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Short communication

Ion-pair reversed-phase high-performance liquid chromatographic separation and determination of ruthenium, rhodium, cobalt and copper as chelates with 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid

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Abstract

Ruthenium(III), rhodium(III), cobalt(II) and copper(II) as chelates with 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid (PAN-6S) were separated by ion-pair reversed-phase high-performance liquid chromatography and detected spectrophotometrically at 580 nm. The optimum conditions for the separation and determination of the Ru(III)–, Rh(III)–, Co(II)– and Cu(II)–PAN-6S chelates were investigated. The chelates were separated on a Nucleosil C_{18} column (250×4.6 mm I.D.) using acetonitrile–water (30:70, v/v) containing 0.01 *M* acetic acid–sodium acetate buffer (pH 5.0) and 0.01 *M* tetrabutylammonium bromide (TBABr) as a mobile phase at a flow-rate of 1.0 ml min^{-1}. The detection limits were 2.6 ng for Ru, 1 ng for Rh and 0.3 ng for both Co and Cu. © 1997 Elsevier Science B.V.

Keywords: Derivatization, LC; Metal chelates; Pyridylazo naphtholsulfonic acid

1. Introduction

The separation of inorganic cations as their chelates with organic chromophoric agents by high-performance liquid chromatography (HPLC) and quantitative detection at visible wavelengths have grown rapidly in recent years. A number of reviews and many papers on this subject have been published [1–4]

The separation and quantitative analysis of precious metals have long been an active field in analytical science. A review on the separation and quantitation of precious metal ions as chelates with organic chromophoric agents, including pyridylazo, thiazolylazo, 8-hydroxquinoline, thiocarbamate and β-diketone, by HPLC, has been published [5].

1-(2-Pyridylazo)-2-naphthol (PAN), used for HPLC separation of precious metal ions, forms water-insoluble metal chelates and when used as a precolumn derivatizing reagent, the metal chelates precipitate as colloidal particles. Thus, the chelates are usually extracted into an organic solvent, such as chloroform, prior to the chromatographic separation. The organic extract can be directly injected onto the separating column when using normal-phase HPLC [6–8]. For reversed-phase HPLC, the organic extract is usually evaporated to dryness and then redissolved in the mobile phase prior to injection [9]. Both techniques lengthen the analysis time and increase the possibility of contamination. A water-soluble analogue of PAN, 4-hydroxy-3-(2-pyridylazo) naphthalene-1-sulfonic acid, has been used for the reversed-phase ion-pair partition chromatography of iron, cobalt and nickel chelates, by direct injection of aqueous sample solution [10].

The purpose of this work is to examine the use of

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1-(2-pyridylazo)-2-naphthol-6-sulfonic acid (PAN-6S) as a precolumn derivatizing reagent for the ion-pair reversed-phase HPLC separation of precious metal ions. The sulfonic groups present in PAN-6S cause its metal chelates to be soluble in water. The solubility and anionic properties of PAN-6S chelates make them ideally suited for ion-pair reversed-phase HPLC. Because the metal chelates are water-soluble, they do not need to be extracted into an organic solvent prior to injection. Since the metal chelates are negatively charged, the resolution of the metal chelates can be controlled by ion pairs being added to the mobile phase. The use of PAN-6S as a precolumn derivatizing reagent provides the basis for the ion-pair reversed-phase HPLC determination of Ru(III), Rh(III), Co(II) and Cu(II) by direct injection of aqueous samples.

2. Experimental

2.1. Apparatus

All experiments were carried out on a Shimadzu Model LC-4A HPLC instrument equipped with a SPD-1 spectrophotometric detector and a Chromatopac C-R2A data processor. A 250×4.6 mm I.D. stainless steel column packed with 5 μm Nucleosil C_{18} was used as the analytical column. A Shimadzu UV-240 recording spectrophotometer was used for spectral measurements. A Shanghai Model pH S-2 pH meter was used to measure the pH values of buffer solutions.

