

CHROM. 21 870

ON-LINE PRECONCENTRATION AND ELUTION OF TRACE METALS BY ION CHROMATOGRAPHY

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SUMMARY

On-line preconcentration of transition metal ions using 8-quinolinol-bonded chelating silica is described. The precolumn was coupled to an ion-pairing chromatographic column and simultaneous determination was achieved using a diode-array UV detector, 0.1 M potassium cyanide (pH 8.5) being used for eluting metals from both the precolumn and the analytical column. Of the metals tested, Cu, Ni, Co and Fe(II) yielded well resolved absorption bands whereas Fe(III) and Mn(II) yielded ill-characterized absorption bands. The working concentration range for Cu and Ni was tested and shown to be linear in the range 10^{-8} – $5 \cdot 10^{-6}$ M. Highly reproducible results were obtained at these concentrations. The sensitivity was found to be limited by background signals and the reason for this background is discussed in detail.

INTRODUCTION

The determination of trace metals at the concentration levels found in natural waters often requires a preconcentration step. Preconcentration of trace metals is most often done off-line, prior to their analysis by a chosen method. Ion chromatography has been widely used for the separation and determination of metal ions. For automation purposes, on-line preconcentration followed by ion chromatography would be necessary. On-line preconcentration has the advantage that no dilution or contamination of the preconcentrated samples is introduced.

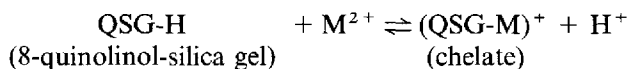
Recently, on-line preconcentration followed by ion chromatographic techniques have been developed^{1–6}. In none of these studies were chelating silicas used for preconcentration purposes. The interesting feature of chelating silicas is their specificity towards transition metals. To our knowledge, chelating silicas have not been used for on-line preconcentration owing to the difficulty in finding a common eluent that could be used for both desorption from the chelating precolumn and for performing separations on a cationic or reversed-phase column.

The eluent usually employed on the precolumn is 0.1 or 1 M hydrochloric or nitric acid. The metals desorbed from the chelating precolumn were determined by techniques such as atomic absorption spectrometry^{7–9} or inductively coupled plasma mass spectrometry¹⁰. Jezorek and co-workers^{11–13} attempted to separate metals

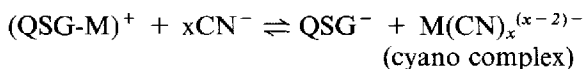
from several chelating analytical columns using these eluents, but the chromatographic peaks were not very well resolved.

In this work we investigated the use of chelating silicas coupled on-line to an ion chromatograph for the simultaneous preconcentration and separation of trace metals. For this purpose, 8-quinolinol-bonded silicas was used in the precolumn. This chelating silica is well known to preconcentrate many transition metal ions⁷⁻¹⁰. Instead of hydrochloric acid, a strong complexant was used to desorb the trace metals. Cyanide ions are known to form very strong complexes with transition metal ions, as can be seen from Table I. The stability constants of cyanide are much higher than those of the 8-quinolinol-silica and hence it was chosen as the eluent. The following processes occur during preconcentration and desorption:

Preconcentration:



Desorption:



The cyanide complexes formed are then separated using an ion-Pairing C₁₈ silica column and detected by UV spectrophotometry. A slightly modified Hilton and Hadad¹⁵ chromatographic procedure was adopted for the purpose of separation and determination of the metals.

EXPERIMENTAL

Apparatus

The chromatographic equipment (Fig. 1) consisted of two Knauer metal-free electric valves, a Dionex QIC preconcentration pump and a Knauer 64 elution pump.

TABLE I

STABILITY CONSTANTS OF METAL-CYANO AND METAL-8-QUINOLINOL COMPLEXES¹⁴

Metal	8-Quinolinol		Cyanide: β_4
	β_1	β_2^a	
Fe(II)	8	(22) ^b	24 ^c
Fe(III)	15	(38) ^b	31 ^c
Co	9	(17)	20 ^c
Ni	10	(19)	22
Cu	13	(24)	25
Zn	9	(17)	17
Cd	8	(14)	18
Pb	9	(17)	10

^a Values in solution.

^b β_3 .

^c β_6 .

