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A New Preconcentration Method for Metal Chelates with Micro Volume of Water Miscible Solvent and Its Application to the Determination of Cobalt by Reversed-Phase High-Performance Liquid Chromatography

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A new effective and simple method has been developed to concentrate trace analytes from the organic phase after conventional extraction. Micro volume of high boiling-point water miscible solvent (solvent A), such as dimethylsulfoxide, is added to the separated organic phase and the low boiling-point organic solvent (solvent B), such as chroloform, is removed by evaporation to concentrate the analytes in the solvent A. This method has been successfully applied to the ion-pair solvent extraction system of cobalt with 2,2'-dihydroxyazobenzene as a powerful preconcentration technique for reversed-phase high-performance liquid chromatography of the metal chelates. The detection limit is 6×10^{-10} mol dm^{-3}.

Solvent extraction and solid phase extraction followed by elution with organic solvent are two of the most popular methods for preconcentration and preliminary matrix simplification for trace analysis. Since these pretreatments often result in a large volume of solvent compared with the volume required for analysis, a variety of evapolation techniques are employed to reduce the volume of the extract or the eluate. The best known examples of such apparatus, although it is very difficult to control the final volume to less than 1 cm^3 even with skilled laboratory support, are a Kuderna-Danish concentrator and a rotary evapolator. Micro-extraction methods by the use of varied glass apparatus are an alternative to reduce the sample sizes without the need for further solvent reduction.[1, 2]

Reversed-phase high performance liquid chromatography (RP-HPLC) is a subject of growing interest as a highly sensitive and selective method for the determination of trace metal ions.[3-7] When a sample is too dilute or too complex, solvent extraction has also been used extensively for RP-HPLC. However, one of the most significant problems currently facing the preconcentration of metal ions by solvent extraction for RP-HPLC is the solubility problem of the solvent in the polar mobile phase as well as its effects on chromatographic peak profiles. Thus, the solvent is usually removed by evaporation to dryness and the sample is reconstituted into 1 cm^3 level of an appropriate solvent which can be injected into a chromatographic system.[8] Salting-out of polar solvent from aqueous solution has been also employed for the extraction of metal ions prior to RP-HPLC.[9, 10] In this approach, however, the possibility of contamination from the salting-out reagent is high. Another problem is the large volume of the solvent compared with the volume injected for chromatographic analysis.

In this study, a new simple method to concentrate the organic phase into micro volume of water miscible solvent has been developed, which is suitable for the preconcentration of trace metal chelate ion-pair prior to the RP-HPLC. The experimental conditions that have been investigated in the study are (1) the extraction of cobalt(III) with 2,2'-dihydroxyazobenzene (DHAB) into chroloform, (2) replacement of chroloform with 0.1 cm^3 of the high boiling-point solvent, dimethylsulfoxide(DMSO), by evapolation of chroloform after the addition of DMSO to the extract in a Teflon beaker, and (3) its subsequent determination by ion-pair reversed-phase partition (IPRP)-HPLC. The effect of the injection solvent on the HPLC peak profiles has been also studied. In our previous studies on the DHAB chelates, it was noticed that the 1:2 chelates of trivalent metal ions are readily extracted as the ion pair, $Q^+[M^{III}L_2]^-$.[11, 12] When the sample volume of 25 cm^3 is used, the enrichment factor of 250 is achieved and the detection limit for cobalt is 6×10^{-10} mol dm^{-3} (35 ng/dm^{-3}). In addition to the greatly increased over-all sensitivity and selectivity, the proposed method serves as a new technique to displace water immiscible phase with water miscible one which can be injected into RP-HPLC system.

