Anal. Chem. 1989, 61, 1494–1496

Exchange Reactions with Zinc Bis[(2-hydroxyethyl)dithiocarbamate] for Automated Monitoring of Metal Ions in Industrial Effluents by Liquid Chromatography with Electrochemical Detection

A. M. Bond* and T. P. Majewski[1]

Division of Chemical and Physical Sciences, Deakin University, Geelong, 3217 Victoria, Australia

On-line mixing of industrial effluents with a buffered aqueous solution of the water-soluble zinc bis[(2-hydroxyethyl)dithiocarbamate] complex (or mixtures of zinc nitrate and ammonium bis(2-hydroxyethyl)dithiocarbamate) leads to the automated formation of dithiocarbamate complexes of metals such as copper, cobalt, nickel, and cadmium. Automated injection of the complexes formed in this way into a slowly flowing (<0.8 mL min^{-1}) 40/60 methanol–water (buffer) solvent mixture followed by oxidative electrochemical detection at +0.9 V vs Ag/AgCl of the dithiocarbamate complexes separated on a C_{18} chromatographic column completes the development of a highly efficient microprocessor-controlled system for trace metal determination in industrial effluents. The high stability of the zinc complex, the absence of any electroactive ligand, the ability to use water-soluble complexes, and the requirement of only small amounts of nonaqueous solvent allow considerable improvements to be made in long-term (7 day) monitoring of metals in industrial effluents relative to existing approaches.

INTRODUCTION

The determination of low concentrations of metal ions by formation of metal complexes with a suitable ligand, chromatographic separation of the mixtures of complexes, and detection of the separated complexes by spectrophotometric, electrochemical, or atomic absorption methods, etc., has become increasingly popular (*1*).

In the case of electrochemical detection, complete automation of the HPLC/EC (high-performance liquid chromatography with electrochemical detection) method has been achieved and continuous monitoring of metal ions in industrial effluents has been attempted for 7-day periods without operator intervention (*2*). In the previously described study (*2*), diethyldithiocarbamate or pyrrolidinecarbodithioate complexes of metal ions were prepared automatically in a reactor coil by using a low-pressure pumping system that mixed the industrial effluent and an acetonitrile solution containing the dithiocarbamate ligand. The acetonitrile–water solvent mixture formed in the complex preparation stage was then used as the solvent medium for the chromatographic separation of the metal dithiocarbamate complexes via the use of a high-pressure pump. Electrochemical detection at a glassy carbon electrode was achieved by oxidation of the metal complex or ligand attached to the metal. After extensive experience with this automated system, it has been recognized that deficiencies in the completely automated procedure arise from the slow decomposition of the dithiocarbamate ligand over the 7-day operation period, the necessary presence of excess electroactive dithiocarbamate ligand which has to be removed prior to electrochemical detection by an anion exchange column, and the use of the relatively expensive and toxic acetonitrile solvent required for the preparation of the water-insoluble dithiocarbamate complexes.

In the present communication we describe the use of the water-soluble, complexing agent zinc bis[(2-hydroxyethyl)dithiocarbamate], $Zn(HEDTC)_2$, as an alternative to salts of diethyldithiocarbamate or pyrrolidinecarbodithioate. $Zn(HEDTC)_2$ has a low stability constant relative to other metals of interest and participates in exchange reactions with many divalent (M^{2+}) and trivalent (M^{3+}) metals

$$\mathrm{Zn(HEDTC)_2 + M^{2+} \rightleftharpoons M(HEDTC)_2 + Zn^{2+}} \quad (1)$$

$$\mathrm{3Zn(HEDTC)_2 + 2M^{3+} \rightleftharpoons 2M(HEDTC)_3 + 3Zn^{2+}} \quad (2)$$

The $Zn(HEDTC)_2$ complex is water soluble and unlike the previously used dithiocarbamate salts can be stored in aqueous media for several weeks without decomposition. Additionally, the $Zn(HEDTC)_2$ complex is more difficult to oxidize than the free ligand and does not need to be removed from the solution by ion chromatography prior to electrochemical detection of most $M(HEDTC)_2$ or $M(HEDTC)_3$ complexes. Finally, $M(HEDTC)_2$ and $M(HEDTC)_3$ complexes formed via the exchange reaction prior to chromatographic separation are also water soluble so that a relatively high percentage of water with a correspondingly smaller quantity of solvents such as methanol can be used instead of the more expensive and more toxic water–acetonitrile mixtures used previously.

