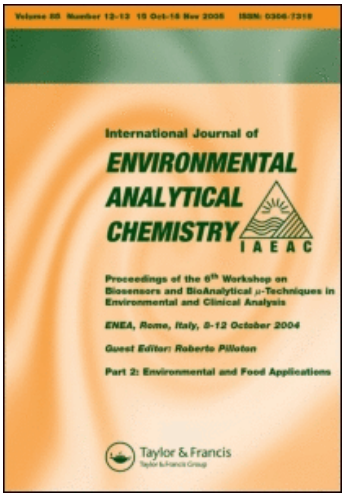

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Photodiode Array Detection as a Fingerprinting Tool for Metal Cyanide Complexes in Gold Processing Solutions

Silvia B. Black[a]; Roger S. Schulz[a]
[a] Chemistry Centre (WA), Western Australia, Australia

To cite this Article Black, Silvia B. and Schulz, Roger S.(1998) 'Photodiode Array Detection as a Fingerprinting Tool for Metal Cyanide Complexes in Gold Processing Solutions', International Journal of Environmental Analytical Chemistry, 72: 2, 129 — 136
To link to this Article: DOI: 10.1080/03067319808035884
URL: http://dx.doi.org/10.1080/03067319808035884

Intern. J. Environ. Anal. Chem., Vol. 72(2), pp. 129-136
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTODIODE ARRAY DETECTION AS A FINGERPRINTING TOOL FOR METAL CYANIDE COMPLEXES IN GOLD PROCESSING SOLUTIONS

SILVIA B. BLACK* and ROGER S. SCHULZ

Chemistry Centre (WA), 125 Hay Street, East Perth, Western Australia 6004, Australia

(Received 8 November, 1997; In final form 26 February, 1998)

Reversed-phase ion-interaction high-performance liquid chromatography with photodiode array detection (PDAD) was used to simultaneously identify and quantify metal cyanide complexes present in gold processing solutions. Identification was achieved using the "fingerprint" or full-scan UV spectrum (190 – 350 nm) obtained from the PDAD. The complexes identified so far were; $Cu(CN)_4^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Ni(CN)_4^{2-}$, $Au(CN)_2^-$ and $Cr(CN)_6^{3-}$. Thiocyanate (SCN) was also detected and identified by this technique.

Keywords: Metal cyanide complexes; thiocyanate; ion chromatography; photodiode array detector; speciation

INTRODUCTION

The identification and quantification of individual metal cyanide complexes, i.e. cyanide speciation, in gold processing liquors are important for both environmental and industrial applications. Knowledge of the type and nature of metal cyanide complexes is of considerable importance in process solutions from metallurgical plants for the recovery of gold. Based on the knowledge that different metal cyanide complexes can exhibit varying degrees of environmental persistence, identification of the kind of metal cyanide complexes present in waters and effluents can result in more effective management of wastes thereby preventing pollution of the environment.

* Corresponding author. Fax: +61–8–93257767. E-mail: sblack@ccwa.wa.gov.au.

The chromatographic method described in this paper is a variation of previously published methods[1–4]. In these and other published work,[5–12] a wide range of detectors have been used including; direct and indirect UV, conductivity, photometry, amperometry, potentiometry, fluorescence and atomic spectroscopy. The combination of photodiode array detection (PDAD) with liquid chromatography is a novel application for detection of inorganic complexes. It is our experience when using chromatographic techniques to analyse complex matrices such as gold processing solutions, that the variability of retention times of analytes complicates identification. These shifts in retention times may be due to the sample matrix or change in the mobile phase composition due to evaporation. In this paper we demonstrate the value of using a photodiode array detector to simultaneously identify and quantify metal cyanide complexes in gold processing liquors and environmental water samples.

EXPERIMENTAL

Instrumentation

The Waters liquid chromatograph system consisted of a 600E pump and delivery system controller, a 700 WISP autosampler, a 991 photodiode array detector, a Nova-Pak C_{18} column (150 × 3.9 mm i.d., 4-μm particle size) and a Nova-Pak C_{18} Guard-Pak pre-column insert housed in a Waters Guard-Pak holder. Data collection and processing were carried out using Waters Photodiode Array and Powerline software.

A Shimadzu UV/VIS spectrophotometer UV-260 was used to obtain full scan spectra of each metal cyanide complex in the wavelength range 190–350 nm.

Reagents and Materials

Potassium thiocyanate and potassium cyanide (both AR grade) were obtained from BDH. Potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), potassium dicyanoaurate (I), potassium hexacyanocobaltate(III), potassium tetracyanonickelate(II) and potassium hexacyanochromate(III) were purchased from Strem Chemicals as pure compounds. Potassium tetracyanocuprate(I) was synthesised using a previously published procedure[13,14]. All standard solutions were prepared with water obtained from a Millipore Milli Q water purification system. Acetonitrile was HPLC grade supplied by EM Science. Low UV PIC® A reagent (containing tetrabutylammonium hydrogen sulphate) was obtained from Waters.

