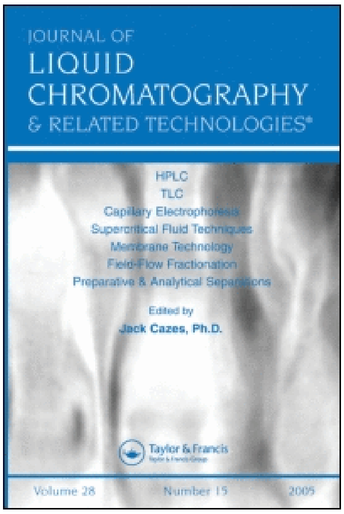

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Simultaneous Determination of Cadmium, Cobalt, Copper, Lead, Mercury and Nickel in Zinc Sulfate Plant Electrolyte Using Liquid Chromatography with Electrochemical and Spectrophotometric Detection

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SIMULTANEOUS DETERMINATION OF CADMIUM, COBALT, COPPER, LEAD, MERCURY AND NICKEL IN ZINC SULFATE PLANT ELECTROLYTE USING LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL AND SPECTROPHOTOMETRIC DETECTION

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ABSTRACT

The current efficiency (cost) of electrolytic production of high purity metallic zinc from zinc sulfate plant electrolyte is critically dependent on the concentration of a number of trace elements. The matrix, containing a very large concentration excess of zinc sulfate in concentrated sulfuric acid presents difficulties for determining low concentrations of other metals with many analytical methods. In this work it is shown that Cd, Co, Cu, Pb, Hg and Ni impurities may be simultaneously determined at concentrations less than or equal to 1 ppm using a combination of solvent extraction, high performance liquid chromatography and electrochemical or spectrophotometric detection. Solvent extraction utilizes the formation of pyrrolidine dithiocarbamate complexes, which after removal of zinc complexes and excess ligand on an anion exchange column can be separated on a C-18 reverse phase chromatographic column and detected by UV/Visible spectrophotometric or electrochemical detection. Other combinations of chromatographic and detection procedures were thwarted by the very large concentration excess of zinc and other problems.

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INTRODUCTION

The determination of trace elements in the presence of a very large excess of another element is a problem frequently encountered by the analytical chemist (1). Even so called specific methods, can exhibit interference effects when confronted with a matrix of this type (2-4).

In the mining industry, the industrial process to produce high purity metals frequently requires the preliminary production of a concentrate where obviously the concentration of the element to be refined is very high. Nevertheless, in many metal refining processes it is extremely important to monitor the concentration of trace impurities present at various stages of the refining. The overall efficiency of the process may be severely decreased in the presence of certain metals, even at trace levels. A number of methods have been reported for the determination of specific elements in various concentrates (5-11). Commonly, electrochemical techniques or atomic absorption spectrometry have been used. These methods become time consuming if a number of elements need to be determined. For example, Beyer and Bond (10) have determined both the major and some minor elements (Cd, Cu, Pb and Zn) simultaneously in lead and zinc concentrates by polarographic techniques. However, in this procedure the number of elements which can be determined simultaneously is limited, which is typically true in problems of this kind.

The electrolytic production of high purity metallic zinc uses a plant electrolyte which is essentially a very concentrated solution of zinc sulfate (100-108 g/L) in sulfuric acid (up to 110 g/L). The current efficiency for zinc production decreases substantially in the presence of trace impurities; i.e. cost of production is increased. Consequently, the zinc sulfate electrolyte has to be monitored very closely during the production process. Unfortunately this is not a matrix conducive to the atomic absorption method and many problems exist in the analytical work (11). In these laboratories, a method has been developed for trace metal analysis using liquid chromatography (LC) with electrochemical (LCEC) and/or UV-Visible spectrophotometric (LCUV) detection (12,13), which can be automated (14) with microprocessor based instrumentation. In the present report, the application to multi-element determination in the presence of a huge excess of zinc is examined on samples of zinc sulfate.

The method is based on formation of dithiocarbamate complexes followed by separation and subsequent electrochemical or spectrophotometric detection. Two modes of operation are available:

(i) The metal-dithiocarbamate complex can be formed external to the chromatographic system and prior to injection onto the separating column. Complex formation may be undertaken in a solvent identical to that for chromatographic separation or in aqueous solution followed by extraction into a suitable organic solvent (15).

(ii) If the kinetics of dithiocarbamate complex formation is sufficiently rapid, the complex can be formed 'in situ' by including the ligand in the chromatographic solvent. This is the method amenable to complete automation (14). With this method, Ni and Cu (14) as well as Pb, Co, Hg and Cd (15) can be determined in a single injection within ten minutes.

