanides under optimized concentrations of cyanide (0.1 mM) and perchlorate (15 mM) in the carrier electrolyte. Cyanides of Hg, Cd, Zn and Mn did not yield peaks in the electropherogram under the conditions chosen

Table 1

Limits of detection (LOD), and preconcentration factors (preconcentration time: 120 min) as well as relative standard deviation (R.S.D.) at a concentration level 50 times higher than the LOD (preconcentration time: 30 min) for membrane preconcentration of metallo-cyanides

Metallo-cyanide complex	LOD (M)	Preconcentration factor	R.S.D. (%)
Fe(II)	$1.4 \cdot 10^{-8}$	70	4.4
Co(III)	$8.5 \cdot 10^{-9}$	300	5.9
Fe(III)	$6.6 \cdot 10^{-9}$	600	6.3
Ni(II)	$1.2 \cdot 10^{-7}$	60	6.9
Pd(II)	$2.2 \cdot 10^{-8}$	220	6.3
Pt(II)	$1.0 \cdot 10^{-7}$	240	7.2
Cr(III)	$3.8 \cdot 10^{-7}$	50	2.9
Au(I)	$1.0 \cdot 10^{-7}$	100	7.3
Ag(I)	$2.0 \cdot 10^{-7}$	200	2.4

Flow-rate 1 ml/min.

in this work and were excluded from further investigations as well as Co(II) cyanide for which three peaks were observed.

3.3. Preconcentration factors, statistical data, interferences

The preconcentration factors obtained by the SLM technique are summarized in Table 1. The highest
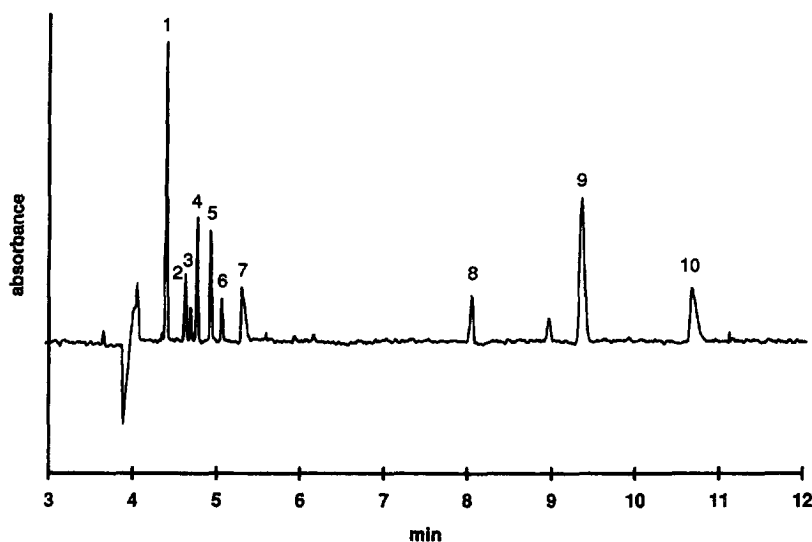

Fig. 3. CZE separation of a standard solution of ten metallo-cyanides. $1 = Fe(CN)_6^{4-}$, $2 = Co(CN)_6^{3-}$, $3 = Fe(CN)_6^{3-}$, $4 = Ni(CN)_4^{2-}$, $5 = Pd(CN)_4^{2-}$, $6 = Pt(CN)_4^{2-}$, $7 = Cu(CN)_4^{3-}$, $8 = Cr(CN)_6^{3-}$, $9 = Au(CN)_2^{-}$, $10 = Ag(CN)_2^{-}$. Voltage: -25 kV. Detection: 214 nm.

preconcentration factor was observed for the Fe(III) complex, and the lowest for the Cr(III) complex. No preconcentration was observed for $Cu(CN)_4^{3-}$ unless an excess of free cyanide was added to the donor solution. Under these conditions a preconcentration factor similar to that of $Au(CN)_2^-$ was obtained. However, $Cu(CN)_4^{3-}$ was excluded from further experiments because of interactions with Fe(III) cyanide and the formation of Fe(II) cyanide, thereby leading to erroneous results. In Table 1, data for the detection limits (defined as three times the signal-to-noise ratio) of the preconcentration procedure in combination with the electrophoretic separation are given; in addition, data on the reproducibility obtained at a level approximately fifty times higher than the detection limits are included.