Procedure

The mobile phase was prepared by diluting the PIC® A reagent in approximately 700 mL water. 10 mL of 1000 mgL^{-1} cyanide (from KCN) and 220 mL acetonitrile were added and the volume was made up to 1000 mL with water. The mobile phase was filtered through a 0.45 μm nylon membrane filter.

All chromatographic separations were carried out at ambient temperature, using a mobile phase flow rate of 1.0 $mLmin^{-1}$ and a 20 μL sample injection volume.

RESULTS AND DISCUSSION

Each metal cyanide complex was found to have a unique UV spectrum (190 – 349 nm). Using PDAD in conjunction with reversed-phase ion-interaction high-performance liquid chromatography, each metal cyanide complex could be simultaneously identified (fingerprinted) and quantified. Figures 1 and 2 show chromatograms and full-scan UV spectra of thiocyanate and metal cyanide complexes. Characteristic UV spectral scan patterns and chromatographic retention times were complimentary information for the positive identification of each complex. The complexes identified were; tetracyanocuprate (I) [$Cu(CN)_4^{3-}$], hexacyanoferrate (II) and (III) [$Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ respectively], hexacyanocobaltate (III) [$Co(CN)_6^{3-}$], tetracyanonickelate (II) [$Ni(CN)_4^{2-}$], dicyanoaurate (I) [$Au(CN)_2^-$] and hexacyanochromate (III) [$Cr(CN)_6^{3-}$]. The derived compound thiocyanate (SCN) was also detected and identified by this technique.

In the case when two analytes were not chromatographically resolved it was still possible to identify and quantify the analytes simultaneously by using PDAD. This eliminated the need to modify methods and repeat analysis.

Figure 3 shows that the chromatographic conditions used here did not resolve the cyanide complexes of Ni(II) and Fe(III). However the PDAD detector provided sufficient information to identify and quantify both analytes. This could be done by measuring absorbance ratios at two wavelengths and preferably at wavelengths of maximum absorbance for each complex. For example, the absorbance ratio of wavelengths 214:265 nm for Ni(II) cyanide complex was 0.4 (Figure 1). The ratio when both Ni(II) and Fe(III) cyanide complexes were present was greater than 0.4 (Figure 3). Quantification was achieved by calculating the concentration of Ni(II) cyanide complex from its absorbance at 265 nm. The concentration of Fe(III) cyanide complex could then be calculated by subtracting the Ni(II) cyanide complex background at 214 nm.

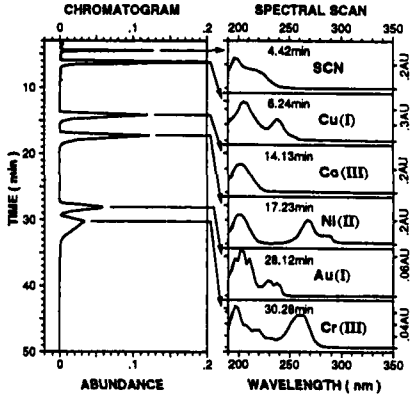

FIGURE 1 Chromatogram and full-scan spectra of a standard solution containing 10 mgL^{-1} SCN and the metal cyanide complexes; 10 mgL^{-1} of each Cu(I), Co(III), 20 mgL^{-1} Ni(II), 50 mgL^{-1} of each Au(I) and Cr(III)

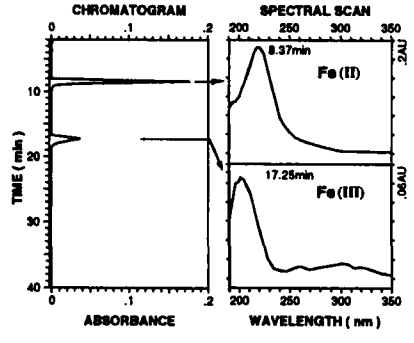

FIGURE 2 Chromatogram and full-scan spectra of 10 mgL^{-1} of each Fe(II) and Fe(III) cyanide complex standards in water

The software used with the PDAD had the capabilities to subtract the Ni(II) background automatically.