The alteration to the methodology as described in this paper therefore achieves simplification to the experiment, a decrease on operational costs, improved performance, and fewer problems with potentially hazardous and toxic organic solvents in the automated continuous 7-day operation of the HPLC/EC method for the on-line fully automated method for the continual determination of metals in industrial effluents. The HEDTC ligand has been used previously for postcolumn complex formation (*3*), the separation of metal complexes following precolumn derivatization (*4*) and in situ ligand exchange chromatography (*5*). Details on the stability of zinc complex and the free ligand under a range of conditions are available from these studies.

EXPERIMENTAL SECTION

Instrumentation. The instrumentation used in the present study is closely related to that described elsewhere (*2*). A reservoir of zinc bis(di-2-hydroxyethyl)dithiocarbamate reagent is automatically mixed with the industrial effluent in a reactor coil. A bubble chamber removes any air bubbles formed during the mixing stage and the sample is then automatically injected onto the HPLC/EC part of the system. The flow rate of the eluting chromatographic solvent can be carefully controlled in the 0.1–0.8 mL min^{-1} range. The glassy carbon working electrode, Ag/AgCl reference electrode, the potentiostat, chromatographic columns as well as other aspects of the instrumentation are the same as those described previously (*2*). Spectrophotometric detection was

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[1] On leave from Institute of General Chemistry, Technical University, 90-924 Lodz, Poland.

0003-2700/89/0361-1494$01.50/0

achieved with a Waters Model 450 variable-wavelength detector.

Reagents. All chemicals and solvents were of analytical or chromatographic grade purity.

Ammonium bis(2-hydroxyethyl)dithiocarbamate was prepared as follows: 10.5 g (0.10 mol) of diethanolamine was dissolved in 50 mL of methanol. A 150-mL portion of tetrahydrofuran and 10 mL (0.15 mol) of concentrated ammonium hydroxide were then added, and the resultant solution was cooled to below 10 °C in an ice bath. To the cooled solution, 5.0 mL (0.11 mol) of carbon disulfide was added dropwise with stirring. After the required product crystallized out from solution over a period of several hours, it was filtered, washed with tetrahydrofuran, and dried under vacuum at ambient temperature. The method is closely related to that described in ref 4.

The metal complexes, $Zn(HEDTC)_2$, $Ni(HEDTC)_2$, $Co(HEDTC)_3$, $Cu(HEDTC)_2$, and $Cd(HEDTC)_2$ were prepared by mixing aqueous solutions of concentrated ammonium bis(2-hydroxyethyl)dithiocarbamate salt, $[NH_4][HEDTC]$, and zinc(II) nitrate, nickel(II) nitrate, cobalt(II) nitrate, copper(II) nitrate, and cadmium(II) nitrate salts or their acetate salts respectively. The resultant precipitates were filtered, washed with water, dried under vacuum, and recrystallized from an ethanol/water mixture.

The chromatographic solvent was prepared by mixing an aqueous buffer (pH 6.5) solution made from conductivity grade water having extremely low metal ion contamination and HPLC grade methanol in the ratio 60:40. Methanol concentrations up to 80% can be used, but these decrease the retention times and increase the problem of organic solvent cost and toxicity. A stock solution of triethylammonium acetate buffer was prepared by dissolving 25.3 g of triethylamine in 300 mL of water and neutralizing to pH 6.5 with acetic acid. The finally recommended chromatographic solvent contains 0.025 M triethylammonium acetate buffer and was degassed with helium sparging during the course of all experiments.