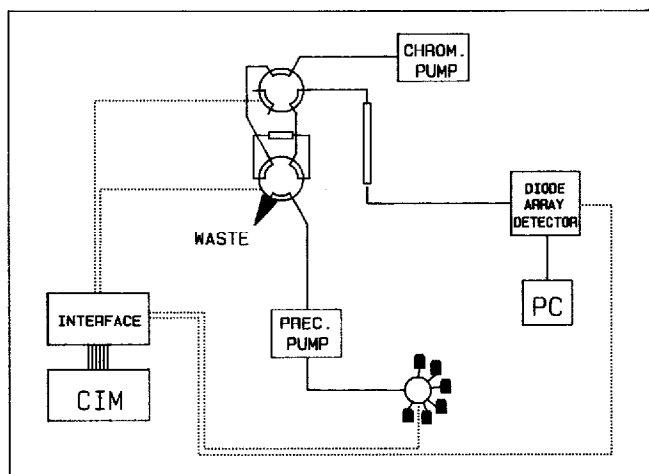


Fig. 1. Chromatographic equipment. PC = Personal computer; CIM = Control interface module.

Only the last pump was made of metal. The precolumn (30×2.5 mm I.D.) (Dionex) was packed manually with 8-quinolinol-silica. The 8-quinolinol-silica was placed in the precolumn with a microspatula and the column was tapped to ensure that the solid was well packed. An SGE glass-lined analytical column was packed with ODS-2 silica ($5 \mu\text{m}$). One Rheodyne six-way low-pressure valve was used with the preconcentration pump for switching between sample and washing solutions. Plastic tubing and connections were used. A Hewlett-Packard 1040 A diode-array UV-visible detector was used. The whole system was automated using a CIM-300 (control interface module) from Autochrom coupled to an interface specially designed in our laboratory.

Reagents

Preconcentration. Unless stated otherwise, all chemicals were of analytical-reagent grade from Merck or Fluka. All solutions were made with freshly prepared doubly distilled water. The 8-quinolinol-silica was synthesized in our laboratory using the procedure described by Fulcher *et al.*¹⁶ Its loading capacity was $360 \mu\text{mol/g}$. Macherey, Nagel & Co. Polygosyl silica 60 ($40\text{--}63 \mu\text{m}$) was used as the starting material for the synthesis.

Eluent. A solution of 0.1 M potassium-cyanide (Biochemica Microselect, Fluka) in 13% acetonitrile (Far-UV, Romil) in water was used as the eluent. Ion pairing was achieved using $1.5 \cdot 10^{-3}$ – $5 \cdot 10^{-3}$ M tetrabutylammonium reagent (Low-UV PIC A, Waters Assoc.). The pH was adjusted to 8.5 with hydrochloric acid, (Suprapur, Merck).

Procedure

A 20-ml volume of solution containing the metal ions was pumped into the chelating silica precolumn, where the metals were preconcentrated, then 6 ml of water were pumped into the precolumn for rinsing. The metals that were retained were desorbed by using the above eluent. For this purpose, the chromatographic pump was used (0.7 ml/min, $P = 115$ bar). During the desorption step, the precolumn and

the analytical column were linked. The metals, after separation on the analytical column, were detected by means of a diode-array detector. The precolumn was disconnected from the analytical column 2 min after passing the eluent. While separation was proceeding, the precolumn cleanup was carried out by washing it with 10 ml of 0.1 *M* potassium cyanide solution (pH 8.5) followed by 10 ml of water.

RESULTS AND DISCUSSION

UV-visible characteristics of metal-cyano complexes

Metal-cyano complexes show well resolved absorption bands in the UV spectrum, *e.g.*, $\lambda_{\text{Cu}} = 238 \text{ nm}$, $\lambda_{\text{Ni}} = 270 \text{ nm}$, $\lambda_{\text{Co}} = 310 \text{ nm}$. The UV-visible diode-array detector allows the simultaneous determination of these complexes at their absorption maxima (λ_{max}) and therefore high sensitivities can be obtained. However, not all metal-cyano complexes are well defined. For instance, the complexes of heavy metals such as Zn, Hg, Cd and Pb do not show UV-visible absorption whereas Fe(III) and Mn(II) show ill-characterized absorption bands. Fe(III) and Mn(II) can nevertheless be determined at 220 and perhaps at 210 nm, but at the latter wavelength the reproducibility of the results may be affected by interferences from cyanide or acetonitrile background absorptions. Even though Fe(II) shows a wellresolved peak, it has a lower molar absorption coefficient and hence the method is not very sensitive for the determination of Fe(II).

Desorption

The cyanide concentration and pH were varied to establish the optimum working conditions. The best results were found using 0.1 *M* potassium cyanide solution at pH 8.0–8.5. At lower concentrations of cyanide the rate of desorption was too slow. Under the optimum conditions, desorption was found to be very efficient even at high metal concentrations, *e.g.*, more than 99% with 1 ml of CN^- (see Fig. 2). The peak tailing in Fig. 2 is due to the decomposition of the 8-quinolinol-silica and not to the presence of the copper complex.