The PDAD could be used as a powerful Quality Assurance tool. For example, small variations in the concentration of acetonitrile in the mobile phase could cause large changes in analyte retention times (Table I, Figures 4 and 5). When the mobile phase contained 26 % (V/V) acetonitrile, the Cr(III) cyanide complex was eluted before the Au(I) cyanide complex. At 24 % (V/V) acetonitrile concentration, the Cr(III) and Au(I) cyanide complexes were not resolved. At 21 % (V/V) acetonitrile concentration, the Cr(III) cyanide was eluted after the Au(I)

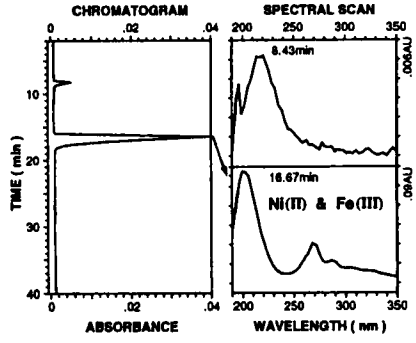

FIGURE 3 Chromatogram and full-scan spectra of 20 mgL^{-1} of each Ni(II) and Fe(III) cyanide complex standards in water

cyanide. Using PDAD, it is possible to identify each peak and determine if peaks were co-eluting or resolved. If a single wavelength UV detector was used, this problem would only be noticed by running individual standards of each complex at intervals throughout the batch run.

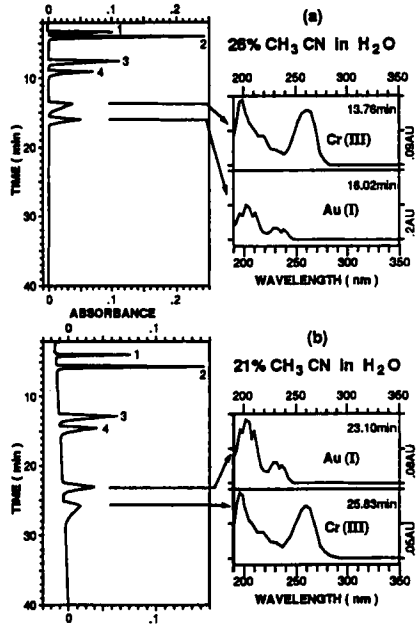

FIGURE 4 Chromatograms and full-scan spectra of SCN and various metal cyanide complexes separated using different mobile phases (a) 26% (V/V) acetonitrile in water and (b) 21% (V/V) acetonitrile in water. Peaks; 1 = SCN; 2 = Cu(I); 3 = Co(III); 4 = Ni(II)

TABLE I Retention of SCN and Metal Cyanide Complexes Affected by Changes of Acetonitrile Concentration in the Mobile Phase

Analyte	*Analyte Rt (min) at different Acetonitrile Concentrations in Mobile Phase (% V/V)*		
	21	*24*	*26*
SCN	4.0	3.6	3.3
$Cu(CN)_4^{3-}$	5.6	4.7	4.1
$Co(CN)_6^{3-}$	12.8	9.7	7.5
$Ni(CN)_4^{2-}$	14.6	11.3	9.0
$Cr(CN)_6^{3-}$	25.8	18.9	13.8
$Au(CN)_2^-$	23.1	18.9	16.0

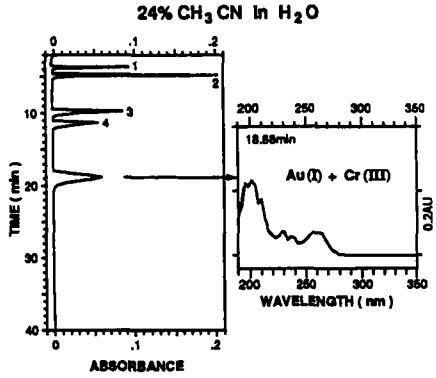

FIGURE 5 Chromatogram and full-scan spectra of SCN and various metal cyanide complexes separated using 24% (V/V) acetonitrile in water as the mobile phase. Peaks; 1 = SCN; 2 = Cu(I); 3 = Co(III); 4 = Ni(II)

The combination of reversed-phase ion-interaction chromatography with PDAD has been successfully applied to the analysis of gold processing solutions (Figures 6 and 7). The sample shown in Figure 6 had to be diluted 10 and 100 fold for the analyte concentrations to fall within the calibration range. Figure 7 shows a sample with very low levels of thiocyanate and metal cyanide complexes.

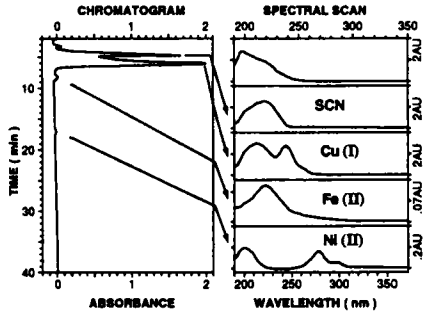

FIGURE 6 Chromatogram and full-scan spectra of SCN and various metal cyanide complexes in a sample of a gold processing solution. The sample contained 220 mgL^{-1} SCN, 380 mgL^{-1} Cu(I), 4.6 mgL^{-1} Fe(II) and 18 mgL^{-1} Ni(II)

Recovery data, detection limits, precision data and linear calibration ranges are given in Table II. Recoveries of spiked samples were between 80 and 110 % and relative standard deviations were between 2 and 9 %.

