

Determination of Metal Ions by High-Performance Liquid Chromatographic Separation of Their Pyrrolidinedithiocarbamate Complexes after Solvent Extraction

Yoshio SHIJO, Kohsuke TAKADA and Nobuo UEHARA

*Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University,
Ishii-cho, Utsunomiya 321, Japan*

Keywords High-performance liquid chromatography, solvent extraction, pyrrolidinedithiocarbamate complex, lead, nickel, cobalt, copper, bismuth, indium

Studies of high-performance liquid chromatography (HPLC) for the determination of metal ions have aroused much interest over the past decade. In particular, the separation of a number of metal complexes by HPLC has been extensively studied.

Both pyrrolidinedithiocarbamate (PDTC) and diethyldithiocarbamate (DDTC) are among the best chelating reagents for the precolumn complexation of many metal ions, owing to their sensitivity and thermodynamic stability. Although a number of papers concerning the determination of metal ions as PDTC complexes by HPLC have been published¹⁻⁹, the detection limits of most HPLC methods using dithiocarbamate complexes are usually at the $\mu\text{g/l}$ level or above. In order to increase the practical value of the HPLC method of metal dithiocarbamate complexes, the most appropriate preconcentration method should be applied.

In this work, a solvent-extraction and reextraction method for PDTC complexes was investigated with the aims to attain a higher concentration factor and to increase the injection volume of the extracts into reversed-phase HPLC (RPHPLC). This method is based on the extraction of PDTC complexes with hexane, followed by reextraction into acetonitrile and subsequent separation by RPHPLC. In the proposed method, a concentration factor of up to about 250 and an injection volume of 50 μl can be attained, thus allowing the determination of metal ions at the sub $\mu\text{g/l}$ level in water.

Experimental

Apparatus and reagents

HPLC separations were performed using a modular system comprising of a Hitachi 655 pump, a Hitachi 638-0430 UV spectrophotometric detector, a Rheodyne 7125

loop injector, and a Shimadzu C-R3A Chromatopac. A Merck LiChrosphere RP-18 column (4 mm \times 250 mm, particle size 5 μm) was used for all of the experiments. The pH measurements were made with a Hitachi-Horiba F-7ss pH-meter.

Analytical reagent-grade acetonitrile was purified by distillation. Water was purified with a Milli-Q system after distillation-deionization. All of the chromatographic mobile phases used were filtered through 0.45 μm filters. Stock solutions (1000 mg/l) of Pb(II), Ni(II), Co(II), Cu(II), Bi(III) and In(III) were of the atomic absorption standard. An ammonium pyrrolidinedithiocarbamate (APDC) solution was freshly prepared by dissolving the requisite amount of APDC in water immediately before use. All of the other chemicals were of analytical reagent grade.

The mobile phase was acetonitrile-water (66/34 v/v) containing 1.5×10^{-5} mol/l APDC and buffered at pH 5.6 with 2×10^{-2} mol/l ammonium acetate. The flow rate was 0.7 ml/min and the detector was operated at 254 nm.

Procedure

Eight milliliters of a 1 mol/l diammonium hydrogen citrate solution was added to a known volume of sample solution containing Pb(II), Ni(II), Co(II), Cu(II), Bi(III) and In(III). After adjusting the pH to 4.0, 8 ml of a 2% APDC solution was added, the mixture was diluted to 400 ml with water. After adding 5 ml of hexane, the mixture was shaken for 5 min in a separatory funnel. Then, after standing for 5 min the aqueous phase was removed and the mixture was allowed to stand for 10 min. Removal of the aqueous phase was repeated. One milliliter of 3 mol/l sodium chloride solution and 2 ml of acetonitrile were added into the separatory funnel; the mixture was then shaken for 1 min. In time, the mixture was separated into three phases: hexane, acetonitrile and sodium chloride solutions as an upper, middle and lower layer, respectively. The acetonitrile

phase was separated and injected into HPLC.

Results and Discussion

A typical chromatogram showing the separation of a mixture of Pb(II), Ni(II), Co(II), Cu(II), Bi(III) and In(III) is given in Fig. 1. All of the peaks are sufficiently resolved for analytical purposes.

Extraction of metal pyrrolidinedithiocarbamate complexes

The optimum pH for extracting PDTC complexes of Pb(II), Ni(II), Co(II), Cu(II), Bi(III) and In(III) with hexane was investigated. The fundamental investigations were carried out using 100 ml of the aqueous phase, 1 ml of hexane and 2 ml of acetonitrile under the procedure described above. The relationship between the pH and the peak height is shown in Fig. 2. Constant peak heights were obtained in the 2–11 pH ranges for Pb(II), 3–8 for Ni(II), 2–8 for Co(II) and Bi(III), 3–10 for Cu(II), and 2–9 for In(III). The solubilities of the PDTC complexes into hexane are usually poor. By shaking during the extraction, although PDTC complexes of Pb(II), Co(II), Bi(III) and In(III) pass into hexane, part of the complexes of Ni(II) and Cu(II) aggregates at the interface between the organic and aqueous phases. Then, all of the PDTC complexes are completely dissolved into acetonitrile by reextraction.