Other elements (e.g., Cr, As, Sb and Se) cannot be determined in this mode for various reasons (13,15), and recourse to the first mentioned method with external complex formation may need to be considered.

In the present work both modes of operation were considered for the simultaneous determination of Ni, Cu, Co, Pb, Hg and Cd in zinc concentrates.

It might be anticipated that the very large concentration of zinc would mitigate against successful development of a chromatographic method based on electrochemical and/or spectrophotometric detection. In principle, the chromatography might be expected to be inadequate to achieve the required separation which must be high with either spectrophotometric or electrochemical detection since zinc dithiocarbamate gives a response with both detectors. However, two major factors influence the possibility of success applying our new method for metal analysis to zinc plant electrolyte: (i) The stability constant of the zinc dithiocarbamate is small compared with most other metal-dithiocarbamates (16-18), (ii) Evidence for the formation of anionic zinc dithiocarbamate complexes has been reported (19-21). In previous work (14) an anion exchange guard column was designed to trap excess negatively charged dithiocarbamate ligand. The same guard column may therefore at least partially remove the zinc dithiocarbamate complex.

EXPERIMENTAL

Reagents and Standard Solutions

All chemicals used were of analytical grade purity unless otherwise stated. Commercially available diethyl and pyrrolidine dithiocarbamate salts were recrystallized from ethanol prior to use.

Standard solutions of the metals concerned were prepared by dissolving copper nitrate, nickel chloride, cobalt nitrate, lead nitrate, mercuric nitrate, cadmium chloride and selenium dioxide in distilled deionized water. Standard solutions were also prepared in a 'zinc sulfate-sulfuric acid' matrix corresponding to "pure" plant electrolyte. These standards were always used in analytical determinations.

Acetate buffer was prepared using the method described by Vogel (22).

Liquid chromatographic grade (LC) grade acetonitrile, methanol, dichloromethane and chloroform were used throughout this work.

Zinc sulfate electrolyte samples were provided by the Electrolytic Zinc Company, Risdon, Tasmania, Australia.

Instrumentation

Instrumental details concerning the chromatographic and electrochemical instrumentation have been described previously (12-14). Chromatography equipment and spectrophotometric detection were based on Waters equipment whilst electrochemical instrumentation was either from Princeton Applied Research (PAR) Corporation, Bioanalytical Systems (BAS), or home built. In this work the electrochemical detector was a Bioanalytical Systems (BAS)

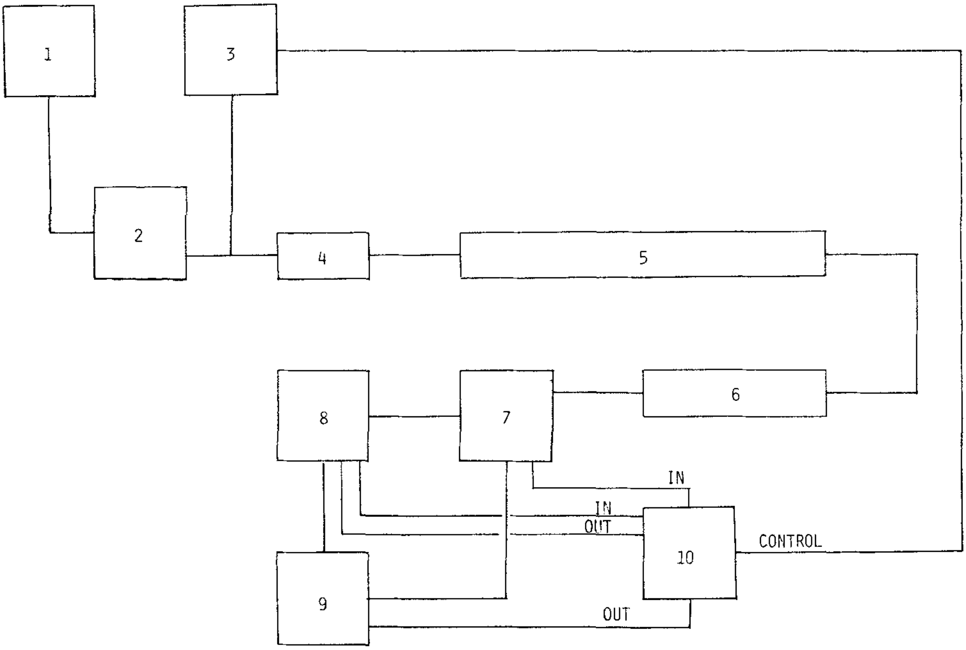

Figure 1

Flow Diagram of Instrumentation.