2.2. Reagents and solutions

PAN-6S was synthesized as described in reference [11]. A $1 \cdot 10^{-3}$ *M* aqueous solution was prepared.

All chemicals were of analytical grade purity. All stock solutions of precious metal ions (1.0 mg ml^{-1}) were made with 1 *M* hydrochloric acid. All working solution of the metal ions were prepared by appropriate dilution with water.

The mobile phase was acetonitrile–water (30:70, v/v) containing 0.01 *M* acetic acid–sodium acetate buffer (pH 5.0) and 0.01 *M* tetrabutylammonium bromide (TBABr).

2.3. Procedure

To a 25-ml volumetric flask, 1–8 ml of a 10-μg ml^{-1} metal ion solution, 4 ml of a $1 \cdot 10^{-3}$ *M* PAN-6S solution and 5 ml of a 0.01-*M* acetic acid–sodium acetate buffer solution (pH 5.0) were added. The mixture was heated in a boiling water-bath for 90 min. After cooling, the prepared solution of chelates was diluted to the mark with water. The sample solution was filtered through a 0.3-μm membrane (mixed cellulose). A 20-μl aliquot of the filtered solution was injected onto the column. The PAN-6S chelates of metal ions were eluted with the acetonitrile–water mobile phase at a flow-rate of 1.0 ml min^{-1} and detected at 580 nm. The calibration curves were constructed by plotting the peak heights against known concentrations of the individual ions.

3. Results and discussion

3.1. Precolumn derivatization and detection wavelength of the chelates

In a solution, pH 4.5–5.5, buffered with acetic acid–sodium acetate, Co(II) and Cu(II) react with PAN-6S to form water-soluble purple–red chelates at ambient temperature and exhibit absorption maxima at 580 nm for Co(II)–PAN-6S and 560 nm for Cu(II)–PAN-6S. The mixed solution of Ru(III) [or Rh(III)], PAN-6S and acetic acid–sodium acetate buffer in the same pH range has to be heated in a boiling water-bath for at least 80 min to accelerate complex formation and to make the reactions more complete. Both chelates of Ru(III)– and Rh(III)–PAN-6S were water soluble and have absorption maxima at 580 nm. The detection wavelength was set at 580 nm because the absorption maxima consistent with those measured by stop-pump and wavelength scanning methods at respective retention time of the chelates.

The experiments indicated that the Co(II)– and Cu(II)–PAN-6S chelates were stable at boiling water temperature and the chelates formed under the above-mentioned conditions gave stable peak heights for at least 48 h.

3.2. Effect of the concentration of acetonitrile in the mobile phase

With a chemically bonded stationary phase, a Nucleosil C_{18} column (250×4.6 mm I.D.), the acetonitrile–water binary system was found to be suitable for the separation of Ru(III)–, Rh(III)–, Co(II)– and Cu(lI)–PAN-6S chelates. To optimize further peak shapes, resolution and sensitivities, acetic acid–sodium acetate buffer (pH 5.0) and TBABr were added to a simple acetonitrile–water binary system. The effect of the concentration of acetonitrile in the mobile phase on the retention time of the chelates is shown in Fig. 1. The optimum results were obtained with acetonitrile–water (30:70, v/v).

3.3. Effect of the concentration of TBABr in the mobile phase

The concentration of TBABr in the mobile phase was changed from 0.005 to 0.015 *M*. As can be seen in Fig. 2, the retention of each chelate increased with increasing TBABr concentration up to 0.01 *M*, but then decreased above 0.012 *M* because the partition of excess TBABr into the stationary phase may interfere with the partition of the chelates. A concentration of 0.01 *M* TBABr in the mobile phase was selected.

