CHROM. 16,752

REVERSED-PHASE ION-PAIR PARTITION CHROMATOGRAPHY OF IRON, COBALT AND NICKEL CHELATES WITH 4-HYDROXY-3-(2-PYRIDYLAZO)NAPHTHALENE-1-SULPHONIC ACID

HIROKO WADA*, SHINJI NEZU, TADAO OZAWA and GENKICHI NAKAGAWA

Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya (Japan)

(Received March 14th, 1984)

SUMMARY

The reversed-phase ion-pair partition chromatography of 4-hydroxy-3-(2-pyridylazo)naphthalene-1-sulphonic acid (α-PAN-4S) and its metal chelates was studied. Cobalt(III), iron(II) and nickel(II) chelates and excess of α-PAN-4S were separated on the column and eluted with acetonitrile–water (37–40:60–63, v/v) containing 0.025 M tetrabutylammonium bromide, 0.005 M 3-(N-morpholino)propanesulphonic acid–sodium hydroxide buffer (pH 7) and 10^{-4} M Na_2(EDTA). Cobalt, iron and nickel were simultaneously determined without interferences from other metals. The effects of the eluent composition and pH on the retention of all species were examined. The method was applied to the determination of cobalt, iron and nickel in a glass sample.

INTRODUCTION

In previous work[1] the reversed-phase ion-pair partition chromatography of cobalt(III), nickel(II) and copper(II) chelates with a water-soluble reagent, 2-(2-thiazolylazo)-5-(sulphomethylamino)benzoic acid (TAMSMB), was studied, and the possibility of the simultaneous spectrophotometric determination of these metals was found. TAMSMB mainly forms chelates with cobalt(III), nickel(II) and copper(II) in the presence of periodate ion. As these chelates are not very stable, the composition of the eluent, *e.g.*, the concentrations of Na^+ as counter ion, H^+ and TAMSMB, was critical in the separation of the chelates.

4-Hydroxy-3-(2-pyridylazo)naphthalene-1-sulphonic acid (α-PAN-4S) is a water-soluble analogue of 1-(2-pyridylazo)-2-naphthol(PAN) which has been widely used for the spectrophotometric determination of various metals. It reacts with many metal ions such as nickel(II), copper(II), zinc(II), cadmium(II), cobalt-(II), -(III), iron-(II), -(III), manganese(II), mercury(II) and lead(II) to form water-soluble chelates, and these chelates can be extracted into chloroform or 1,2-dichloroethane in the presence of tetraphenylarsonium chloride or tetraphenylphosphonium chloride[2]. Cobalt(III)–, nickel(II)– and iron(II)–α-PAN-4S chelates extracted as the ion-pair

complexes are not decomposed by shaking the organic phase with EDTA solution. Therefore, α-PAN-4S was applied to the simultaneous spectrophotometric determination of cobalt, nickel and iron by reversed-phase ion-pair partition chromatography, and to the analysis of a glass sample.

EXPERIMENTAL

Apparatus

A JASCO UVIDEC-100WB detector (Japan Spectroscopic Co., Tokyo), wavelength 550 nm and cell volume 8 μl, a Kyowa Seimitsu KHU-16 reciprocal pump (Kyowa Seimitsu Co., Tokyo), a Kusano Kagaku C.I.G. prepacked glass column CPO-042, 200 mm × 4.0 mm I.D., with silica-ODS (particle diameter 10 μm) and a double four-way valve injector (Kyowa Seimitsu), sample volume 114 μl, were employed.

Chemicals and reagents

α-PAN-4S was synthesized as described previously[3]. A 5×10^{-3} M aqueous solution was prepared.

Standard cobalt(II) and nickel(II) solutions were prepared from the analytical reagent-grade nitrates. A standard iron(III) solution was prepared by dissolving analytical reagent-grade iron(III) ammonium sulphate in 1 M nitric acid. The concentrations of the colbalt(II), nickel(II) and iron(III) solutions were determined by EDTA titrations with xylenol orange–1,10-phenanthroline, TAMSMB[4] and Variamine Blue-B as indicators, respectively. The metal ion stock solutions were diluted as required.