RESULTS AND DISCUSSION

The stability of $Zn(HEDTC)_2$ was examined over a range of conditions. At a concentration of 1×10^{-4} M and in the presence of 0.025 M triethylammonium acetate buffer, no detectable change in $Zn(HEDTC)_2$ concentration was observed over a 2-week period. These zinc complex concentration and buffer conditions were therefore considered to be suitable for the HPLC/EC method which requires a 1-week continuous operation period without replacement of reagents or operator intervention. As an alternative, a mixture of 1×10^{-4} M $Zn(NO_3)_2$ and 1×10^{-4} $[NH_4][HEDTC]$ can be used in the buffered solution. This has the advantage of ensuring that only a minimal amount of uncomplexed and readily oxidized free ligand $[HEDTC]^-$ is present because the equilibrium

$$Zn^{2+} + 2HEDTC^- \rightleftharpoons Zn(HEDTC)_2 \qquad (3)$$

is shifted further to the right-hand side by the presence of excess zinc ions. The 10^{-4} M $Zn(HEDTC)_2$ complex in aqueous buffered media is stored in the HPLC/EC instrument related to that described in detail in ref 2 and is available for mixing when required with the industrial effluent or other aqueous sample via the use of a low-pressure pump (*2*). The exchange reactions given in eq 1 and 2 enable $M(HEDTC)_2$ and $M(HEDTC)_2$ complexes to be formed after zinc reagent and industrial effluent or other water sample are mixed. It is assumed that the metal ions of interest rapidly form the $M(HEDTC)_2$ and $M(HEDTC)_3$ complexes in the reaction chamber described in ref 2. In the industrial effluents examined in this work the metal ions are present at a concentration below 10^{-4} M so there is a significant excess of $Zn(HEDTC)_2$ present to ensure that the equilibrium positions in eq 1 and 2 lie well to the right.

The complexes of the metals of interest formed by the exchange reaction, along with excess $Zn(HEDTC)_2$, are automatically injected into the flowing chromatographic solvent. A potential of +0.9 V vs Ag/AgCl gives a very sensitive response for oxidation of nickel, copper, cobalt (metal based oxidation), and cadmium (ligand based oxidation) complexes and an insensitive response for $Zn(HEDTC)_2$ (ligand based oxidation) so that this potential is very suitable for multielement determinations. Measurement of the $Zn(HEDTC)_2$ response is a useful marker to ensure that an excess of the reagent was actually present and the decrease in peak height of this response relative to a control experiment provides information on how much $[HEDTC]^-$ has been complexed by other metals present. If the $Zn(HEDTC)_2$ response is not observed, then an insufficient concentration of this reagent is present and calculated values of metal ions in the industrial effluents represent lower limits, rather than correct values.