1. Chromatographic solvent: e.g. External mode : 70% acetonitrile : 30% acetate buffer, pH = 6 (.02 M), .01 M $NaNO_3$. In situ mode : as above but add 10^{-4} M NH_4pydtc.
2. Solvent Delivery System : Typical flow rate = 1-3 mL/min.
3. Injection System : can be either manual or automatic. Typical injection is 10-100 µL.
4. Guard column : containing (i) separator resin to protect separator column, e.g. C-18 resin and (ii) ion exchange resin to trap excess dithiocarbamate (external mode), e.g. Amberlite CG-400.
5. Separator column : e.g. C-18 reverse phase from Waters Assoc. Length = 30 cm; i.d. = 3.9 mm.
6. Suppressor column : to remove excess dithiocarbamate (in situ mode), packed with ion exchange resin as in guard column. Length = 20 cm; i.d. = 3.9 mm.

TL5 cell with glassy carbon working electrode, and an aqueous Ag/AgCl (3M KCl) reference electrode. Columns were basically as described in reference 14. A typical experimental arrangement is shown schematically in Figure 1.

Electrochemical experiments in a conventional cell were performed using glassy carbon working and auxiliary electrodes and a Ag/AgCl (satd. LiCl : methanol or dichloromethane) reference electrode.

Unless otherwise stated all data were obtained at (22 ± 1)°C and all solutions were degassed with nitrogen.

RESULTS AND DISCUSSION

The two methods of dithiocarbamate complex formation described in the introduction were examined to ascertain the effect of the large zinc concentration present in zinc sulfate electrolyte.

(i) External Dithiocarbamate Complex Formation

In this mode, diethyl or pyrrolidine dithiocarbamate complexes need to be formed in a buffered aqueous sample of zinc sulfate electrolyte by addition of an aqueous solution of diethyl or pyrrolidine dithiocarbamate salt. The metal complexes are then extracted into an organic phase (dichloromethane or chloroform were found to be suitable) prior to injection onto the column. The

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7. Spectrophotometric detector.
8. Electrochemical detector.
9. Readout device.
10. Microprocessor.

buffer solution was made 1% (w/v) in $NaNO_3$ to enhance the extraction efficiency (23). Injection of very pure zinc sulfate electrolyte without any guard column gives an extremely large zinc dithiocarbamate response using spectrophotometric detection (λ = 254 nm) or electrochemical detection (DC potential = 0.80 V) as shown in Figure 2(a,c). However, insertion of an anion exchange guard column is very efficient in removing this response, as shown in Figure 2 (b,d). This method can therefore be used for trace metal determination in zinc sulfate electrolyte with considerable advantage since Cd, Co, Cu, Pb, Hg and Ni may be determined simultaneously if no interference effects are in operation.

Initial studies to examine the extraction behaviour of the various metals in the presence and absence of zinc sulfate were undertaken with differential pulse voltammetry at a glassy carbon working electrode. Each of the dithiocarbamate complexes gives very well defined oxidation responses in organic solvents (19,24). The metal complexes were extracted into dichloromethane, and the electrochemistry then investigated in this solvent after addition of 0.1 $\underline{M}$ Bu_4NClO_4 as a suitable supporting electrolyte.

The extraction efficiency and stability of the metal complexes in the presence and absence of zinc sulfate electrolyte could be investigated conveniently in this manner. For those metal complexes which could be measured directly by voltammetry in a conventional electrochemical cell in the presence of a large excess of zinc, data agreed well with that found in liquid chromatographic work after chromato[illegible] removal of zinc. In all cases it was found that the

TABLE 1

Extraction of Metal Pyrrolidine Dithiocarbamate Complexes in Presence and Absence of Zinc Sulfate Electrolyte[a,b].

Metal	Percentage of metal dithiocarbamate signal obtained for extraction in presence and absence of zinc sulfate electrolyte.	Percentage of original metal dithiocarbamate signal remaining after two hours.	
		Without Zn	With Zn
Ni	18%	95%	100%
Co	15%	100%	100%
Pb	75%	100%	100%
Hg	85%	100%	100%
Cd	10%	100%	100%
Cu	100%	100%	100%

(a) Percentages quoted typically have a mean deviation of ± 3%.

(b) Extractions were performed with dichloromethane as in text (see later). Results are average values obtained by two methods.

(i) Differential pulse voltammetry (conventional cell). Scan rate = 5 mV/sec. Duration between pulses = 0.5 sec. Modulation amplitude = 50 mV.