The detection limits were determined for a 2 h preconcentration step, whereas relative standard deviations were calculated from 8 consecutive experiments based on preconcentration for 30 min. The technique yielded a linear range from the detection limit to concentrations twenty times higher than the detection limits. At higher concentrations, the calibration for some of the metallo-cyanides remained linear, whereas for others (especially for the Fe(II) complex) significant deviations from linearity were observed. The reason for this behavior is not yet fully clear, although the limited capacity of the membrane might be responsible for these effects. However, an increase of the capacity by increasing the concentration of the ion-pairing reagent is not feasible, because then also the perchlorate concentration in the acceptor phase needs to be increased and causes problems in the CZE separation.

Anionic species present in the sample can be potential interferents in the preconcentration step. The extent of the interference depends on the stability constant of the ion pair between the anion and methyltrioctylammonium chloride. Moreover, some anions which can be preconcentrated absorb at 214 nm and cause interferences in the CZE separation step. The interference in the preconcentration step was evaluated from the peak areas of all the metallo-cyanides in Table 1, without and with addition of appropriate amounts of the interfering anion into the donor phase. No preconcentration or interference in separation was observed for chloride, sulfate and cyanide at concentrations up to 1000

ppm. Nitrite and nitrate did not cause any interferences in the preconcentration step up to 50 and 100 ppm, respectively, but caused problems in the separation step. Co-migration of nitrite with Fe(II) cyanide and nitrate with Co(III) cyanide was observed, whereby nitrate at levels above 50 ppm led to some overlapping with the peaks of Fe(III) and Ni(II) cyanide. A possible approach to remove some of the interferences in the separation step is the detection at a different wavelength, e.g., 254 nm. This approach was successfully used for the determination of free and labile cyanide (see below). Perchlorate and thiocyanate present in the sample did not disturb the CE separation, but decreased the preconcentration factors [especially for Fe(II) and Cr(III) cyanide] when present at concentrations above 10 ppm.

4. Analysis of free and labile cyanide

In addition to the analysis of different metallo-cyanides, the determination of free cyanide and weakly bound cyanide (e.g., metallo-cyanides with a low stability constant) can provide valuable information on industrial as well as environmental samples. Free cyanide in waste waters has been determined by liquid chromatography after conversion of the cyanide into the silver cyanide complex [7]. Alternatively, the conversion of free cyanide into the nickel cyanide complex followed by electrophoretic separation might have several advantages. The $[Ni(CN)_4]^{2-}$ complex has an absorption maximum at 267 nm and a molar absorptivity of 11 300, so that a much higher detection selectivity can be achieved than in the case of $[Ag(CN)_2]^-$, which requires a considerably lower detection wavelength and has a lower molar absorptivity (2200 at 214 nm). Furthermore, at 267 nm most of the commonly present anions do not absorb light and do not interfere. In the present work, a detection wavelength of 254 nm was chosen, as the instrument was equipped with a fixed-wavelength detector.

In a series of experiments nickel sulfate at a level of 1 mM was added to a mixture of metallo-cyanides and free cyanide and the sample was subjected to the preconcentration and separation procedure. The addition of nickel ions resulted in a disappearance of the

peaks for Fe(II) cyanide and Cr(III) cyanide and in a corresponding increase in the peak area of Ni(II) cyanide. The calibration plot for free cyanide was linear from the detection limit of $5 \cdot 10^{-7}$ M (pre-concentration time 2 h at a flow-rate of 1 ml min) up to $2 \cdot 10^{-5}$ M. The value for the limit of the detection (LOD) is given for an injection time of 10 s and can be easily improved by a factor of three if the injection time is increased to 30 s. The conversion of free cyanide into its nickel complex was quantitative. On the other hand, it should be mentioned that the conversion of labile cyanide from metallo-cyanides into the nickel cyanide complex can depend on the pH of the sample solution. Details of this conversion have not yet been studied.

Fig. 4 shows a typical electropherogram of a surface water sample spiked with 50 ppb of free cyanide. No interferences were observed at a detection wavelength of 254 nm, so that this technique seems to have considerable potential for monitoring free and labile cyanide in environmental samples.