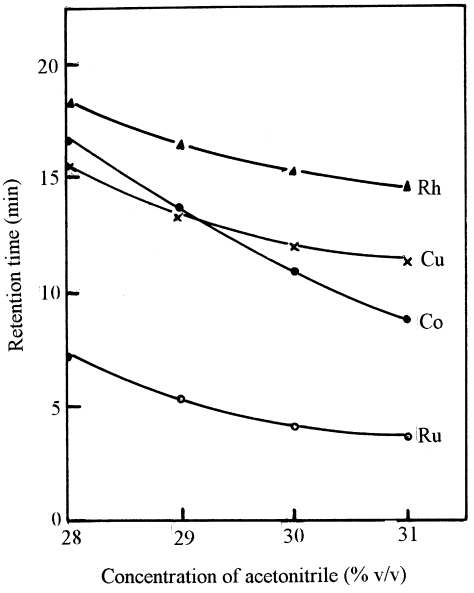

Fig. 1. Effect of the concentration of acetonitrile in the mobile phase on the retention times of the chelates of Ru(III)–, Rh(III)–, Co(III)– and Cu(II)–PAN-6S. Mobile phase, 0.01 *M* acetic acid–sodium acetate (pH 5.0) and 0.01 *M* TBABr; flow-rate, 1.0 ml min^{-1}; column, Nucleosil C_{18} (250×4.6 mm I.D.)

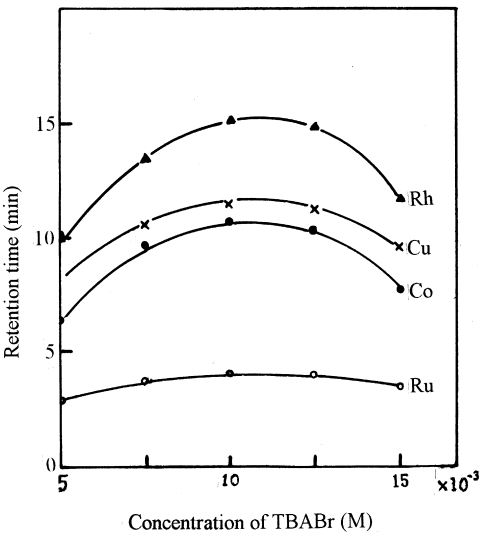

Fig. 2. Effect of the concentration of TBABr in the mobile phase on the retention times of the chelates of Ru(III)–, Rh(III)–, Co(II)– and Cu(II)–PAN-6S. Mobile phase, acetonitrile–water (30:70, v/v) containing 0.01 *M* acetic acid–sodium acetate buffer (pH 5.0). Other conditions as in Fig. 1.

3.4. Effect of the pH of buffer added to the mobile phase

To examine the optimum pH range of the mobile phase, acetic acid–sodium acetate buffer solutions (0.01 *M*) in the pH range 4.0–6.0 were used. At pH values higher than 4.6, the peak heights were constant for all species, but the retention decreased with increasing pH. It is believed that these variations are from interaction of the polar metal chelates with residual silanol groups on the C_{18} packing. The addition of acetic acid–sodium acetate buffer effectively blocks the effect of the residual silanols and led to the formation of well-defined peak shapes, and to high and reproducible chelate peak heights. An acetic acid–sodium acetate buffer solution of pH 5.0 was selected for use in the mobile phase.