The buffer comprised 3-(N-morpholino)propanesulphonic acid (MOPS)–sodium hydroxide solution (0.1 M, pH 7.0–7.1). Tetra-*n*-butylammonium bromide (TBABr), potassium periodate and acetonitrile were of reagent grade and used as received. Water was redistilled from a hard glass vessel.

Preparation of metal chelate solution

In a 25-ml volumetric flask, 0.1–4.5 ml of 4×10^{-4} M metal ion solution were taken, and 5 ml of 5×10^{-3} M α-PAN-4S solution, 5 ml of 0.1 M MOPS buffer and 1 ml of 0.4% (w/v) potassium periodate solution were added. The solution was diluted to the mark in water.

Procedure

The sample solution (114 μl) was placed on the column via the injection valve and the eluent [acetonitrile–water (37–40:60–63, v/v)] containing 0.025 M TBABr, 0.005 M MOPS buffer (pH 7) and 10^{-4} M Na$_2$ (EDTA) was pumped at a flow-rate of 0.73 ml min^{-1}. The elution of the excess of α-PAN-4S and the metal chelates was monitored at 550 nm. The amount of metal was determined from the peak height.

RESULTS AND DISCUSSION

Detection wavelength

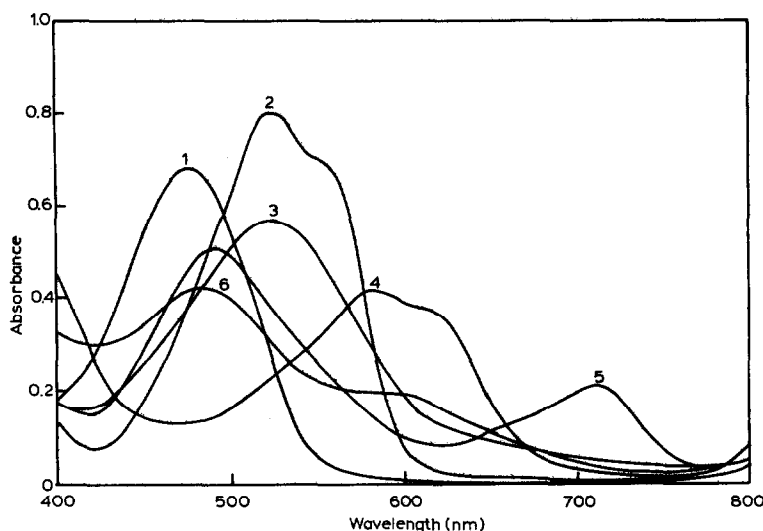Absorption spectra of iron(II), iron(III), cobalt(II), cobalt(III) and nickel(II)

Fig. 1. Absorption spectra of α-PAN-4S and the chelates. Concentrations: α-PAN-4S, 3×10^{-5} M; metal, 8×10^{-4} M. Curves: 1, α-PAN-4S; 2, nickel(II) chelate; 3, cobalt(II) chelate; 4, cobalt(III) chelate; 5, iron(II) chelate; 6, iron(III) chelate.

chelates with α-PAN-4S are shown in Fig. 1. The molar absorptivities of these chelates are high but that of α-PAN-4S is low at 550 nm, thus the absorbances were measured at 550 nm.

