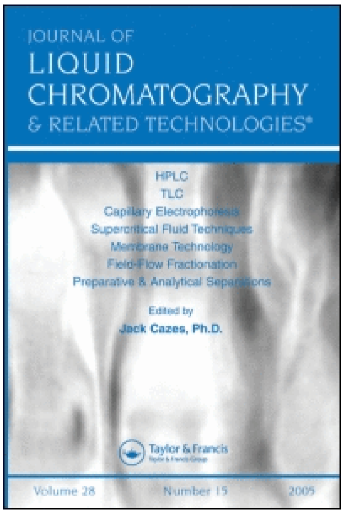

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Cobalt(II) by Reversed-Phase Liquid Chromatography with Electrochemical and Spectrophotometric Detection

Yukio Nagaosa[a]; Toru Mizuyuki[a]
[a] Department of Applied Chemistry and Biotechnology Faculty of Engineering, Fukui University Bunkyo, Fukui, Japan

To cite this Article Nagaosa, Yukio and Mizuyuki, Toru(1995) 'Determination of Cobalt(II) by Reversed-Phase Liquid Chromatography with Electrochemical and Spectrophotometric Detection', Journal of Liquid Chromatography & Related Technologies, 18: 15, 3139 — 3146

To link to this Article: DOI: 10.1080/10826079508010439

URL: http://dx.doi.org/10.1080/10826079508010439

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(15), 3139-3146 (1995)

DETERMINATION OF COBALT(II) BY REVERSED-PHASE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL AND SPECTROPHOTOMETRIC DETECTION

YUKIO NAGAOSA AND TORU MIZUYUKI
Department of Applied Chemistry and Biotechnology
Faculty of Engineering
Fukui University
Bunkyo, Fukui 910, Japan

ABSTRACT

A reversed-phase liquid chromatographic method for the selective and sensitive determination of cobalt (II) with ethyl xanthate (EX) is described. The method is based on the pre-column derivatization of cobalt(III)-EX chelate, injection of the sample onto a C_{18} column, and elution with 4:1 acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 0.02 mol dm^{-3} potassium nitrate as the mobile phase. The detection of the metal in eluate has been made by electrochemical (at +1.40 V *vs*. Ag/AgCl) and spectrophotometric (at 330 nm) methods. The detection limits (S/N=3) for cobalt(II) by the proposed method are 0.23 and 0.56 $\mu g\ dm^{-3}$ for the electrochemical and spectrophotometric detection, respectively. Cobalt in pepperbush has been determined with satisfactory precision.

INTRODUCTION

In recent years, the separation and determination of metal ions by liquid chromatography (LC) has been increasing popular (1). These methods involve the formation of metal chelates with coordinating reagents such as diethyldithiocarbamate (2), β-diketones (3), quinolinol-8-ol (4), 4-(2-pyridylazo) resorcinols (5,6) and so on, followed by LC separation with spectrophotometric and electrochemical detections. It has been recognized that the spectrophotometric detection after LC separation of metal chelates makes it possible to simultaneously determine multielments in a variety of samples. The electrochemical detection, on the other hand, is a very effective method for the selective determination of some components of interest, because only electroactive (oxidative or reductive) species can be detected amperometrically at a glassy carbon. Deficiencies in the use of the electrochemical detection arises from the necessary presence of excess electroactive ligand (*e.g.* dithiocarbamates) which has to be eliminated prior to electrochemical detection by an anion exchange column (7). Further, the slow decomposition of certain chelates under the conditions of the reversed-phase LC system is observed due to solubility problems. In order to overcome such problems, Bond et. al have used the exchange reaction with zinc bis-(2-hydroxyethyl)dithiocarbamate for automated monitoring of metal ions by LC with electrochemical detection (8).

In this work we describe the use of ethyl xanthate (EX) as an electroactive ligand for the electrochemical detection of the Co(III) chelate after the reversed-phase LC separation. The ligand has been utilized for normal-phase LC of such metal ions as Bi(III), As(III) and Sb(III) (9), but not for the reversed-phase LC system in which only the Co(III) chelate is the most stable than the other metals; the Co(III) chelate does not decompose in the C_{18} column even when the elution was made with the mobile phase containing no ligand. The results suggest that the use of EX as a precolumn derivatization achieves decrease of background current and detection limit, unchanged response and selective detection of the metal chelate at working electrodes. We have developed a selective and sensitive method for the determination of low levels of cobalt(III) by the reversed-phase LC with electrochemical detection as well as spectrophotometric one. It is demonstrated that the proposed method is virtually free from interferences such as Cu(II), Ni(II), Pb(II), Cd(II) and has been applied to the determination of cobalt in pepperbush (Standard Reference Material No.1 from the National Institute of Environmental Science, NIES 1, Japan).