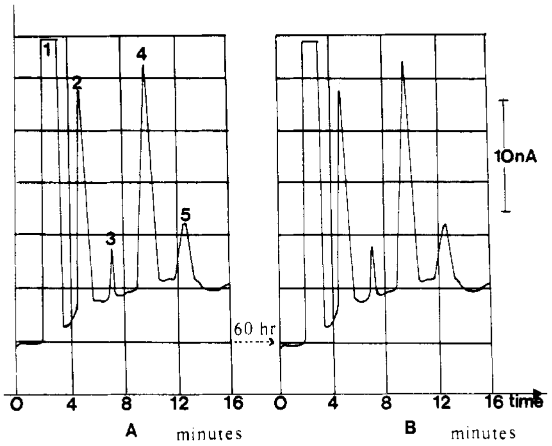

Figure 1. Chromatogram of 20-μL injection of a solution containing 500 ppb of Cu, Ni, and Co and 1000 ppb of Cd. A is the response observed initially and B the response after 60 h of continual operation of the automated HPLC/EC system. Responses are due to (1) excess of $Zn(HEDTC)_2$, (2) $Co(HEDTC)_3$, (3) $Cd(HEDTC)_2$, (4) $Ni(HEDTC)_2$, and (5) $Cu(HEDTC)_2$. Experimental parameters and conditions were as follows: complexing reagents 10^{-4} M $Zn(HEDTC)_2$; Altex C_{18} Spherisorb column; chromatographic solvent, 40:60 methanol–water (buffer); flow rate, 0.8 mL min^{-1}; electrode detection potential, +0.9 V vs Ag/AgCl; temperature, 18 °C.

In the absence of the triethylammonium acetate buffer in the chromatographic solvent, peak heights were nonreproducible. The buffer presumably blocks residual silanol groups on the C_{18} column which would otherwise be available for metal complexation (*4*). The presence of this buffer in the zinc reagent also ensures that reproducible conditions are available for metal complex formation in the reaction chamber.

Figure 1A shows a chromatogram of the observed response for a mixture of Cu, Co, Cd, and Ni metal ions in a standard solution of known composition. A low flow rate of 0.8 mL min^{-1} or less can be used because of the high resolution obtained with the column and conditions used. In the experiment described in Figure 1 a new injection of the same solution was undertaken every 20 min. The response in Figure 1B, which was observed after 60 h of running time, is virtually identical with the initially observed response.

After a 1-week continual operating period with a sample injected every 20 min, less than 5% variation in peak height was found in data obtained via the automated HPLC/EC method and the use of the exchange reaction with $Zn(HEDTC)_2$, provided the glassy electrode was cleaned every 10 h (or approximately every 60 injections) by application of a potential of −1.2 V vs Ag/AgCl for 30 s. In the absence of this cleaning pulse, a gradual deterioration in response is observed (peak diminishes in height). The application of the pulsed potential restores the response to the initial value. Data in Table I illustrate the gradual decay of the response and the restoration achieved by application of the pulse.

While the calibration curves are linear for each element, the sensitivity (peak current per unit concentration) is metal dependent (Figure 1). The limits of detection for each element are given in Table II.

Table I. Variation of the Measured Current Peak Height for Copper, Nickel, Cobalt, and Cadmium as a Function of Time of Continuous Operation of the Automated HPLC/EC System[a]

	% decrease in peak height with respect to the initial peak height			
time, h	Cu	Ni	Co	Cd
2	0.5	0.5	0.4	0.3
4	1.3	1.2	1.2	1.0
6	3.4	3.0	3.2	2.8
8	4.2	4.3	4.0	4.2
10	5.4	5.2	5.3	5.0
10[b]	0.1	0.0	0.1	0.0

[a] Experimental conditions are given in caption to Figure 1. [b] Data obtained after a cleaning potential of −1.2 V vs Ag/AgCl has been applied for 30 s.

Table II. Limits of Detection for Determination of Copper, Nickel, Cobalt, and Cadmium by the Fully Automated HPLC/EC Method[a]

metal	detection limit,[b] ppb
copper	20
nickel	10
cobalt	10
cadmium	100

[a] Complex forming reagent, aqueous, buffered 1×10^{-4} M $Zn(NO_3)_2$/1×10^{-4} M $[NH_4][HEDTC]$; chromatographic solvent, 40/60 methanol/water (buffer); flow rate, 0.8 mL min^{-1}; detection potential +0.9 V vs Ag/AgCl; Altex C_{18} Spherisorb column; temperature, 18 °C. [b] Calculated as a signal to noise ratio of 3:1.

