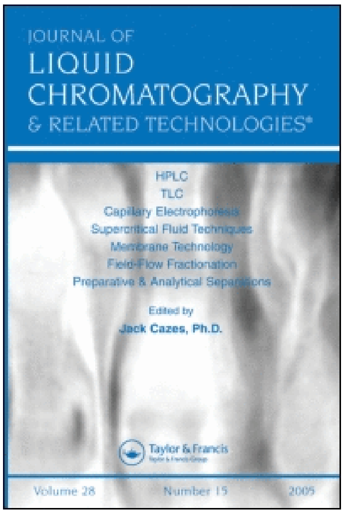

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A Comparative Study of Ion-Exchange and Ion-Pair Reversed-Phase Liquid Chromatography of Metal 4-(2-Pyridylazo)Resorcinol Complexes as Methods of Trace Metal Analysis

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A COMPARATIVE STUDY OF ION-EXCHANGE AND ION-PAIR REVERSED-PHASE LIQUID CHROMATOGRAPHY OF METAL 4-(2-PYRIDYLAZO)RESORCINOL COMPLEXES AS METHODS OF TRACE METAL ANALYSIS*

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ABSTRACT

The behaviour of heavy metals as complexes with 4-(2-pyridylazo)resorcinol in ion-exchange and ion-pair reversed-phase HPLC was investigated. Retention mechanism of metal pyridylazoresorcinolates on columns with a low capacity anion-exchanger and an octadecylsilanized silica gel was discussed in dependence of the mobile phase composition (concentrations of organic modifier, eluent competing ion, ion-pairing reagent, pH). Anion-exchange and adsorption mechanisms

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are realized simultaneously during the ion-exchange chromatographic separation, while the retention behaviour of metal complexes in ion-pair chromatography is best described by the ion-interaction model. The conditions of metal determination using spectrophotometric detection and the procedures of galvanic production waste waters analysis were developed. The analytical possibilities of ion-exchange and ion-pair HPLC in trace metal analysis were compared.

INTRODUCTION

The development of HPLC in heavy and transition metal analysis occurs along several directions, the majority of them being connected with the application of the complex-formation reactions to a greater or lesser degree. They are the following: cation-exchange chromatography with complex-forming eluents and post-column reaction detection of metals as chelates; anion-exchange chromatography of metal cyanide, chloride and other complexes; adsorption chromatography of neutral metal chelates; chromatography on chelating stationary phases ion-exchange (IE) and ion-pair (IP) chromatography of charged metal chelates, etc. Among these the latter two methods, united by the application of spectrophotometric reagents complexes, are of our particular interest.

In this paper we have investigated the chromatographic behaviour of metal complexes (on the example of pyridylazoresorcinolates) and compared the analytical possibilities of IE- and IP-HPLC with spectrophotometric detection for metal separation and determination at trace levels.

MATERIALS AND METHODS

Apparatus and Chromatographic Materials

All chromatography was performed on the models Zvet-306 and Zvet-3003 high performance liquid chromatographs (Dzerzhinsk, Russia) equipped by stainless steel columns (6 mm i.d. x 200 mm) and spectrophotometric detector set at 500 nm. A low capacity resin-based anion-exchanger HIKS-1 (particle diameter 25-40 µm; Estonia) (IE-HPLC) and a Silasorb C_8 (Hemapol, Czechoslovakia) with 10-µm particles (IP-HPLC) were used as a stationary phase. Isocratic elutions were done at a flow rate of 1 ml/min.

Chemicals and Eluents

Metal nitrates were used for the preparation of metal standard solutions (0.01 M). 1-(2-Pyridylazo)resorcinol (PAR) (Reanal, Hungary) was dissolved in deionized water to give a 2.10^{-3} M solution. Metal complexes were formed directly before the chromatographic analysis by adding PAR solution (in 2-3-fold excess) to metal solution (1.10^{-3} M).

The eluents for IE-HPLC were prepared by dissolving Na_2CO_3 in deionized water with the addition of acetone or isopropanol (up to 40 vol.%) and pH 11-13 was adjusted with NaOH. In IP-HPLC the eluents were water-organic mixtures containing up to 20 vol.% of organic modifier (acetonitrile, ethanol or acetone), 4-16 mM tetrabutylammonium hydroxide (TBAOH; Reakhim, Russia) and 0.1 M Na_2CO_3 (pH 11-13). All the chemicals used were of analytical-reagent grade.