(ii) Extractions were performed and samples injected into the LCEC/UV system described in Fig. 1. Injection volume = 10 µl. Flow rate = 2 mL/min. UV detection λ = 254 nm. Electrochemical detection DC (+ 1.20 V) vs Ag/AgCl (3 M KCl).

stability of the metal dithiocarbamates was increased in the presence of zinc dithiocarbamate as has been reported by other workers (25,26). Results are summarized in Table 1.

The ligand chosen for extraction in all quantitative studies was pyrrolidine dithiocarbamate ($pydtc^-$) rather than diethyldithiocarbamate, ($dedtc^-$) for a number of reasons. Firstly, $pydtc^-$ has been shown to exchange more readily than

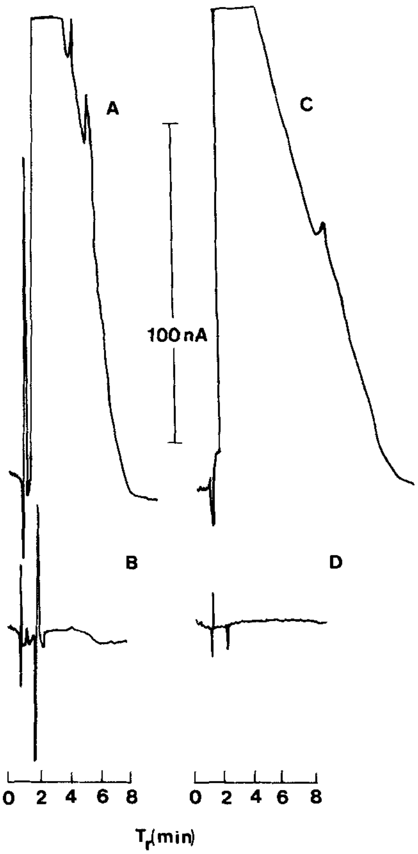

Figure 2

Injection (10 μL) of a $ZnSO_4$ solution (108 g Zn/L) in distilled H_2O. Chromatographic system as described in Fig. 1. Solvent flow rate = 3 mL/min.

(a) spectrophotometric detection (λ = 254 nm).

(b) as for (a) but insert ion exchange guard column.

(c) electrochemical detection DC (potential = + 1.20 V).

(d) as for (c) but insert ion exchange guard column.

dedtc$^-$ (18). Secondly, pydtc$^-$ is more stable than the dedtc$^-$ ligand in acidic solutions, such as encountered with zinc sulfate electrolyte. Finally, a significant response attributable to $Zn(dedtc)_2$ is observed when the dedtc$^-$ ligand is used. This complex has a retention volume similar to $Cu(dedtc)_2$ and causes interference.

Acetate buffer (pH = 4) was found suitable for extraction of all metals considered.

The basis of the extraction is shown in the reaction scheme below.

$$M_1^{x+} + M_2^{y+} + M_3^{z+} + \ldots + Zn^{2+} + pydtc^-$$

$$\Big\downarrow \text{Fast}$$

$$\text{"}Zn(pydtc)_n\text{"} + M_1^{x+} + M_2^{y+} + M_3^{3+} + \ldots + Zn^{2+}(\text{excess})$$

$$\Big\downarrow \text{Slower}$$

$$\text{"}Zn(pydtc)_n\text{"} + Zn^{2+} + M_1(pydtc)_x + M_2(pydtc)_y + M_3(pydtc)_3 + \ldots$$

"$Zn(pydtc)_n$" is then trapped on anion exchange guard column and

$$M_1(pydtc)_x + M_2(pydtc)_y + M_3(pydtc)_3 + \ldots$$

are separated on a reverse phase C-18 chromatographic column and detected. Zn^{2+} does not respond at either detector operating under appropriate conditions.

In this reaction scheme, "$Zn(pydtc)_n$" is probably a mixture of neutral and anionic complexes. Upon injection some of these complexes break down to give free (pydtc)$^-$ (15) which is trapped on the guard column.

M_1^{x+}, M_2^{y+}, M_3^{3+} ... are trace metals and Zn^{2+} is in a very large concentration excess over other metal ions being detected.

In such an extraction it would be ideal to use as much ligand as possible in order to increase the rate of formation of the metal dithiocarbamate complexes. However, if more than 5 mL of 1% (w/v) $pydtc^-$ is used with 1 mL of zinc sulfate electrolyte and 10 mL of extracting solvent, "$Zn(pydtc)_n$" begins to precipitate at the organic/aqueous interface.