Metal chelates eluted

In order to examine the elution of the metal chelates, three solutions were prepared: I, as described in Experimental; II, as solution I but with ascorbic acid in place of potassium periodate; III, containing only iron(III)–α-PAN-4S chelate in chloroacetate buffer at pH 2.5. As shown in Fig. 2, when solution I was injected, good separation of cobalt(III), iron and nickel chelates was obtained. When solution II was injected, the peaks of cobalt(II) and nickel chelates overlapped, while the retention of iron chelate was the same as that in the case of solution I (Fig. 3). Therefore, when solution I was injected, cobalt(III) chelate was eluted, but the cobalt(II) chelate with solution II. When solution III was injected the retention of iron chelate was the same as those with solutions I and II. Although the absorption spectrum of solution III indicated the formation of iron(III) chelate, the eluted solution of iron chelate absorbed at 710 nm (see Fig. 1). This showed that the iron(III) chelate was reduced to iron(II) chelate on the column. On the other hand, the iron(II)–α-PAN-4S chelate once formed at pH 7 was not oxidized to iron(III) chelate even by the addition of potassium periodate.

Eluent composition and pH

The chelates on the column may be adsorbed to the stationary phase as the ion pairs $Co(III)L_2^- \cdot R^+$, $Ni(II)L_2^{2-} \cdot 2R^+$ and $Fe(II)L_2^{2-} \cdot 2R^+$, where L^{2-} and R^+ represent the completely deprotonated form of α-PAN-4S and the counter ion, respectively. Water–methanol or water–acetonitrile mixtures as the solvent, and Na^+,

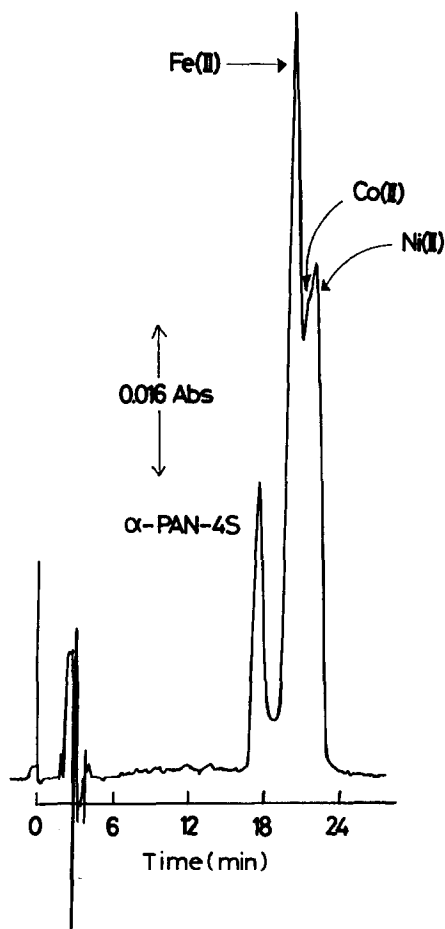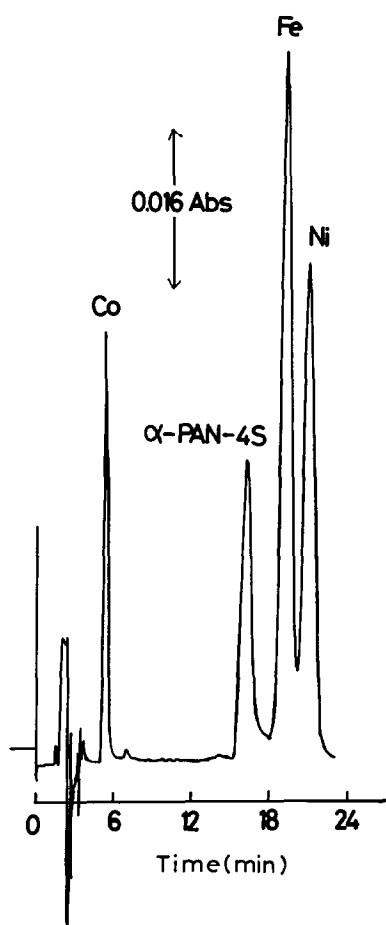Fig. 2. Chromatogram of α-PAN-4S and the chelates. Column: 200 mm × 4 mm I.D. silica-ODS (10 μm). Eluent: acetonitrile–water (40:60, v/v) containing 0.025 M TBABr, 0.005 M MOPS buffer (pH 7) and 10^{-4} M EDTA. Flow-rate: 0.73 ml min^{-1}. Amount of metal injected: Co, 32 ng; Ni, 57 ng; Fe, 215 ng.