TABLE II Recovery, linearity, detection limit and precision data for thiocyanate and metal cyanide complexes

Metal Oxidation State	*Analyte*	*Linear Calibration range* (mgL^{-1})*	*Average recovery** (n = 5) (%)*	*Precision (R.S.D.,%)*	*Detection limit (mgL^{-1} as metal)*
	SCN	0.1 – 10	88	3.5	0.1
Cu(I)	$Cu(CN)_4^{3-}$	0.1 – 10	94	1.3	0.1
Co(III)	$Co(CN)_6^{3-}$	0.1 – 10	87	6.7	0.1
Fe(II)	$Fe(CN)_6^{4-}$	0.1 – 10	103	2.2	0.1
Fe(III)	$Fe(CN)_6^{3-}$	0.1 – 10	80	4.4	0.1
Ni(II)	$Ni(CN)_4^{2-}$	0.2 – 20	114	4.8	0.2
Cr(III)	$Cr(CN)_6^{3-}$	0.5 – 50	99	6.4	0.5
Au(I)	$Au(CN)_2^-$	1.0 – 50	107†	7.9†	1.0

* Quantification was done at $\lambda = 265$ nm for Cr(III) and Ni(II) and at 214 nm for all other metal cyanide complexes.

** Recovery studies were carried out by spiking (with metal cyanide complexes) an environmental sample containing 0.55 mgL^{-1} SCN, 2.2 mgL^{-1} Cu(I) and 1.0 mgL^{-1} Fe(II) with 0.45 mgL^{-1} of each SCN, Cu(I), Fe(II), Fe(III), 0.90 mgL^{-1} Ni(II), 2.25 mgL^{-1} of each Au(I) and Cr(III).

† n = 3.

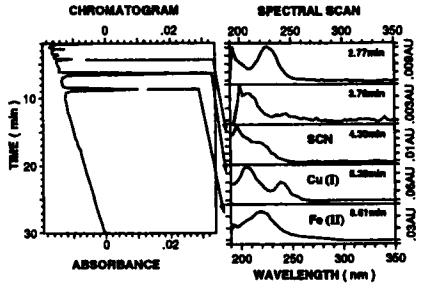

FIGURE 7 Chromatogram and full-scan spectra of SCN and metal cyanide complexes in an environmental sample. The sample contained 0.55 mgL^{-1} SCN, 2.2 mgL^{-1}Cu(I) and 1.0 mgL^{-1} Fe(II)

CONCLUSION

The use of a photodiode array detector provides a wealth of information that allows the analyst to operate at optimum conditions. The characteristic UV spectra obtained for each metal cyanide complex enabled fast identification and assisted troubleshooting. Even when two analytes were not chromatographically resolved it was still possible to identify and quantify the analytes simultaneously without needing to repeat the analysis.

The combination of PDAD with reversed-phase ion-interaction high-performance liquid chromatography has been successfully applied to the quantitative analysis of industrial and environmental samples.

Acknowledgements

The authors would like to thank the Director of the Chemistry Centre (WA) for permission to publish this work.

References

[1] D.F. Hilton and P.R. Haddad, *J. Chromatogr,* **361**, 141–150 (1986).
[2] L. Giroux and D.J. Barkley, *Can. J. Chem,* **72**, 269–273 (1994).
[3] B. Grigorova, S.A. Wright and M. Josephson, *J. Chromatogr,* **410**, 419–426 (1987).
[4] P.R. Haddad and C. Kalambaheti, *Anal. Chim. Acta,* **250**, 21–36 (1991).
[5] M. Nonomura, *Anal. Chem,* **59**, 2073–2076 (1987)
[6] C. Pohlandt, *S. Afr. J. Chem,* **38**, 110–114 (1985).
[7] C. Pohlandt, *S. Afr. J. Chem, 37,* 133–137 (1984).
[8] W. Buchberger and P.R. Haddad, *J. Chromatogr,* **687**, 343–349 (1994).
[9] Q. Huang, B. Paull and P.R. Haddad, *Chemistry in Australia,* **July**, 310–311 (1996.)
[10] D.M. Muir, *Chemistry in Australia,* **October**, 582–583 (1994).
[11] E.O. Otu, C.W. Robinson and J.J. Byerley, *Analyst,* **117**, 1145–1149 (1992).
[12] E.O. Otu, C.W. Robinson and J.J. Byerley, *Analyst,* **118**, 1277–1280 (1993).
[13] E. Staritzky, *Anal. Chem,* **28**, 419–423 (1956).
[14] H. Basset and A.S. Corbet, *J. Chem. Soc,* **125**, 1660–1675 (1924).