EXPERIMENTAL

Apparatus

The liquid chromatograph used consisted of a Tosoh CCPD pump, a Rheodyne 7125 loop injector equipped with a 100 mm^3 sample loop, a Fuso Model HECS 318 High Sensitive Potentiostat equipped with a BAS LC-17A thin-layer electrochemical cell (a glassy carbon working electrode, a stainless steel auxiliary electrode and a Ag/AgCl reference electrode), a Shimadzu SPD-10A ultraviolet-visible spectrophotometric detector and Shimadzu Chromatopac CR-6A data processor. Tosoh TSK-Gel ODS 80TM chromatographic columns (250 x 4.6 mm i.d. and 150 x 4.6 mm i.d.) were used. A PAR 174A polarographic analyzer equipped with a Rika Denki RW-11 x-y recorder was used for differential-pulse voltammetric measurements. A Toa Denpa HM-30S pH meter was also used.

Reagents and Solutions

Acetonitrile was of LC grade from Kanto Chemicals. Potassium EX salt and metal ion standards for atomic absorption spectrometry were purchased from Wako Junyaku Chemicals. The water used was obtained from a Millipore Milli-Q water purification system. The mobile phase was 4:1 (v/v) acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 0.02 mol dm^{-3} KNO_3. Potassium EX salt was dissolved in acetonitrile to give a concentration of 2 x 10^{-3} mol dm^{-3}. All other chemicals used were of analytical-reagent grade.

Procedure

A slightly alkaline solution (pH ca.9) containing Co(II) was taken in a 10-cm^3 mol dm^{-3} calibrated flask, and 5.0 cm^3 of 2 x 10^{-3} mol dm^{-3} potassium EX salt solution in acetonitrile was added. The total volume was made up to 10.0 cm^3 with water. A 100-mm^3 aliquot of the resultant solution was injected onto the analytical column, and eluted with the mobile phase at a flow rate of 1.0 cm^3 min^{-1}. The eluate after LC separation was detected by the electrochemical (+1.40 V *vs*. Ag/AgCl) and spectrophotometric (330 nm) detection methods. The amount of the metal was determined by measuring the peak height on the chromatogram.

Treatment of pepperbush sample

The sample was dried at 110 °C to obtain constant mass and was then weighed by 0.3790 g in this experiment. The weighed sample was transferred to a 500-cm^3 beaker, and treated with 10 cm^3 of nitric acid, 10 cm^3 of sulfuric acid and 30 cm^3 perchloric acid at 150-200°C. The solution was evaporated to almost dryness. The residue was dissolved in 10 cm^3 of 2 mol dm^{-3} hydrochloric acid, and the pH was then adjusted to *ca.* 9.0 by adding 5.0 cm^3 of 0.1 mol dm^{-3} sodium citrate and an appropriate volume of 6 mol dm^{-3} ammonia. The sample solution was made up to 100 cm^3 with water, and was mixed with 2 x 10^{-3} mol dm^{-3} EX solution in acetonitrile at a 1:1 volume ratio, as described in the section of procedure.

RESULTS AND DISCUSSION

Chromatographic studies of metal EX-chelates

Fig.1 shows a typical chromatogram for the Cu(II), Ni(II), Pb(II), Hg(II), Cd(II), Bi(III) and Co(III) chelates by the reversed-phase LC system using 4:1 acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 10^{-3} mol dm^{-3} EX as the mobile phase. At the stage of the precolumn

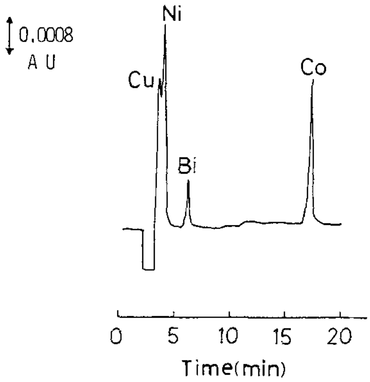

Fig.1 A chromatogram for metal-EX chelates by reversed-phase LC with spectrophotometric detection (330 nm): the mobile phase was 4:1 acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 2 x 10^{-3} mol dm^{-3} EX and 0.02 mol dm^{-3} KNO_3; the metal concentration was 1.0 mg dm^{-3}; the analytical column was Tosoh ODS 80TM (4.6 x 250 mm).