Fig. 3. Chromatogram of iron(II), nickel(II) and cobalt(II) chelates. See Fig. 2 for conditions.

tetra-*n*-butylammonium ion(TBA$^+$) or tetraphenylarsonium ion (TPhA$^+$) as the counter ion, were examined. With water–acetonitrile and TBA$^+$ a better separation of all species and higher absorbances of each chelate were obtained than with water–methanol as eluent.

The effect of the content of acetonitrile in the eluent on the retention of each species is shown in Fig. 4. The capacity factor, k', was plotted against the acetonitrile content. An acetonitrile content of 37–40% (v/v) was best for both separation and retention.

The concentration of TBABr in the eluent was changed from 0.002 to 0.077 M. As can be seen in Fig. 5 the retention of each chelate increased with increasing TBABr concentration up to 0.04 M, but then decreased above 0.05 M because the
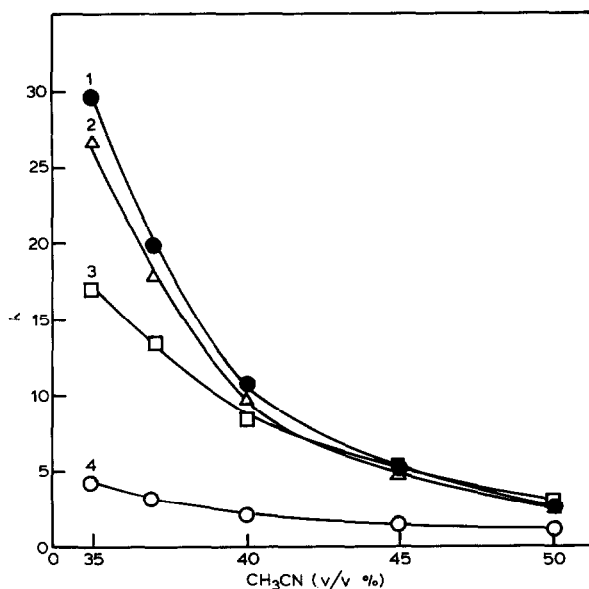
Fig. 4. Effect of acetonitrile concentration on the retention of α-PAN-4S and the chelates. Eluent: acetonitrile–water (40:60, v/v) containing 0.025 M TBABr, 0.005 M MOPS buffer (pH 7) and 10^{-4} M EDTA. Curves: 1, Ni; 2, Fe; 3, α-PAN-4S; 4, Co.

partition of excess of TBABr into the stationary phase may interfere with the partition of the chelates. When tetrapropylammonium bromide (TPABr) was used, the capacity factors of all species were smaller than those with TBABr: 1.13 for cobalt, 2.03 for iron, 2.21 for nickel and 3.70 for α-PAN-4S with 0.05 M TPABr. The retention of α-PAN-4S was larger than those of the nickel and iron chelates, in contrast to TBABr.

When TBAClO₄ was used in place of TBABr the capacity factors decreased, as can be seen in Table I. The order of elution of α-PAN-4S was reversed. The reason for the smaller capacity factors compared with those with TBABr may be due to the greater partition of TBAClO₄ into the stationary phase, but it is not yet clear that the retention of α-PAN-4S is larger than those of the nickel and iron chelates.

The effect of Na⁺ on the retention of each species was examined by adding sodium chloride to the eluent. As shown in Fig. 6 the retention of all the species decreased with increasing sodium ion concentration. Sodium ion may compete with TBA⁺ in forming the ion pair with α-PAN-4S and its chelates, and the ion pair with Na⁺ may be less hydrophobic. Therefore, a low concentration of Na⁺ in eluent was preferred.