Procedure

A 10-ml portion of PAR standard solution was added to 10-ml sample and after 10 min a 10-50-µl aliquot of the mixture was injected into the IE-HPLC or IP-HPLC column. The metal contents were determined from calibration plots of peak height against concentration.

RESULTS AND DISCUSSION

Ion-exchange HPLC

IE-HPLC of metals as chelate complexes with spectrophotometric reagents is refered to a comparatively new chromatographic method. The ion-chromatographic determination of nickel and zinc by on-column formation of the anionic complexes with xylenol orange (1) is one of a few examples. This predetermined our increased interest in the investigation of metal pyridylazoresorcinolates under IE-HPLC conditions.

Optimization of Separation Conditions

The metal complexes as well as the reagent itself, are strongly retained by the surface-modified polymer-based anion exchanger when eluting with aqueous eluents. The strong hydrophobic adsorption on the polysterene-divinylbenzene

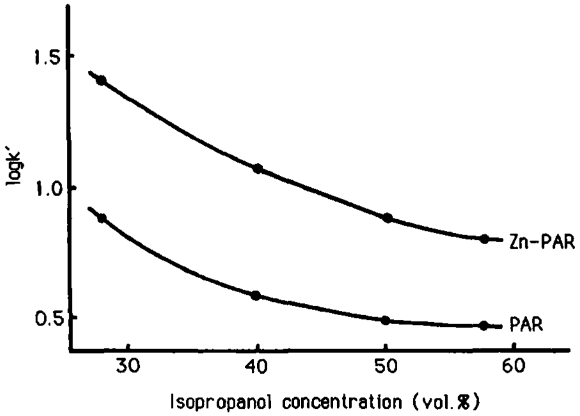

Figure 1. Dependences of the retention times of PAR and Zn-PAR on the concentration of isopropanol. Mobile phase: 0.05 M sodium carbonate - isopropanol, pH 11.8.

resin is the most probable reason. The sorption on the ion-exchanger matrix (polymethyl methacrylate resin Spheron 100000) constitutes negligible retention. This has been demonstrated by the elution of metal complexes on the column filled with Spheron only.

It is necessary to add the organic solvent to a mobile phase to reduce the non-ion-exchange sorption. The dependence of retention time of PAR and Zn-PAR chelate on isopropanol concentration in the eluent is shown in Figure 1. At isopropanol concentration lower than 20 vol.%, the complexes are retained irreversibly. The optimal concentration of organic modifier (acetone, isopropanol) is about 40 vol.%; at greater content the separation becomes worse.

None of the investigated eluents with pH<10 (potassium hydrogen phthalate; sodium hydroxide, hydrocarbonate or carbonate; borate, phthalate or ammonia buffer) elute metal PAR complexes. This result may be explained by the fact that the complexes are in undissociated highly hydrophobic form at such acidity of the mobile phase.

It should be especially emphasized that sufficiently high chromatographic stability of transition metal PAR chelates in strongly basic eluents is provided by their extremely high thermodynamic stability (see below). From this point

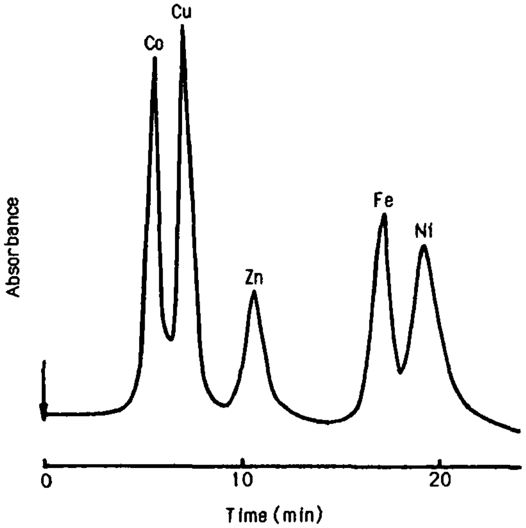

Figure 2. Chromatogram of metal pyridylazoresorcinolates. Mobile phase: 0.05 M Na_2CO_3 - acetone (60:40, v/v), pH 11.8.

of view the chelate preparation method is also very important (2). We use the precolumn complex formation in the presence of excess reagent (the complex-forming conditions indicated in Procedure correspond to a ligand-to-metal ion ratio equal to 5-10).