derivatization, the labile Co(II) chelate was oxidized to the inert Co(III) derivative in the presence of air. It was found that the retention time of the metal chelates increased as the percentage of acetonitrile decreased. An acetonitrile content of 80% was chosen as the mobile phase, because the Bi(III) and Co(III) chelates were well separated from the others at retention times of 6 and 17 min, respectively. The two chromatographic peaks were unaffected even when the ligand was not present in the mobile phase; however, the other metal chelates gave no peak because they decomposed through the LC elution. The results indicate that the C_{18} column acts as a reactor to separate certain coexisting species. In addition, the detection limit could also be lowered as a result of decreased background noises on the chromatogram. In the present paper, we have studied the determination of Co(II) as the EX chelate by the reversed-phase LC separation using the mobile phase containing no ligand, followed by electrochemical and spectrophotometric detection.

Electrochemical detection after LC separation as the Co(III)-EX chelate

As described above, 4:1 acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 0.02 mol dm^{-3} KNO_3 was selected as the best mobile phase for the LC separation of the Co(III)-EX chelate from the others. In the analysis of real samples, a C_{18} column (Tosoh ODS 80TM, 4.6 x 150 mm) was recommended in order to shorten the analytical time. Fig.2 shows a chromatogram obtained for a mixture of 0.1 μg cm^{-3} Cu(II), Ni(II), Bi(III), Pb(II), Cd(II), Hg(II) and Co(II) by the

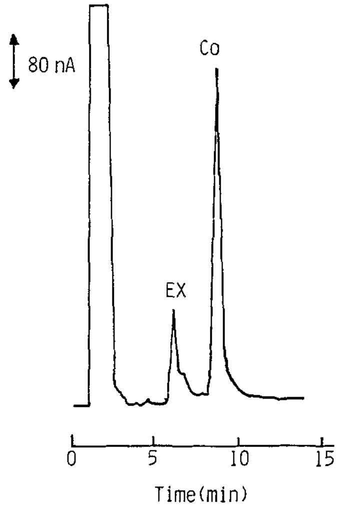

Fig.2 A chromatogram for the Co(III)-EX chelate by reversed-phase LC with electrochemical detection (+1.40 V *vs.* Ag/AgCl): the mobile phase was 4:1 acetonitrile/sodium acetate solution (0.02 mol dm^{-3}, pH 7.8) containing 0.02 mol dm^{-3} KNO_3; the metal concentration was 0.1 mg dm^{-3}; the analytical column was a Tosoh ODS 80 TM (4.6 x 150 mm).

reversed-phase LC with electrochemical detection +1.40 V *vs.* Ag/AgCl. Only Co(II) and excess ligand showed chromatographic responses at 9.3 and 6.5 min, respectively. Therefore, the proposed LC method is free from interferences due to the other metals. The differential-pulse voltammogram for the ligand EX in 9:1 acetonitrile/0.02 mol dm^{-3} sodium acetate solution was recorded in a conventional cell. The oxidation of EX to form thiuram disulfide was observed at +0.35 V *vs.* Ag/AgCl, above which potentials no further response of the ligand was seen. On the addition of Co(II) to the ligand solution, as shown in Fig.3, an oxidative response from Co(III) to Co(IV) appeared at +1.34 V *vs.* Ag/AgCl under the experimental conditions: scan rate 5 mV s^{-1}, modulation amplitude 50 mV, duration time between pulses 1s. The peak current for the Co(III) response increased with applied potentials commencing +1.30 V *vs.* Ag/AgCl. An applied potential of +1.40 V was chosen for the determination of Co(II) by the reversed-phase LC with electrochemical detection.

Calibration graphs and detection limits

According to the above procedure, the precolumn derivatization and sample injection of 100 mm^3 were made, followed by chromatographic elution. When the eluate was detected electrochemically at +1.40 V, the calibration graph of peak current *vs.* Co(II) concentration was linear in the range of

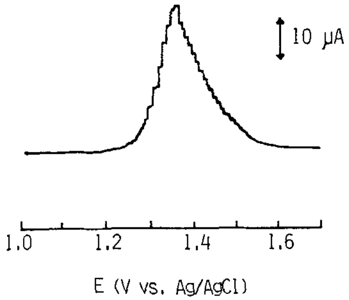

Fig.3 A differential-pulse voltammogram for the Co(III)-EX chelate in 9:1 acetonitrile/aqueous solution containing 0.05 mol dm^{-3} EX, 0.02 mol dm^{-3} sodium acetate and 0.02 mol dm^{-3} KNO_3; scan rate: 5 mV s^{-1}; modulation amplitude: 50 mV; pulse interval: 1 s; the metal concentration: 50 mg dm^{-3}.