To examine the optimum pH range of the eluent, three buffers (0.005 M) were used: chloroacetic acid–sodium chloroacetate (pH 2.59, 3.49); acetic acid–sodium acetate (pH 4.32, 5.38) and MOPS–sodium hydroxide (pH 6.08, 7.09). At pH higher than 3.5 the peak areas were constant for all species, but retention decreased with increasing pH. The peak heights were greatest at pH 7.
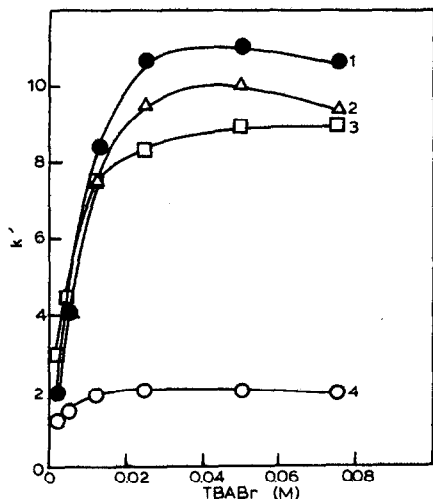
Fig. 5. Effect of TBABr concentration on the retention of α-PAN-4S and the chelates. Eluent: acetonitrile–water (40:60, v/v) containing 0.005 M MOPS buffer, 10^{-4} M EDTA and TBABr. Curves as in Fig. 4.

Calibration curves and detection limits

Calibration curves were linear for 2.4×10^{-6}–1.2×10^{-5} M cobalt, 1.3×10^{-5}–6.8×10^{-5} M iron and 5.0×10^{-6}–2.5×10^{-5} M nickel, when the absorbances were measured with a detector sensitivity of 0.16 absorbance units full scale. At the midpoint of the concentration range on the calibration curves, the coefficients of variation for cobalt, iron and nickel were 2.34, 1.88 and 1.70% from ten determi-
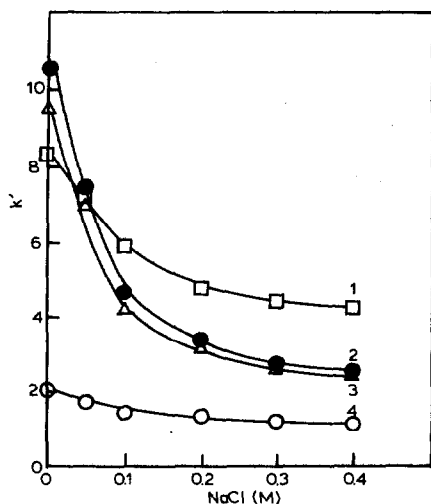

Fig. 6. Effect of NaCl concentration on the retention of α-PAN-4S and the chelates. Eluent: acetonitrile–water (40:60, v/v) containing 0.025 M TBABr, 0.005 M MOPS buffer (pH 7), 10^{-4} M EDTA and NaCl. Curves: 1, α-PAN-4S; 2, Ni; 3, Fe; 4, Co.

TABLE I

INFLUENCE OF Br⁻ AND ClO₄⁻ ON THE CAPACITY FACTOR OF α-PAN-4S AND THE CHE-
LATES

Eluent: acetonitrile–water (37:63, v/v) solution containing 0.005 M MOPS buffer (pH 7), 10^{-4} M EDTA
and 0.025 M tetrabutylammonium salt.