The best separation was achieved with the use of water-organic solutions of sodium carbonate. A typical chromatogram is presented in Figure 2. Under these conditions PAR, apparently, is eluted as a unicharged ion HR^-. The comparatively small retention time (t_R 6.50 min) and the growth of ionization constants of the reagent during the increase of organic solvent content (3) indicate this.

The retention of the complexes naturally decreases with increase of Na_2CO_3 concentration (Figure 3). The linear character of presented dependences indicates the ion-exchange mechanism of separation (4):

$$2R_n\text{-}M(PAR)_n + nCO_3^{2-} == nR_2\text{-}CO_3 + 2M(PAR)_n^{n-} \qquad (1)$$

However, the slope (-0.4 - -0.7) is less than the theoretical value. According to the equation suggested by Sevenich and Fritz (5):

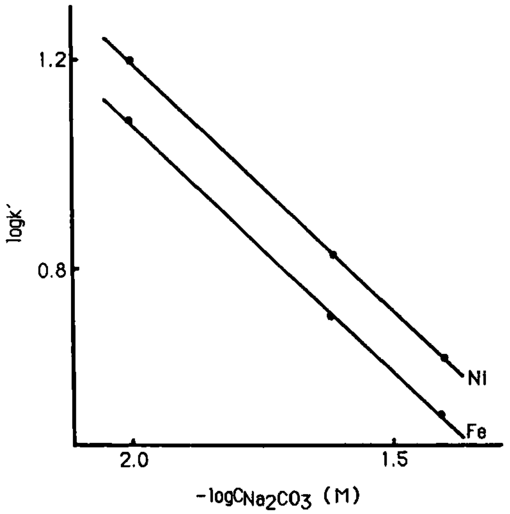

Figure 3. Dependences of the capacity factors of Fe-PAR and Ni-PAR on the concentration of sodium carbonate in the mobile phase. Mobile phase: Na_2CO_3 - isopropanol (60:40, v/v).

$$\log t_R = (n/2)\log(C/2) + \log t_0 - \log[CO_3^{2-}] + (1/2)\log K_m \qquad (2)$$

where n is the charge of complex, C is the exchange capacity of resin, t_0 and t_R are the retention time of unsorbed component and metal complex, respectively, and K_m is the selectivity coefficient of the corresponding complex, the slope must be equal to -1, as the majority of complexes have 1:2 composition (n=2) and the eluent competing ion is double-charged in this pH range. We can attribute the smaller slope values to the partial retention by the hydrophobic mechanism. The pH increase also considerably decreases the retention time of complexes, Na_2CO_3 concentration is less, pH influence is stronger (Figure 4). The optimal conditions are 0.04 M Na_2CO_3 and pH 12.0.

Thus, the metal pyridylazoresorcinolates retention in IE-HPLC occures obviously by both ion-exchange and adsorption mechanisms. This peculiarity of their chromatographic behaviour allows one to regulate the separation selectivity by varying independently eluent competing ion and organic modifier concentration.

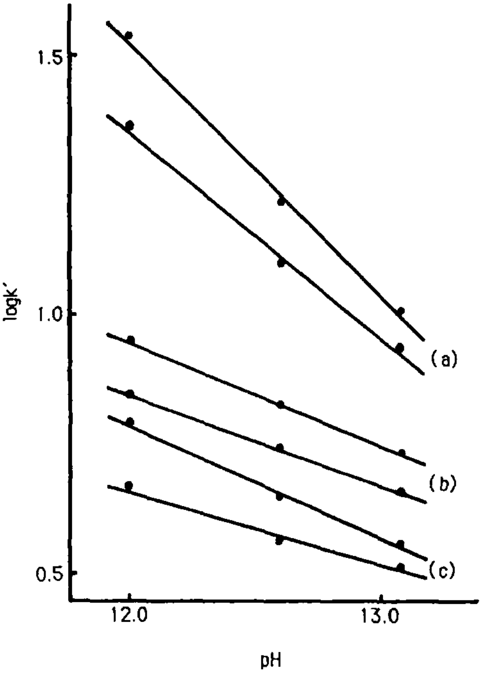

Figure 4. Effect of pH on the retention of Ni-PAR (o) and Fe-PAR (o) at different concentration of sodium carbonate. (a) 0.01 M; (b) 0.025 M; (c) 0.04 M. Mobile phase: Na_2CO_3 - isopropanol (60:40, v/v).