In addition, process solutions from a gold leaching plant were investigated. These samples contained large amounts of both free cyanide (approximately 100 ppm) and copper cyanide. They were diluted 1:1000 and nickel sulfate was added to a final concentration of 1 mM. The diluted sample was then subjected to a 30 min preconcentration procedure and analyzed by CZE. The electropherogram shown

in Fig. 5 reveals the possibility for free cyanide monitoring in process solutions. It should be noted that for this type of monitoring of industrial samples the preconcentration step was only necessary to remove the excess of nickel ions in the sample; otherwise, the nickel ions would react with the cyanide of the carrier electrolyte. On the other hand, it is also possible to use a cyanide-free electrolyte for the analysis of the nickel(II) cyanide, so that the sample containing an excess of nickel ions can be injected directly into the CE instrument without any pretreatment.

5. Conclusions

Preconcentration techniques using SLMs can lead to a considerable improvement of the detection limits in the analysis of cyanide species by CE. The results presented in this paper have been obtained with a very simple preconcentration device; a refined design can further enhance the efficiency of the preconcentration step. Cyanide species can be detected well below the limits stated for drinking water. Fine-tuning of the technique for various industrial waste waters or process solutions should be easily possible. In addition to metallo-cyanides, other negatively charged metal-complexes (like complexes of metals with aminopolycarboxylic acids) can be subjected to
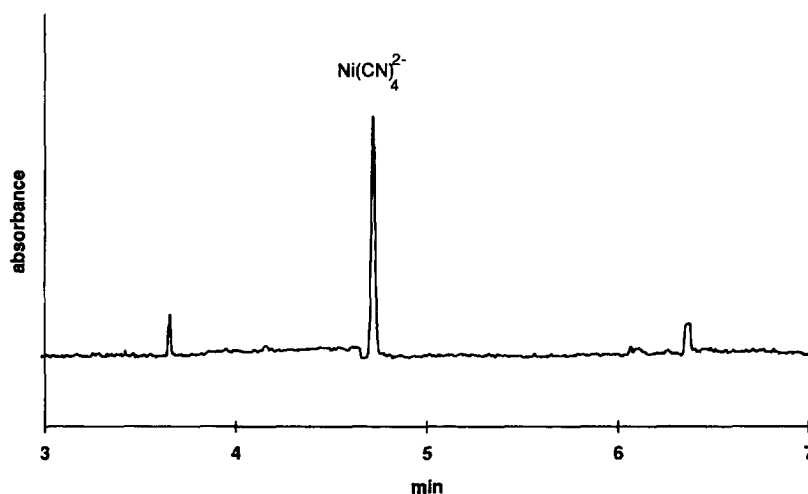

Fig. 4. Electropherogram of a surface water sample spiked with 50 ppb of free cyanide which was converted into the Ni(II) complex. Preconcentration time: 2 h. Voltage: -25 kV. Detection: 254 nm.
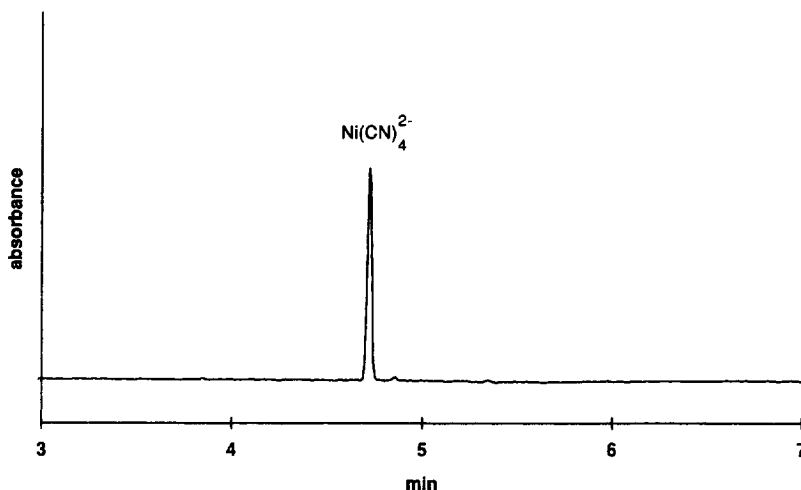
Fig. 5. Electropherogram of a gold leaching process solution containing 100 ppm of free cyanide. The sample was diluted 1:1000 and after conversion of the cyanide into the Ni(II) complex subjected to a 30 min preconcentration step. Voltage: −25 kV. Detection: 254 nm.

similar preconcentration procedures at SLMs prior to CE. Results will be published elsewhere.

Acknowledgments

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