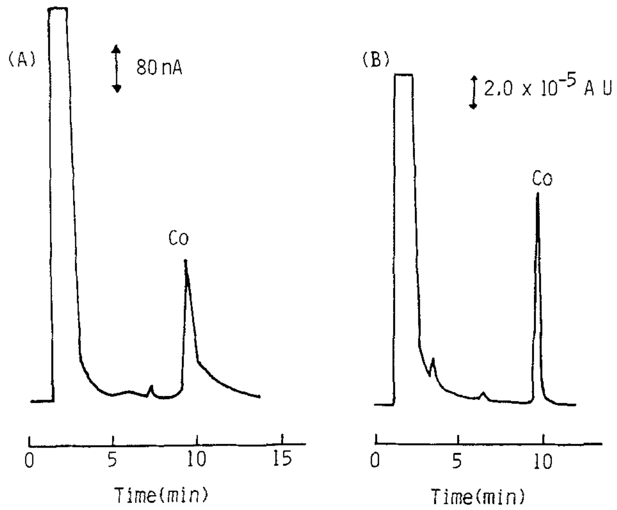

Fig.4 Determination of cobalt in pepperbush by the reversed-phase LC with electrochemical (A) and spectrophotometric detection (B); the experimental conditions are described in Fig.2 and the procedure of the experimental section.

0.5~200 μg dm^{-3}. The straight line can be expressed by the equation Y (peak current, nA) = 4.76 x 10^3 X(concentration, mg dm^{-3}) + 3.9, and the correlation coefficient (γ) was 0.9992. The detection limit was 0.23 μg dm^{-3} Co(II) at a signal-to-noise (S/N) ratio of 3.

When the spectrophotometric detection was made at 330 nm, the calibration graph was a straight line of Y (peak height, absorbance unit) = 3.06 x 10^{-3} X (concentration, mg dm^{-3}) + 4.16 x 10^{-6}, γ = 0.9994 in the concentration range of 1.0 ~ 200 μg dm^{-3}. The detection limit was 0.56 μg dm^{-3} at S/N = 3 (0.002 absorbance unit full scale).

Determination of cobalt in pepperbush

Pepperbush sample (NIES No.1) was analyzed by the proposed LC method. The chromatogram are shown in Fig.4 (A) and (B). Before injection, a 2.0-cm^3 aliquot of the sample solution (3.79 mg cm^{-3}) was mixed with the equal volume of 10^{-3} mol dm^{-3} EX in acetonitrile. The analytical results (n=5) obtained by the electrochemical and spectrophotometric detection were 22.8 ± 0.9 and 22.6 ± 0.5 μg g^{-1} respectively, which both coincided well with the certified value 23 ± 3 μg g^{-1}. The proposed method is very sensitive and free from interferences, and in addition it would be able to determine traces levels of cobalt in environmental and biological samples.

CONCLUSIONS

The results presented here indicate that the use of EX as a derivatization reagent is of analytical utility for the electrochemical and spectrophotometric detection after LC separation of metal species. The chromatographic system permits the oxidative detection of the Co(III) chelate to be discriminated against excess ligand in the mobile phase. As the result, the S/N ratio can be improved to obtain lowered detection limits. As seen from the successful application, we have also expected that the other real samples containing cobalt can be analyzed with good precision and accuracy.

REFERENCES

(1) A. R. Timerbaev, O. M. Petrukhin, Y. A. Zolotov, Fresenius' Z. Anal. Chem., 327, 87(1987).

(2) A. M. Bond, G. G. Wallace, Anal. Chem., 55, 718(1983).

(3) J. D. Willet, M. M. Knight, J. Chromatogr., 237, 99(1982).

(4) Y. Nagaosa, H. Kawabe, A. M. Bond, Anal. Chem., 63, 28(1991).

(5) D. A. Roston, Anal. Chem., 56, 241(1984).

(6) S. J. Tsai, Y. Lee, Analyst, 116, 615(1991).

(7) A. M. Bond, G. G. Wallace, J. Liq. Chromatogr., 6, 1799(1983).

(8) A. M. Bond, T. P. Majewski, Anal. Chem., 61, 1494(1989).

(9) H. Eggers, H. A. Russel, Chromatographia, 17, 486(1983).

Received: January 12, 1995
Accepted: April 12, 1995