For the determination of low concentrations of metals it is also obviously desirable to use as much zinc electrolyte (sample) as possible. However, use of too much electrolyte introduces too much zinc and therefore decreases the signals (extraction efficiency) of most of the other metals. Variation of zinc concentration at the ± 10% level was found experimentally to produce a constant trace metal signal (± 3%). There are obviously a number of constraints on the extraction procedure that can be used prior to chromatography and detection. In summary, the recommended analytical method is as follows:

(i) Add 10 mL 1 M acetate buffer (pH = 4.2) containing 1% $NaNO_3$ (w/v) to 1 mL of zinc plant electrolyte.

(ii) Add 5 mL of 1% aqueous $pydtc^-$ (w/v). Shake mechanically for ten minutes.

(iii) Add 10 mL extracting solvent (dichloromethane, or chloroform).

(iv) Shake for a further ten minutes.

(v) Leave to separate for five minutes.

(vi) Draw off sample from organic layer and inject a 10 µL sample into the chromatographic system consisting of 70% acetonitrile/30% buffer etc. as the running solvent, a guard column to remove excess pydtc$^-$ and "zinc dithiocarbamate" and a reverse phase C-18 separating column (see Figure 1).

(vii) Detect the metal with electrochemical or spectrophotometric detection after chromatographic separation.

With the above procedure, calibration curves were constructed for the metals concerned. All were linear for concentrations from the detection limit to at least 20 ppm. Fig. 3 shows a typical chromatogram. Chromatographic resolution between the Cu and Hg responses can be achieved by replacing 70% acetonitrile with (50% acetonitrile + 20% methanol) in the chromatographic solvent.

The only chemical interference observed with other elements known to be present was when mercury was monitored in the presence of selenium. In this situation, complex behaviour was observed in that the mercury response was split into two peaks (Fig. 4), implying that mercury selenium complexes are being formed via exchange reactions. (Results are similar with or without $ZnSO_4$ present).

Detection limits for both electrochemical and spectrophotometric detection are listed in Table II. Note that in previous work (13-14) the electrochemical detector has proved superior with respect to sensitivity. However in this work, even though the guard column does trap most of the pydtc$^-$ and "Zn(pydtc)$_n$" some

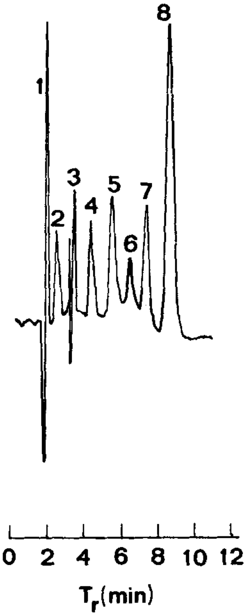

Figure 3

Determination of cadmium (2 ppm), lead (5 ppm) [peak 5], nickel (5 ppm) [peak 6], cobalt (5 ppm) [peak 7], mercury (5 ppm) and copper (5 ppm) [peak 8] in $ZnSO_4$ (108 g Zn/L). Peak 4 is due to thiuramdisulfide.

Extraction performed as in text using dichloromethane as extracting solvent. Peaks (1), (2) and (3) in blank. Chromatographic system as in Fig. 1. Injection volume = 10 µL, flow rate = 2 mL/min. Spectrophotometric detection (λ = 254 nm).

material(s) inhibiting the electrochemical response must be entering the detector since the current per unit concentration is less than that obtained in the absence of zinc when relatively positive DC potentials are used for detection.

Examination of plant electrolyte zinc samples was successfully carried out (see Fig. 5). Data obtained using the method of

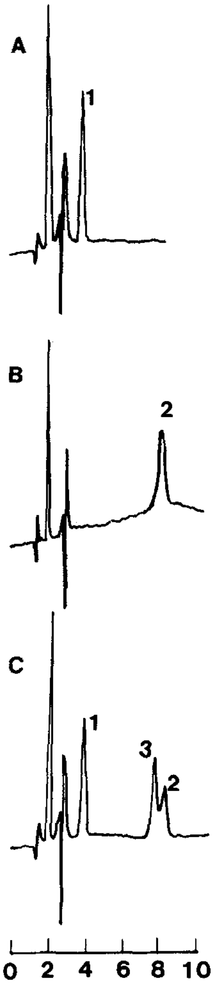

Figure 4

Injection of mercury (peak 2) in the presence of selenium (peak 1) results in another discrete response (peak 3). System as in Fig. 1. Flow rate = 3 mL/min. Injection volume = 10 µL.

(A) 10 ppm selenium. Peak 1 may be the thiuram disulfide dimer rather than selenium.

(B) 10 ppm mercury.