Fifty cycles can be achieved using this procedure with a loss of only 20% of the loading capacity of the precolumn. It should be pointed out that under the working conditions, the precolumn is used much below its maximum loading capacity and hence the results will be unaffected for a very long period.

Chromatographic separation

The method described by Hilton and Haddad¹⁵ was found to be reasonable for the separation of Cu, Co and Ni but it was impossible to separate Fe and Mn. We therefore modified their experimental conditions slightly because of the high concentration of cyanide used here. A lower proportion of acetonitrile (18%) and a lower concentration of tetrabutylammonium ($1.5 \cdot 10^{-3} \text{ M}$) were used. A typical chromatographic separation is shown in Fig. 3.

It should be pointed out that the analytical column undergoes slow decomposition and the experimental conditions have to be changed accordingly, *e.g.*, over a period of 2 months the following modifications were necessary: a reduction in acetonitrile concentration from 18 to 13% and an increase in tetrabutylammonium ion concentration from $1.5 \cdot 10^{-3}$ to $3 \cdot 10^{-3} \text{ M}$.

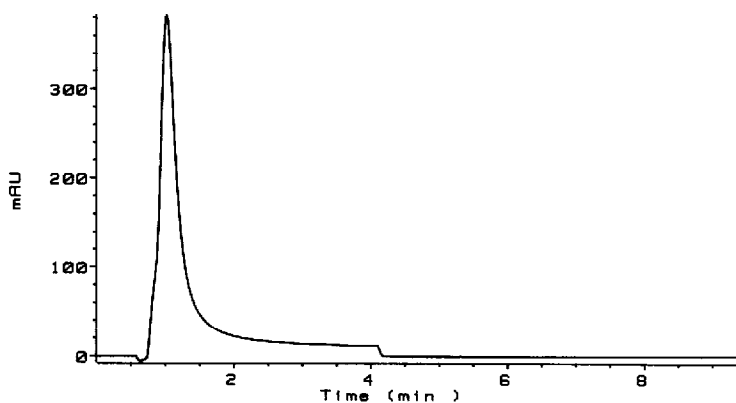


Fig. 2. Desorption of pre-concentrated copper on 8-quinolinol-bonded silica. Preconcentration: 20 ml of 10^{-6} M Cu^{2+} . Eluent: 0.1 M potassium cyanide (pH 8.5) without analytical column.

On-line preconcentration

We chose Cu and Ni ions for on-line preconcentration. These metals have been preconcentrated previously on materials other than chelating silica¹⁻⁶. The reasons for selecting Cu and Ni are that well defined peaks are obtained and high sensitivities can be achieved owing to their high molar absorption coefficients. Co was omitted because at low concentrations the very high solvent peak masks the Co peak. The Cu peak was found to be masked by a degradation peak from 8-quinolinol-silica and it was necessary to modify the experimental conditions slightly to avoid interferences from this peak. Under the modified conditions ($5 \cdot 10^{-3}$ M tetrabutylammonium, 13% acetonitrile), well defined peaks were obtained (Fig. 4).

Sensitivity. The calibration graphs in Fig. 5 show that excellent linearity is obtained in the concentration range $5 \cdot 10^{-6} - 10^{-8}$ M, indicating that the method is highly sensitive for these metal ions. The method could not be extended to lower

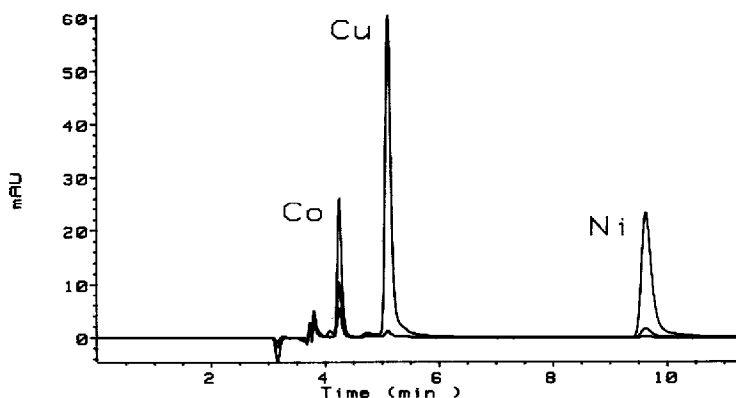


Fig. 3. Chromatographic separation of metal-cyano complexes. Injection: 20 μl of samples containing $2 \cdot 10^{-5}$ M of metal ions. Eluent: 0.1 M potassium cyanide (pH 8)– $1.5 \cdot 10^{-3}$ M tetrabutylammonium reagent in 18% (v/v) acetonitrile–water, flow-rate 0.7 ml/min. Detection: 310 nm for Co, 238 nm for Cu and 270 nm for Ni.