The HPLC setup consisted of a JASCO 880-PU pump unit, a JASCO 870-UV spectrophotometric detector with a 1 cm cell, and a Rheodyne 7125 loop injector (0.1 cm^3). The detector setting of 0.02 absorbance unit full scale (AUFS) at 510 nm was used for 1 mV recorder output. A Cica-Merck LiChroCART RP-18 column (4 mm i.d. x 120 mm length) was used. Metal ion stock solutions were prepared from the chloride or the nitrates. The reagent, DHAB, was used as received from Dojindo Laboratories and the solution (ca. 2×10^{-4} mol dm^{-3}) was prepared by dissolving it in an aqueous solution of 0.04% trimethyl (hydroxyethyl)ammonium hydroxide (TMK-12, electronic grade) from Kanto Chemical Co. Inc. . All other reagents used were of guaranteed reagent grade. As the mobile phase, an aqueous methanol (61.0 wt%, pH 8.0) containing 6×10^{-3} mol kg^{-1} tetrabutylammonium bromide (TBABr), 2×10^{-3} mol kg^{-1} trihydroxy(methylamino)methane (THMAM), and 10^{-4} mol kg^{-1} disodium salt of EDTA was used.

The typical procedure is as follows: transfer an aliquot (not more than 23 cm^3) of an acidic sample solution, containing less than 70 ng of cobalt(II) ion, to a Teflon bottle. Add 0.5 cm^3 of the DHAB solution, 1 cm^3 of 0.1 mol dm^{-3} Borax-NaOH buffer solution (pH 10), and 0.1 cm^3 of 1×10^{-3} mol dm^{-3} TBABr and dilute to 25 cm^3 with water. Extract with 5 cm^3 of chroloform by stirring with a magnetic stirrer for 10 min. Separate the organic layer with a hydrophobic filter paper (ADVANTEC 2S, 125 mm) into a 50-cm^3 Teflon beaker. After the addition of 0.1 cm^3 of DMSO, remove the extracting solvent, chroloform, by evaporation in a water bath at 60 °C. To the residual DMSO solution, add 0.1 cm^3 of water and inject an aliquot of it to the HPLC column with a 0.1 cm^3 loop injector.

In the IPRP-HPLC with DHAB, the chelates of V^V, Co^{II}, Al^{III}, and Fe^{III} ions cannot be destroyed along the HPLC column without addition of the chromogenic reagent in the eluent, even in the presence of EDTA, and are separated on the column.[6, 7, 13] Figure 1 shows the typical chromatogram obtained when the proposed method is applied to the preconcentration of cobalt prior to the HPLC separation. The largest source of the peaks of aluminium and iron shown in Fig.1 is the impurity of the reagents used. The blank value was not detected for cobalt throughout the study. Although aluminium at higher concentrations tends to interfere with the determination of cobalt in the HPLC separation owing to the relatively low resolution of their elution peaks, the extraction process employed in this study serves as a preseparation method of cobalt from aluminium as well as a preconcentration method. Figure 2 shows the effect of the pH of the aqueous phase on the over-all recovery of cobalt, together with that of aluminium. Thus aluminium at concentrations up to 1.6×10^{-6}