Metal Determination

Calibration graphs of peak height against metal concentration are linear in the range not less than two orders of magnitude under optimal separation conditions. The lower determined concentration varies from 1.10^{-6} M (cobalt) to 2.10^{-5} M (zinc). Detection limits at a signal-to-noise ratio of 3 are from 0.9 to 6.0 ng with a 100-µl injection. The relative standard deviation is 0.9-2.3%. The method is tested by analysing waste waters after galvanic bath washing. The results of analysis are given in Table 1.

TABLE 1

Determination of Transition Metals in Waste Waters

Sample	Metal	Method	Found[a] (mg/l)	R.s.d. (%)	Certified[b] (mg/l)
1	Cu	IE-HPLC	4.10±0.15	3	-
	Ni		0.80±0.04	4	-
2	Cu		0.51±0.03	5	0.5
	Ni		0.37±0.02	5	0.4
	Zn		0.82±0.04	3	0.8
3	Cu	IP-HPLC	0.08±0.005	4	0.07
	Ni		0.04±0.003	5	0.04

[a] Mean and standard deviation from 4 or 5 separate samples.

[b] Photometric method.

Ion-pair HPLC

Metal pyridylazoresorcinolates behaviour in IP-HPLC is studied in more detail (6). However, until now there is no common opinion about the retention mechanism. Available literature data does not allow us to prefer any retention model. This, of course, makes the interpretation of the chromatographic behaviour and the selection of separating conditions of metal complexes difficult.

Optimization of Separation Conditions

To select optimal separation conditions and to elucidate the retention mechanism we successively investigated the influence of mobile phase parameters.

Acidity. For metal pyridylazoresorcinolates separation the neutral mobile phases (pH 6-8) and tetraalkyl ammonium salts (often in bromide form) as an ion-pairing reagent (IPR) have been used in all works without exclusion (6). However, under such conditions some metals form uncharged complexes and practically do not retain (7). Moreover, the ionization constants of complexes

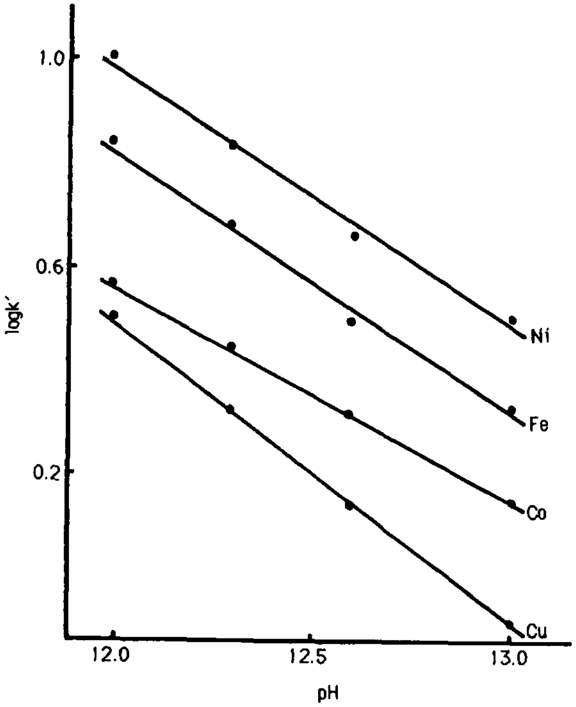

Figure 5. Dependences of the retention parameters of metal pyridylazoresorcinolates on pH of the mobile phase. Mobile phase: ethanol - water (20:80, v/v) containing 4 mM TBAOH.

decrease in the presence of organic solvent in accordance with the increase of its concentration (2). Therefore, we used highly alkali mobile phases (pH 11-13) and TBAOH as IPR to achieve the complete ionization.