(C) 10 ppm selenium + 10 ppm mercury.

Extraction performed as outlined in text using dichloromethane as extracting solvent (no $ZnSO_4$ present). Spectrophotometric detection (λ = 254 nm).

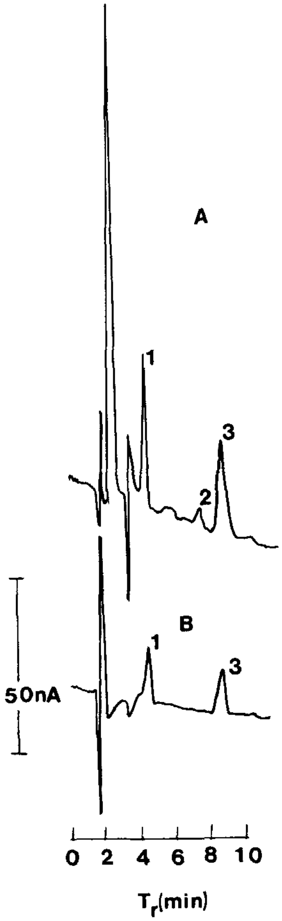

Figure 5

Injection (10 μ L) of a zinc plant electrolyte. Determination of 13 ppm cadmium (peak 1), 2 ppm cobalt (peak 2) and 7 ppm Cu(peak 3). Chromatographic system as in Fig. 1. Flow rate = 3 mL/min. Injection volume = 10 μL. Extraction as outlined in text using dichloromethane as extracting solvent.

(A) spectrophotometric detection (λ = 254 nm).

(B) electrochemical detection. DC (potential = +1.20 V).

standard additions were in excellent agreement with those obtained by conventional techniques based on individual determinations by atomic absorption spectrometry (100 fold dilution) or polarography (11), implying that the method is relatively interference free. No problems from other major constituents in the electrolyte (e.g. Mn, 12 g/L) were observed. Direct rather than standard addition methods of calibration was also satisfactory, except for the mercury-selenium combination noted above. This again is indicative that interferences are generally minimal.

(ii) <u>'In situ' Dithiocarbamate Complex Formation</u>

Several problems arise with this mode of operation.

The highly ionic zinc concentrate (~ 100 g/L Zn) needs to be miscible with a suitable chromatographic solvent. Both acetonitrile-water and methanol-water chromatographic solvents previously employed (14) were investigated with respect to miscibility. The zinc electrolyte was found to be immiscible with 70% acetonitrile solution, although this problem can be eliminated by a preliminary twenty-fold dilution and a corresponding loss in sensitivity. Although the zinc concentrate is in fact miscible with 70% methanol, zinc dithiocarbamate is not as soluble in methanol and precipitation may occur in the chromatographic system which is undesirable. If the UV-visible spectrophotometric detector is set at 254 nm or the electrochemical detector operated at potentials more positive than +0.80 V a very large zinc dithiocarbamate response is observed as shown in Fig. 6. Tuning of the spectrophotometric detector to λ = 400 nm or electrochemical detector to +0.60 V alleviates this problem significantly. However,

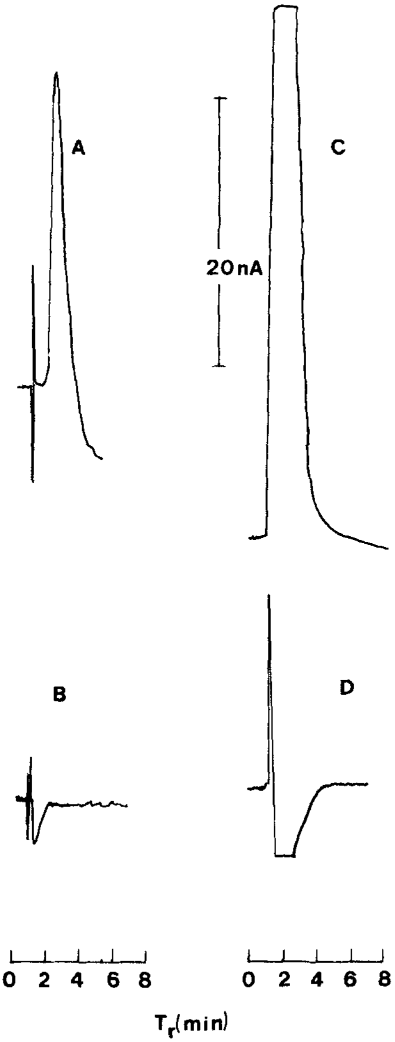

Figure 6

Blank (10 μL injection of $ZnSO_4$ electrolyte (108 g Zn/L) diluted twenty fold) determinations under various conditions.