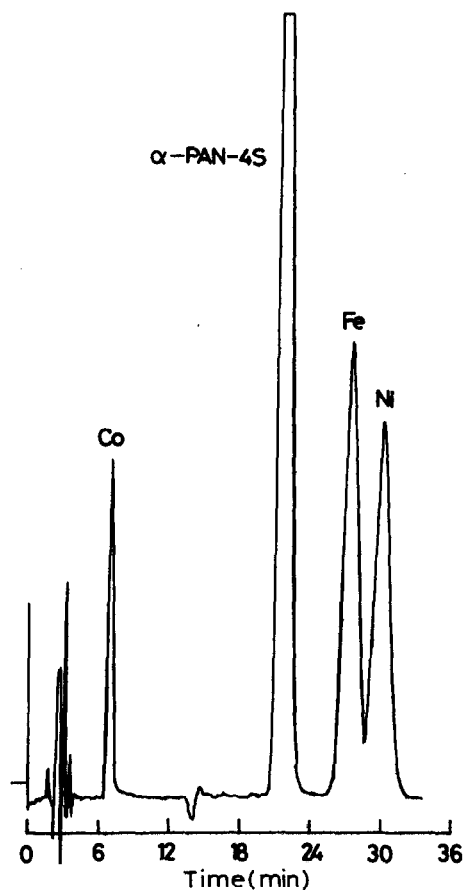| Salt (0.025 M)	Capacity factor, k'			
	Cobalt chelate	Nickel chelate	Iron chelate	α-PAN-4S
TBABr	3.26	19.9	17.9	13.4
TBAClO₄	2.15	6.32	5.78	8.37

Fig. 7. Determination of Co, Fe and Ni in glass. Conditions: as Fig. 2 but acetonitrile–water (37:63 v/v).

TABLE II

DETERMINATION OF Co, Fe AND Ni IN GLASS

Values are percentages. HPLC = High-performance liquid chromatography; AAS = atomic absorption spectrometry; VIS = visible spectrophotometry.

Metal	This method	HPLC with TAMSMB	AAS	VIS	
				TAMSMB	Nitroso-DMAP
Co	0.0093	0.0093	0.0087	0.0095	0.0094
Fe	0.0355	–	0.0356	–	–
Ni	0.0134	0.0140	0.0134	–	–

nations. The detection limits at a signal/noise ratio of 3 were 1 ng for cobalt, 5 ng for iron and 2 ng for nickel (amounts injected).

Effects of other metals

Copper(II)–, zinc(II)–, cadmium(II)–, mercury(II)–, lead(II)– and manganese(II)–α-PAN-4S chelates gave broad absorption bands near the reagent band. In the cases of copper and cadmium chelates, double peaks were obtained. Since these metals interfered with the determinations of nickel and iron, EDTA was added to the eluent. 10^{-4} M EDTA in the eluent could decompose copper(II), zinc (II), cadmium(II), mercury(II), lead(II) and manganese(II) chelates on the column without any decomposition of the colbalt(III), iron(II) and nickel(II) chelates. The retentions and the peak heights of the latter chelates were not changed by addition of EDTA.

Application to the determination of cobalt, iron and nickel in glass

This method was applied to the determination of cobalt, iron and nickel in a glass sample. Finely powdered glass (0.5 g) was weighed into a platinum crucible, and 1 ml of 60% perchloric acid and 5 ml of concentrated hydrofluoric acid were carefully added. After the exothermic reaction had ceased, the crucible was heated gently until the contents became syrupy. The contents were transferred with water to a 50-ml volumetric flask and the solution was diluted to the mark. A 10-ml aliquot of the solution was taken, the sample solution was prepared as described above. In this case, potassium periodate was not added because cobalt was readily oxidized. A 114-μl portion of the sample solution was injected. Cobalt, iron and nickel were determined from the peak heights.

The results are given in Fig. 7 and Table II together with the results obtained by atomic absorption spectrometry and spectrophotometric methods with TAMSMB[5] and 2-nitroso-5-dimethylaminophenol (nitroso-DMAP)[6]. The results for nickel and iron were in good agreement with those obtained by atomic absorption spectrometry. The result for cobalt agreed with those obtained by spectrophotometry with TAMSMB and nitroso-DMAP, but was slightly different from that obtained by atomic absorption spectrometry.

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