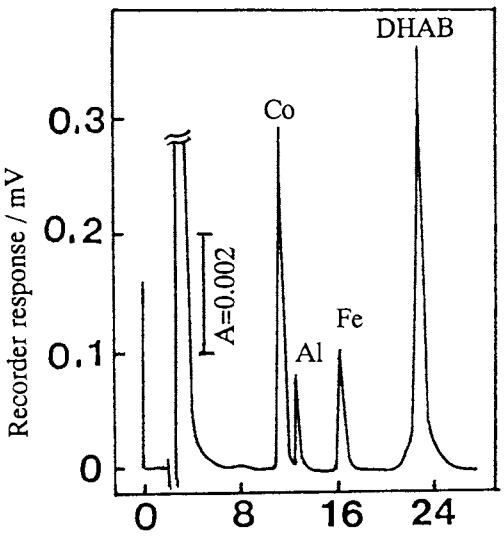

Fig.1. Typical chromatogram for cobalt after preconcentration by the proposed method.
Conditions for concentration
Sample: 8×10^{-9} mol dm^{-3} Co (25 cm^3); Solvent for extraction: $CHCl_3$; $[DHAB]_T$: 4×10^{-6} mol dm^{-3}; [TBABr]: 4×10^{-6} mol dm^{-3}; pH: 10; Final solvent: DMSO 0.1 cm^3.
Conditions for HPLC
Solvent for injection: 1:1 DMSO-water; Column: LiChroCART RP_{18}; Detection wavelength: 510 nm; Mobile phase: (TBABr: 6×10^{-3} molal; EDTA: 1×10^{-4} molal; THMAM: 2×10^{-3}molal (pH 8.0); MeOH: 61.0 wt %); Flow rate: 0.5 cm^3 min^{-1}; AUFS: 0.02.

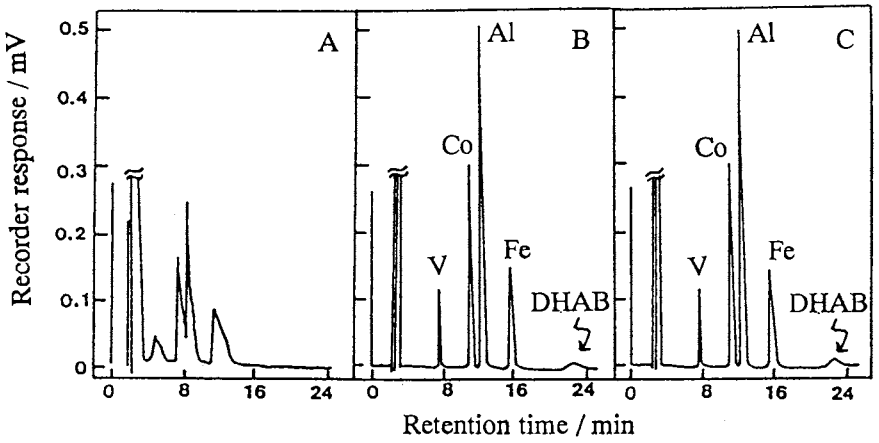

Fig.2. Effect of pH on the recovery of cobalt and aluminium. ●:$[Co]_{initial}$= 1.6×10^{-8} mol dm^{-3}; ○ :$[Al]_{initial}$= 4×10^{-8} mol dm^{-3}. The other conditions are the same as those in Fig.1.

Fig.3. Effect of injection solvent on peak profiles.
C_M=1 x 10^{-6} mol dm^{-3} (without preconcentration), injection solvent: A (DMSO 80 %-water), B (DMSO 50 %-water), C (water). The other conditions for HPLC are the same as those in Fig.1.

mol dm^{-3} has no significant effect due to the low recovery of aluminium under the analytical condition (pH 10) in addition to the chromatographic separation.

Earlier works showed that organic solvents in sample solutions gave significant effects on chromatographic peak profiles in RP-HPLC.[14-17] Although DMSO causes peak broadening at higher concentrations of the solvent in the injection sample, no interference on the peak profiles is observed when the injection solvent is water-DMSO (1:1, V/V) (Fig.3). This allows the use of aqueous standards for calibration.

The peak height calibration curve was linear up to 5 x 10^{-8} mol dm^{-3} (3 μg dm^{-3}). The detection limit, defined as three times the standard deviation of the base line noise level, was 6 x 10^{-10} mol dm^{-3} (35 ng dm^{-3}). Between-run coefficient of variation for 5 samples of 1.6 x 10^{-8} mol dm^{-3} Co was 1.9%. The over-all recovery of cobalt ranged between 95.7% and 102% (mean = 99.1%, n = 5) at 1.6 x 10^{-8} mol dm^{-3}. The reflux of chloroform along the wall of the beaker during evapolation was useful for the quantitative recovery, eliminating further washing step.

Preconcentration with a large enrichment factor and replacement of sample solvent with an appropriate one for subsequent analysis can be realized by the proposed method simultaneously, requiring minimal sample manipulation and no special apparatus. Future work will focus on preconcentration from smaller quantities of a sample solution into nl (0.1 mm^3) level of final volume.

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