(A) spectrophotometric detection (λ = 254 nm).

(B) spectrophotometric detection (λ = 350 nm).

(C) electrochemical detection DC (potential = +0.80 V).

(D) electrochemical detection DC (potential = + 0.60 V).

Chromatographic system as in Fig. 1 (in situ mode). Flow rate = 3 mL/min.

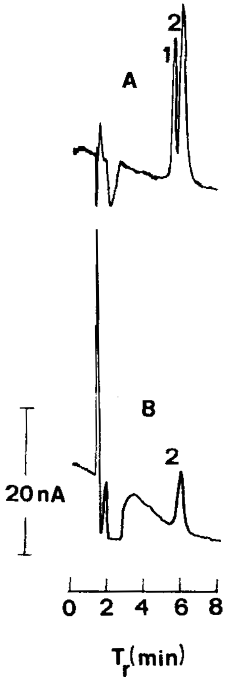

Figure 7

Determination of cobalt (20 ppm) [peak 1] and copper (260 ppm) [peak 2] in a zinc plant electrolyte (2 g/L H_2SO_4) sample after a twenty fold dilution.

(A) spectrophotometric detection (λ = 350 nm).

(B) electrochemical detection. DC (potential = + 0.60 V).

Chromatographic system as in Fig. 1 (in situ mode). Flow rate = 3 mL/min. Injection volume = 10 μL.

under these conditions, detection is limited to Ni, Cu and Co (spectrophotometric detection) and Ni and Cu (electrochemical detection). Data obtained in the presence and absence of zinc electrolyte show that the trace metal response is not the same as that observed when no zinc is present for metals other than Cu. The ratio of signal observed in the presence and absence of zinc is 100% for copper, 65% for nickel and 48% for cobalt. Thus, whilst copper determinations retain their sensitivity, the sensitivity for nickel and cobalt are decreased. Fig. 7 shows an example of an injection of a zinc plant electrolyte sample which demonstrates that the method does work. Data are presented in Table 2.

However, a further problem which mitigates against the long term use of the 'in situ' complex formation method was observed with long term monitoring under automated conditions. Repeated injections of the zinc electrolyte lead to relatively rapid deterioration in the performance of the separating column and column regeneration is required at more frequent intervals than required on zinc free samples. In an endeavour to provide improved performance, the 'in situ' complex formation mode was examined with a suppressor column in the system prior to the detectors in order to trap the excess ligand as well as the zinc dithiocarbamate complex. However under the conditions of ligand being included in the running solvent, this can only work for a few injections until the suppressor column is overloaded and fails to work.

In summary, for the particular example of trace metal determination in zinc plant electrolyte, the external dithiocarbamate complex formation method is considerably superior

TABLE 2

Limits of detection[a] in presence of zinc sulfate electrolyte.

	Detection Limits			
	External Mode[b,c]		'In situ' mode[d,e]	
Metal	spectrophotometric detection (ppm)	electrochemical injection (ppm)	spectrophotometric detection (ppm)	electrochemical detection (ppm)
Cu	0.1	0.1	0.1	0.1
Ni	0.5	2	0.5	0.5
Co	0.2	2	0.2	
Pb	0.1	1		
Hg	1	1		
Cd	0.5	0.5		

(a) For signal to noise ratio of 2, using a 10 μL injection.

(b) Using recommended extraction procedure (see text) with dichloromethane.

(c) External mode: λ = 254 nm - DC (+ 1.20V) linear to 20 ppm.

(d) Direct injection.

(e) 'In situ' mode: λ = 400 nm - DC potential = + 0.60 V.

Results obtained on chromatographic system as outlined in Fig. 1.

and must be recommended, even though it requires more time consuming procedures.

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REFERENCES

1. Smith, R.G. and Windom, H.L., A solvent extraction technique for determining nanogram per litre concentrations of cadmium, copper, nickel and zinc in seawater, Anal. Chim. Acta., 113, 39, 1980.

2. Durst, R.A., Ion Selective Electrodes, Nat. Bur. Stand. (U.S.) Spec. Publ. 314, Washington, 1969.

3. Pinta, M., Modern Methods for Trace Element Analysis, Ann Arbor Science, Mich., 1978.

4. Bond, A.M., Modern Polarographic Methods in Analytical Chemistry, Marcel Dekker, New York, 1980.

5. Donaldson, E.M., Spectrophotometric determination of selenium in concentrates and high-purity copper metal with 3,3'-Diaminobenzidine after separation by xanthate extraction, Talanta, 24, 441, 1977.