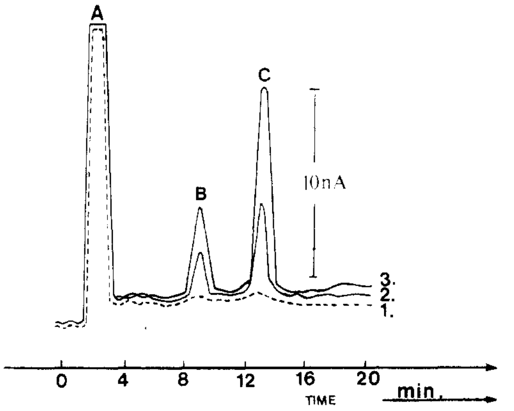

Figure 2. Determination of copper and nickel by HPLC/EC in (1) distilled water, (2) river water, and (3) drinking water: (A) excess $Zn(HEDTC)_2$; (B) $Ni(HEDTC)_2$; (C) $Cu(HEDTC)_2$. Experimental parameters and conditions are given in Figure 1.

Table III. Determination of Copper and Nickel in Water Samples by HPLC with Automated Electrochemical and Spectrophotometric Detection[a]

		concn found,[b] ppm	
sample	metal	electrochemical	spectrophotometric
drinking water	Cu	0.395 ± 0.012	0.420 ± 0.015
	Ni	0.120 ± 0.005	0.135 ± 0.010
river water	Cu	0.140 ± 0.015	0.160 ± 0.010
	Ni	0.090 ± 0.008	0.095 ± 0.010

[a] Experimental details are given in caption to Figure 1. [b] Average of five experiments obtained by using the fully automated sample preparation and injection system with direct calibration.

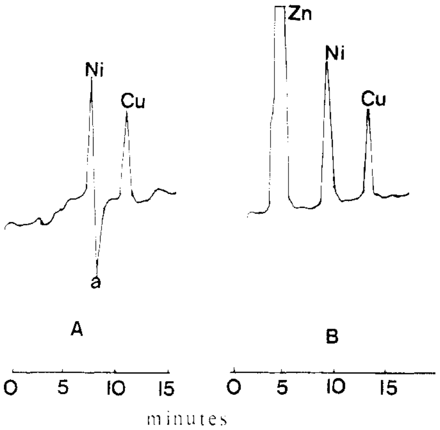

Figure 3. Determination of copper and nickel in drinking water by HPLC with electrochemical and spectrophotometric detection: (A) spectrophotometric detection at a wavelength of 300 nm; (B) electrochemical detection at +0.8 V vs Ag/AgCl. Other experimental parameters and conditions are given in Figure 1.

Figure 2 shows the chromatogram observed on drinking water which passes through copper pipes and from river water. Both these samples were obtained from sources on the Deakin University campus in Geelong, Victoria, Australia. In these two examples, nickel and copper levels may be determined but cobalt and cadmium levels are too low to be detected. Table III and Figure 3 provide a comparison of data obtained by electrochemical and spectrophotometric detection for nickel and copper. Excellent agreement is obtained for both methods of detection and the performance appears to be superior to that reported in ref 5. The "dip" in the chromatogram with spectrophotometric detection is caused by depletion of $Zn(HEDTC)_2$ (*5*). This elution dip is not observed under the conditions of the present study with electrochemical detection at +0.8 V vs Ag/AgCl.

Industrial liquors and effluents from electroplating or electrorefining industries often have considerably elevated cobalt and cadmium levels that can be routinely monitored by the method described in this work for 1-week periods, without operator intervention or maintenance. The concept of using an exchange reaction with $Zn(HEDTC)_2$ instead of in situ complex formation with an excess of dithiocarbamate ligand (*6*) or ex situ complex formation in the reaction chamber (*2*) offers a considerable improvement in reproducibility, stability, cost of reagents, and safety and has enabled objectives of the kind outlined in ref 2 for long-term monitoring of metal ion concentrations by the HPLC/EC method to be achieved more efficiently and effectively.

Registry No. $Zn(HEDTC)_2$, 94023-61-7; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Cd, 7440-43-9; water, 7732-18-5.

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RECEIVED for review December 27, 1988. Accepted March 14, 1989.