As can be seen from Figure 5, the basicity of the mobile phase essentially affects retention times of metal PAR complexes up to pH 13. The character of presented dependences unanimously points to the ion-exchange mechanism of retention under such conditions. If the ion-partition mechanism was to be valid, the dependences of t_R on pH must be opposite, since with pH increase, the ionization degree of both complexes and IPR increases. Consequently, their association and the retention of ion-associate grows. Additionally, similar influence of pH

TABLE 2

Dependence of Metal Pyridylazoresorcinolates Retention Time (min) on Concentration of Sodium Carbonate

Chromatographic conditions: ethanol - water (20:80, v/v), 12 mM TBAOH, pH 12.2

Metal Complex	Concentration (M)	
	0.1	0.5
Co	8.8	6.5
Cu	9.0	7.5
Fe	10.0	7.5
Ni	14.5	9.5

on the retention was observed during ion-exchange separation of metal PAR complexes (cf. Figures 4 and 5).

The influence of sodium carbonate on elution of metal pyridylazoresorcinolates (Table 2) is another indication in favour of the ion-interaction model. As in IE-HPLC, the increase of $C_{Na_2CO_3}$ decreases retention of all complexes because of rise eluent strength. It is interesting to note that when the adsorption mechanism prevails the salt addition into the mobile phase must have the opposite effect. The surface-tension increase accompaning the rise of ionic strength increases retention (salting-out effect) (8).

The best separation of studied metal complexes was observed at pH 12.6 and $C_{Na_2CO_3}$ 0.1 M.

Ion-pairing reagent concentration. The dependences of PAR-complexes retention shown in Figure 6, are typical for IP-HPLC (particularly for the cobalt complex which has a distinct maximum on the curve). The decreasing slope of the discussed dependences, beginning at ca. 12-16 mM TBAOH, testifies to the completion of a dynamically modified layer formation at this concentration of IPR when the composition and properties of a stationary phase cease to change. However, simultaneously the selectivity and speed of separation became worse. Thus 4-8 mM is recommended as an optimal C_{TBAOH}.

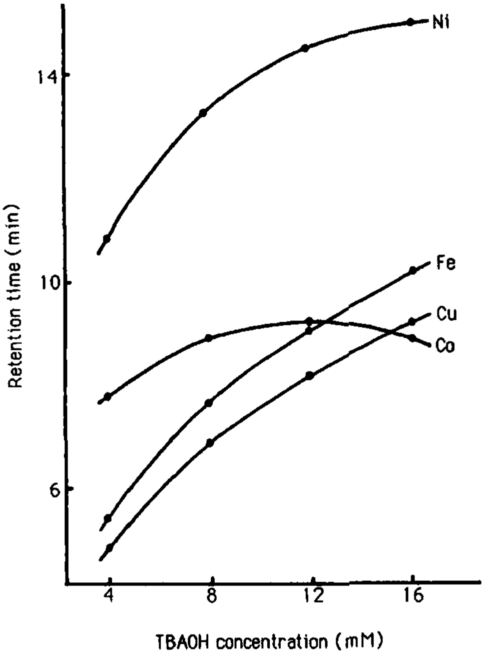

Figure 6. Influence of TBAOH concentration on the retention time of metal PAR complexes. Mobile phase: ethanol - water (20:80, v/v), pH 11.8.

<u>Nature and concentration of organic solvent</u>. Independent of the retention model in systems with dynamic modification of a stationary phase, the following correlation should be accomplished (at constant IPR concentration):

$$\log k' = a - b\log[E] \quad (3)$$

where E is an organic solvent and a,b are the constants. Indeed, with the increase of organic modifier concentration, the retention times gradually decrease. Analysis of the above dependences showed that under the ion-pair mode conditions (as in reversed-phase HPLC) the following equation applies:

$$\log k' = a - bc \quad (4)$$

where c is the volume concentration of organic solvent (Figure 7).