The effect of the concentration of APDC in the aqueous phase on the extraction of PDTC complexes was investigated at pH 4.0. Constant peak heights were obtained in the APDC concentration ranges of more

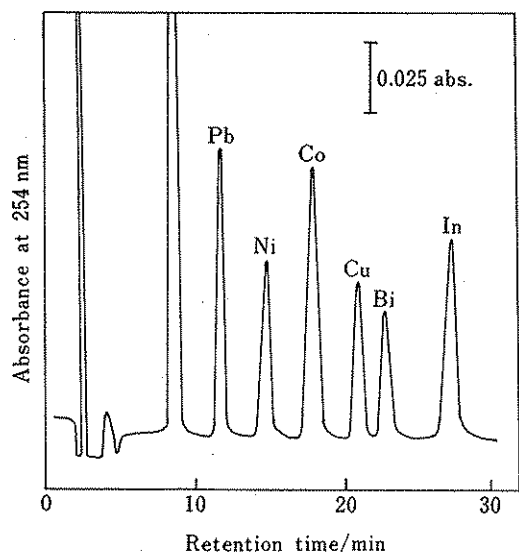


Fig. 1 Chromatogram of PDTC complexes. Sample, Pb(II) 125 ng, Ni(II) 50 ng, Co(II) 50 ng, Cu(II) 50 ng, Bi(III) 50 ng, In(III) 50 ng, injection volume 50 μ l. Mobile phase, acetonitrile–water (66/34, v/v) containing 1.5×10^{-5} mol/l APDC and 2×10^{-2} mol/l acetate buffer (pH 5.6), flow rate 0.7 ml/min. Detection, absorbance at 254 nm. Column, LiChrosphere RP-18 (4 mm \times 250 mm, 5 μ m).

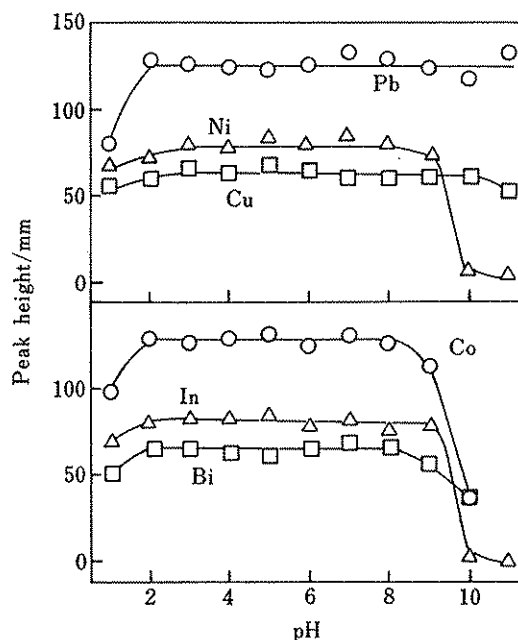


Fig. 2 Effect of the pH on the extraction of PDTC complexes with hexane. Aqueous phase 100 ml, APDC 2.4×10^{-3} mol/l, hexane 1 ml, acetonitrile 2 ml, injection volume 20 μ l. All other conditions as in Fig. 1 except pH.

than 6×10^{-7} mol/l for Pb(II) and In(III), 6×10^{-5} mol/l for Ni(II), 6×10^{-4} mol/l for Co(II), 6×10^{-6} mol/l for Cu(II), and 6×10^{-8} mol/l for Bi(III).

The extraction of PDTC complexes was studied by varying the volume ratio of the aqueous-to-organic phase. Constant peak heights were obtained at a volume ratio of the aqueous-to-organic phase $< 100:1$ for the first extraction, except for the complex of Pb(II). The peak height of the PDTC complex of Pb(II) decreased with increasing volume ratio of the aqueous-to-organic phase.

Reextraction of PDTC complexes with acetonitrile

The PDTC complexes of Pb(II), Ni(II), Co(II), Cu(II), Bi(III) and In(III) extracted with hexane were reextracted by acetonitrile for subsequent injection into RPHPLC. After removing the aqueous phase in the first extraction, the amount of water remaining on the internal wall of the separatory funnel varies somewhat in each case. Therefore, at the time of the reextraction, 1 ml of 3 mol/l sodium chloride solution was added in order to suppress the volume change of the acetonitrile phase by salting out. A quantitative reextraction of the PDTC complexes was achieved with 2 ml of acetonitrile from 5 ml of hexane.

Injection volume

The effect of the injection volume of the extracts in acetonitrile was investigated using loop injectors of various volumes, such as 5, 10, 20, 50, 100, and 200 μ l. The peak heights of the complexes increase linearly with

Table 1 Detection limits, precisions and recoveries

Metal	Detection limit $\mu\text{g/l}$	RSD, %	Recovery, %
Pb(II)	0.21	3.0	88.7
Ni(II)	0.15	3.9	94.5
Co(II)	0.028	2.2	98.0
Cu(II)	0.023	9.2	100
Bi(III)	0.057	6.3	95.6
In(III)	0.040	2.7	100

increasing injection volume up to 50 μl . The retention time and peak shape of the complexes remain unchanged in the 5 – 50 μl range of the injection volume.

Calibration graph, detection limit and recovery

The calibration graphs were linear over the 0 – 10 $\mu\text{g/l}$ range of the metal ions under the recommended conditions when the peak height was measured at 50 μl injection. The detection limits were defined as being the metal-ion concentrations giving a peak height that is three-times larger than the background noise. The detection limits, precision and recovery are summarized in Table 1. The recovery of the metal ions studied were

determined by repeating the extraction and reextraction three times.

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(Received September 3, 1992)

(Accepted December 15, 1992)