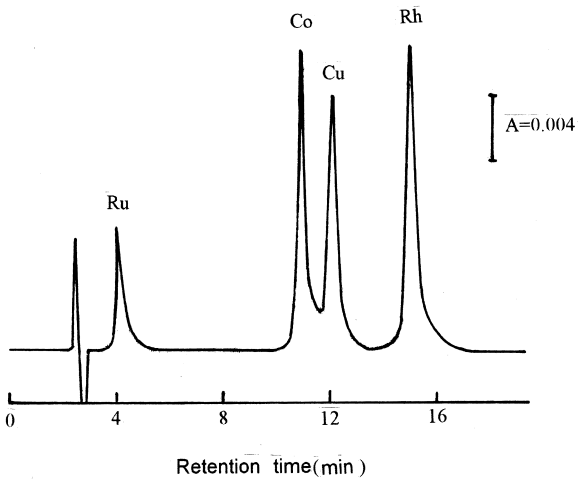

Fig. 3. Chromatogram of Ru(III)–, Rh(III)–, Co(II)– and Cu(II)–PAN-6S chelates. Mobile phase, acetonitrile–water (30:70, v/v) containing 0.01 *M* each of acetic acid–sodium acetate buffer (pH 5.0) and TBABr: Detection wavelength, 580 nm. Sample solution, 2 μg ml^{-1} each of Ru and Rh, 0.5 μg ml^{-1} each of Co and Cu; $1.6 \cdot 10^{-4}$ *M* PAN-6S. Other conditions as in Fig. 1.

3.5. Calibration curves and detection limits

A typical chromatogram for the separation of the chelates of Ru(III), Rh(III), Co(II) and Cu(II) is shown in Fig. 3. The slopes and intercepts of calibration curves for the simultaneous determination of ruthenium, rhodium, cobalt and copper, calculated by linear regression analysis of the peak heights versus metal ion concentration (μg ml^{-1}), are given in Table 1. The calibration curves were linear for 0.4–8.0 μg ml^{-1} ruthenium, 0.2–9.0 μg ml^{-1} rhodium, 0.1–3.6 μg ml^{-1} cobalt and 0.3–4.8 μg ml^{-1} copper. The detection limits, calculated as the amount injected that gave a signal that was three times the background noise (i.e., signal-to-noise ratio of 3:1), were 2.6 ng for ruthenium, 1 ng for rhodium and 0.3 ng for both cobalt and copper.

3.6. Effect of other metal ions

The effect of possible interference was studied by adding each metal ion in turn to the sample before precolumn derivatization of Ru(III)–, Rh(III)–, Co(II)– and Cu(II)–PAN-6S chelates. The maximum level (in μg) of other metal ions that caused a change of less than ±5% in the peak heights of the PAN-6S chelates in simultaneous determinations of 20 μg each of ruthenium and rhodium and 2 μg each of cobalt and copper was: Pt(II), Os(VIII), Pd(II) and Au(I), 100; Fe(II), Ni(II), Zn(II), Cd(II), Hg(II), Pb(II) and Mn(II), 10. Although these metal ions react with PAN-6S to form red chelates, which have absorption maxima at around 580 nm, they are unstable in the chromatographic system.

3.7. Application

An anode mud sample from the copper smelter was dissolved in concentrated HCl–HNO_3 (2:1, v/v) and evaporated to near dryness. The process was repeated twice. A 1-ml volume of 1 *M* HCl, a small amount of water and two drops of concentrated H_2SO_4 [to precipitate Pb(II)] were added, and the mixture was heated to dissolve all soluble salts. The solution was adjusted to a slightly acidic value with dilute NaOH, then filtered into a 100-ml volumetric flask and diluted to the mark with water. An aliquot of the last sample solution was taken and a given amount of Ru(III), Rh(III), Co(II) and Cu(II) were added. The PAN-6S chelates of the metal ions were formed and detected as described above. The results are given in Table 2.

Table 1
Coefficients of linear regression analysis for calibration of the chromatographic detector

Parameter	Metal ion			
	Ru(III)	Rh(III)	Co(II)	Cu(II)
Concentration (μg ml^{-1})	0.4–8.0	0.2–9.0	0.1–3.6	0.3–4.8
Amount injected (ng)	8–160	4–180	2–72	3–96
Slope (*A* ml μg^{-1})	0.00350	0.00912	0.0351	0.0315
Intercept (*A*)	0.00081	−0.00054	0.00048	−0.00075
Correlation coefficient	0.993	1.00	0.999	1.00

Table 2
Recovery results for Ru, Rh, Co and Cu in anode mud

Added (μg)				Found[a] (μg)			
Ru	Rh	Co	Cu	Ru	Rh	Co	Cu
20.0	20.0	10.0	10.0	19.2	19.5	10.6	9.8

[a] Average of three parallel determinations.

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