The eluting ability of water-organic mixtures is determined not only by the volume ratio of components, but also by the nature of the organic solvent. For

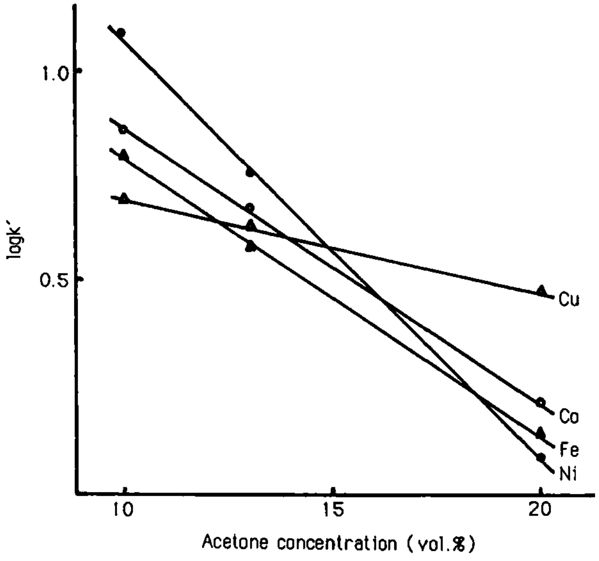

Figure 7. Dependences of the retention of metal PAR complexes on the concentration of acetone in the mobile phase. Mobile phase: 6mM TBAOH, pH 11.8.

its quantitative estimation in HPLC, the following widely used characteristics are applied: Snyder P′ parameter of solvent polarity, hydrophobic parameter P_S, empirical parameters expressing the solvation activity of a solvent (Kamle-Taft, Dimroth-Reichardt, Kosower and Brounstein parameters), eluent macroscopic characteristics (viscosity, dielectric constant, surface tension). For example, a good confirmation of this is presented by Figure 8, which depicts a typical dependence of logk′ on P_S values, described by the equation

$$\log k' = a - b\log P_S \qquad (5)$$

(P_S is the distribution constant of a solvent between n-octanol and water). It should be noted that the elution order of metal complexes changes, both in organic solvent nature change and in its concentration (see Figures 7 and 8). We shall show below that it is connected with the retention mechanism conversation.

The best separation efficiency of metal PAR complexes is observed for water-acetonitrile mixtures (as the least viscous). At 20 vol.% content of organic component the number of theoretical plates reaches 18000 per meter.

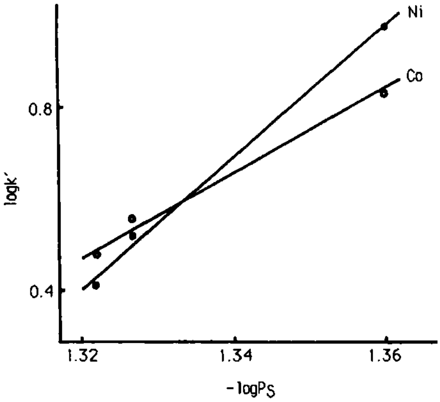

Figure 8. Effect of the mobile phase hydrophobicity on logk' values of Co-PAR and Ni-PAR. Mobile phase: organic solvent - water (20:80, v/v) containing 4 mM TBAOH, pH 12.0.

Metal atom nature

Model design, describing the metal atom influence on chelates retention in IP-HPLC, is not a simple task because of the varying nature of the separation mechanism. The latter is expressed by changes in the elution sequence of the complexes. Depending on eluent conditions, this can result in practically complete conversion of retention (Figure 9).

During sorption by the ion-exchange mechanism, and in case of the same metal complex charge, the influence of metal atom on the oxygen atom basicity of free ligand hydroxyl group (i.e. on the pK_{p-OH} value) should be taken into account first of all. This influence is determined by the metal atom electron-acceptor effect connected with the electron density distribution in the chelate ring and in the complex as a whole. Therefore, the higher the effective charge of metal atom, the less the basicity of oxygen atom and the stronger the retention of complex. One can approximately estimate the effective metal charge by the atomic electronegativity values, which diminish in the order Cu (2.1) - Co (2.0) - Fe (1.95) - Ni (1.9) for metal pyridylazoresorcinolates presented on Figure 9a. That is how the elution sequence of these complexes for water-ethanol eluents looks. The elution order of metal PAR complexes obtained in (9,10) using water-methanol mobile phases, are analogous.

There are many reasons to believe that the dependence of retention values on metal atom properties of pyridylazoresorcinolates in IE-HPLC should be similar.