6. Donaldson, E.M., Spectrophotometric determination of bismuth in concentrates and non-ferrous alloys by the iodide method after separations by diethyldithiocarbamate and xanthate extraction, Talanta, 25, 131, 1978.

7. Donaldson, E.M., Determination of antimony in concentrates, ores and non-ferrous materials by atomic-absorption spectrophotometry after iron-lanthanum collection or by the iodide method after further xanthate extraction, Talanta, 26, 999, 1979.

8. Donaldson, E.M., Determination of bismuth in ores, concentrates and non-ferrous alloys by atomic-absorption spectrophotometry after separation by diethyldithiocarbamate extraction or iron collection, Talanta, 26, 1119, 1979.

9. Gallego, M., Garcio-Vargas, M. and Valcarcel, M., Pyridine-2-carbaldehyde 2-Hydroxybenzoylhydrazone as a selective reagent for the extraction and spectrophotometric determination of Iron(II), Analyst, 104, 613, 1979.

10. Beyer, M.E. and Bond, A.M., Simultaneous determination of cadmium, copper, lead and zinc in lead and zinc concentrates by

AC polarographic methods - comparison with atomic absorption spectrometry, Anal. Chim. Acta., 75, 409, 1975.

11. Pilkington, E.S., Weeks, C.E., Bond, A.M., Determination of zinc plant electrolyte by differential pulse polarography and anodic stripping voltammetry, Anal. Chem., 48, 1665, 1976.

12. Bond, A.M. and Wallace, G.G., Determination of copper as a dithiocarbamate complex by reverse-phase liquid chromatography with electrochemical detection, Anal. Chem. 53, 1209, 1981.

13. Bond, A.M. and Wallace, G.G., Simultaneous determination of copper, nickel, cobalt, chromium(VI) and chromium(III) by liquid chromatography with electrochemical detection, Anal. Chem. 54, 1706, 1982.

14. Bond, A.M. and Wallace, G.G., Automated monitoring of nickel and copper by high performance liquid chromatography with electrochemical and spectrophotometric detection, Anal. Chem. (In Press).

15. Bond, A.M. and Wallace, G.G., Simultaneous determination of copper, nickel, cobalt, chromium(VI), chromium(III), lead, mercury, cadmium and selenium as dithiocarbamate complexes using liquid chromatography with electrochemical and/or spectrophotometric detection. Unpublished work, Deakin University, 1983.

16. Hulanick, A., Complexation reactions of dithiocarbamates, Talanta, 14, 1371, 1967.

17. Busev, A.I., Byr'ko, V.M., Yen, H.K. and Kvesitadze A.G., Translated from Zhurnal Analiticheskoi Khimii, Vol. 26, No. 11, pp. 2069 - 2074. November 1971 : page 1849.

18. Sachinials, J. and Grant, M.W., Metal exchange reactions between divalent metal ions and their dithiocarbamate complexes in dimethyl sulfoxide : a kinetic and mechanistic study, Aust. J. Chem. 34, 2195, 1981 and references cited therein.

19. Coucouvanis, D., The Chemistry of dithioacid and 1,1 dithiolate complexes, 1968-1977, Progr. Inorg. Chem. 26, 301, 1979 and references cited therein.

20. McCleverty, J.A. and Morrison, N.J., Metal dithiocarbamates and related species. Part 2, J. Chem. Soc. Dalton, 2169, 1976.

21. Nieuwpoort, A., Dix, A.H., Porskamp, P.A.T.W. and van der Linden, J.G.M., Preparation and electrochemical behaviour of tris dithiocarbamato complexes $[Bu_4N]$ M - $(Et_2dtc)_3$ with M = Ba, Zn, Cd and Hg, Inorg. Chim. Acta, 35, 221, 1979.

22. Vogel, A., A Textbook of Quantitative Inorganic Analysis, Longmans, London, 1968.

23. Morrison, G.H. and Freiser, H., Solvent Extraction in Analytical Chemistry, John Wiley & Sons, New York, 1957.

24. Bond, A.M., Hendrickson, A.R. and Martin, R.L., Redox behaviour of 1,1 dithio and related chelates of transition metals (In Press) 1983.

25. Taddia, M., Atomic absorption spectrometry of cadmium after solvent extraction with zinc dibenzldithiocarbamate, Microchem. J. 26, 340, 1981.

26. Bajo, S. and Wyttenbach, A., Lead, cadmium and zinc bis(diethyldithiocarbamate) and diethyldithiocarbamic acid as reagents for liquid-liquid extraction, Anal. Chem. 51, 376, 1979.