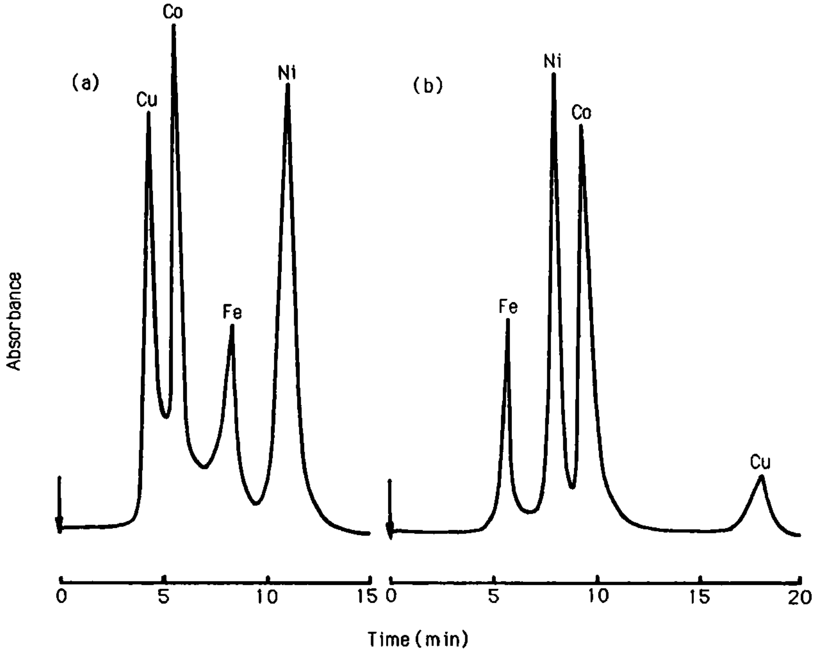

Figure 9. Influence of the organic modifier nature on the retention mechanism of metal PAR complexes. (a) ethanol; (b) acetone. Mobile phase: organic solvent - water (20:80, v/v) containing 8 mM TBAOH, pH 11.8.

However, because of the considerable contribution of non-ion-exchange sorption, the elution sequence is disturbed (see Figure 2).

The elution order of the complexes must be reverse if the adsorption mechanism dominant. The behaviour of ion-associates of anionic chelates in RP-HPLC are well described in terms of modern theory of liquid adsorpton chromatography of neutral metal chelates (11). According to this theory, the specific interactions of ligand electronegative atoms with polar components of a mobile phase are determined by the differences in distribution of these compouds between water-organic eluents and non-polar alkylmodified sorbents. The energy of these interactions is proportional to the metal atom effective charge. Therefore, the ion-associates of more electronegative metals should have greater retention. An elution sequence close to theoretical is observed in water-acetonitrile mobile phases (see Figure 9b).

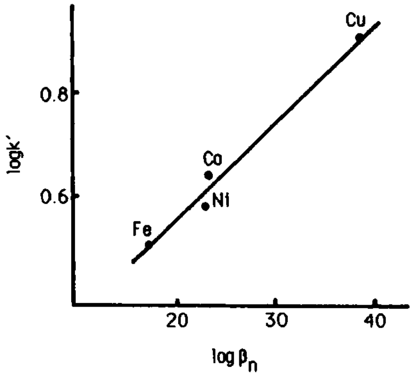

Figure 10. A plot of logk' vs. logβ_n values for metal PAR complexes.

Hence, the influence of the organic solvent on the retention mechanism of metal pyridylazoresorcinolates becomes clear. IPR sorption is reduced, owing to the growth of organic solvent concentration or by its replacement with a solvent of greater eluting ability. As a result, the association of metal complex and ion-pairing cation shifts from the stationary phase into mobile phase. Thus, for example, at 10 vol.% acetone concentration in the mobile phase, the ion-exchange sorption is advantageous (see Figure 7), while at 20 vol.% concentration the adsorption mechanism is dominating. In the intermediate concentration range the contributions of both mechanisms are comparable.

The other structure-dependent parameter of the metal complex is the stability constant, β_n. One can show that under definite experimental conditions the correlation between retention parameters and β_n values is observed (Figure 10) which is well described by the following equation:

$$\log k' = a + b\log\beta_n \qquad (6)$$

Metal Determination

The limits of detection varies from 1.2 ng (nickel) to 15 ng (copper) (at injected volume of 50 µl) depending on the chromatographic properties of corresponding complexes. Calibration plots are linear in the range up to three orders of magnitude (the lower limit is from 4.10^{-7} M (Ni) to 6.10^{-6} M (Cu)).

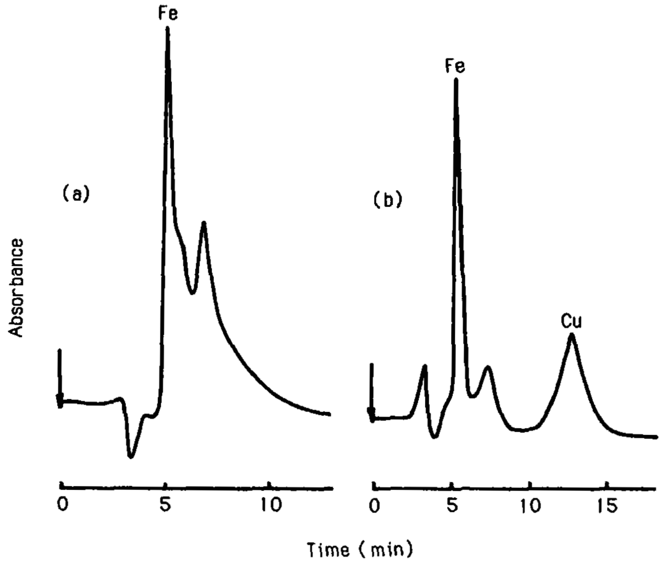

Figure 11. Analysis of real samples by IP-HPLC. (a) tap water; (b) apple-grape juice. Mobile phase: acetone - water (20:80, v/v) containing 6 mM TBAOH, pH 12.0.

The relative standard deviation for metal concentrations 2.10^{-5}-2.10^{-4} M is about 1.5-3.0%. This method was applied to the analysis of transition metals in waste water of electroplating production (before and after refinement) (Table 1) and to the quality control of drinking water, juices and wines (Figure 11).

Comparison of Ion-Exchange and Ion-Pair Chromatography

The above-mentioned regularities of metal pyridylazoresorcinolates retention behaviour and the results of metal analysis by IE- and IP-HPLC allow us to compare and distinguish the common features, peculiarities and advantages of each method.

First of all, both methods are characterized by sufficiently high sensitivity which is determined by the application of spectrophotometric reagents (like metalchromic indicators) forming intensively coloured water-soluble metal chelates (for instance, the molar absorbtivities of metal PAR complexes reach to 10^5). The detection limits are better in IP-HPLC due to the higher separation efficiency. However, the lower sensitivity of IE-HPLC can be compensated by a possibility of concentration of analysed complexes directly on the analytical column (by increasing injected volumes up to 500 µl or on average 10 times more than in ion-pair mode). Detection in visual range decreases the requirements on spectral purity of a mobile phase and allows to use solvents which absorb in the UV range (i.e., acetone).

Owing to the high sensitivity of these HPLC variants, the necessity of preconcentration - the obligatory stage in trace metal analysis by normal- or reversed-phase HPLC of neutral chelate (11) - is often absent. As a result, the analysis is accelerated and simplified.

Metal chelates formed by polydentate reagents (like heterocyclic azodyes) and having macrocyclic structure, are distinguished by high stability in the chromatographic conditions. The possibility of separation of metal complexes in the presence of excess reagent due to the differences in spectral characteristics and, in certain instances, in retention, results in chromatographic stability of these chelates.

At last, both methods are characterized by wide possibilities of regulating the separation (in particular, IP-HPLC) both by multicomponent composition of the mobile phase and the complex retention mechanism. It is this peculiarity that advantageously distinguishes IE- and IP-HPLC from adsorption HPLC of neutral metal chelates. As in the other chromatographic methods, where metal complexes are used, the selectivity of metal determination can be increased by varying the complex-forming conditions (including the on-column formation).

CONCLUSION

The method of transition metal analysis based on the separation of their anionic PAR complexes by IE- or IP-HPLC and spectrophotometric detection, has potential and competes against other variants of HPLC by its analytical characteristics. It should be also noted that PAR, as many others heterocyclic azo reagents, depending on the complex-forming conditions and metal nature can also form neutral and mixed-ligand chelates (for example, with rare earth elements). This ability, caused by complex chemistry of coordination compounds, not only increases the number of determined metals, but also can be considered as an important advantage of chelates application in metal HPLC analysis.

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