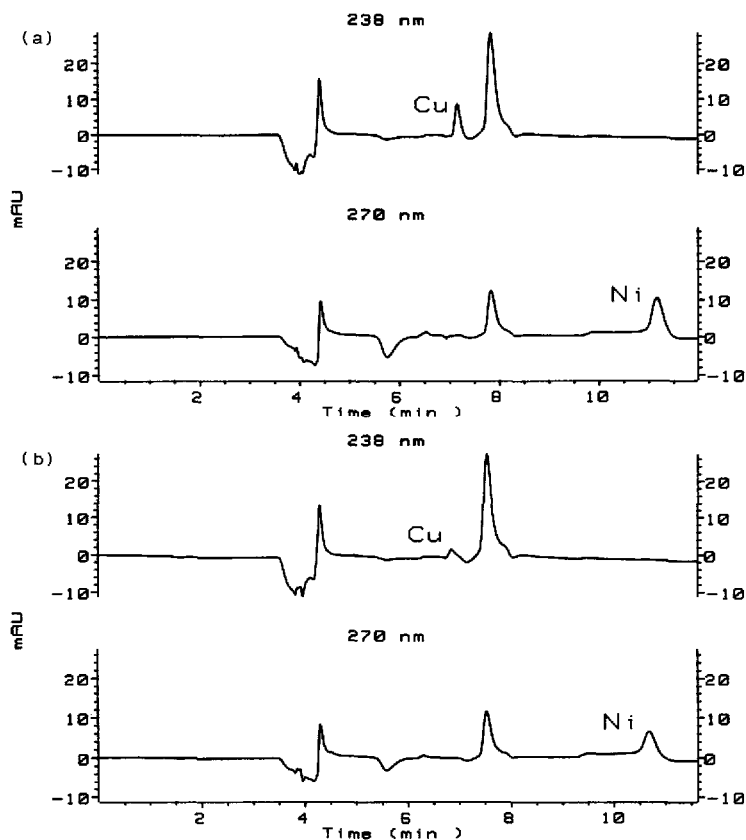


Fig. 4. Chromatographic separation of preconcentrated samples. (a) 20 ml of 10^{-8} M Ni^{2+} and Cu^{2+} ; (b) blank, 20 ml of doubly distilled water. Eluent: 0.1 M potassium cyanide (pH 8.5)– $5 \cdot 10^{-3}$ M tetrabutylammonium reagent in 13% (v/v) acetonitrile–water, flow-rate 0.7 ml/min.

sensitivity owing to the high background absorption (about 0.006 absorbance units, which correspond to a concentration of metal of $5 \cdot 10^{-9}$ M; see Fig. 4). The high background signals may be due to inability to remove ultra-trace amounts of metals from doubly distilled water. It may also be due to incomplete desorption of the metal ions. This is supported by the fact that the background increased after eluting high concentrations of metals ($5 \cdot 10^{-6}$ M). This finding is not unique to cyanide ions but also occurs with other eluents, e.g., hydrochloric acid¹⁷.

Reproducibility. The reproducibility of the method was tested by making replicate measurements using 10^{-7} M Ni(II) on different days. At constant cyanide concentration, reproducible results are obtained (standard deviation 5.4% for desorption times of 2 min). It should be pointed out that a desorption time of less than 2 min is insufficient to achieve complete transfer. It is interesting that slight variations in the acetonitrile of tetrabutylammonium ion concentrations do not affect the reproducibility of the results.

Similar studies with Cu posed problems owing to the degradation of the 8-quinolinol-silica, as mentioned earlier.

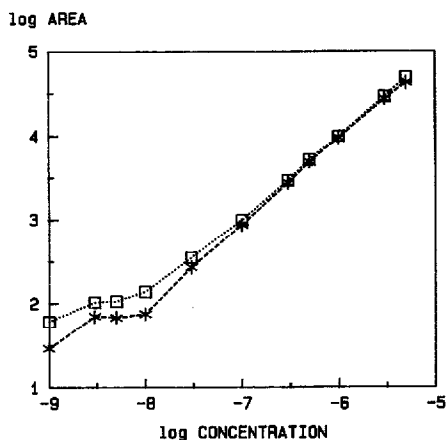


Fig. 5. Calibration graphs for (*) Cu and (□) Ni. Conditions as in Fig. 4.

CONCLUSION

The results indicate that it is possible to use the method described here to determine concentrations of Cu and Ni at levels of 10^{-8} M. The background contamination limits the extension of the method to lower levels. Provided that the doubly distilled water is ultra-pure, the sensitivity limit can be extended if larger volumes of the sample are preconcentrated. The maximum sample volume that can be used will depend on the breakthrough volume (ca. 200 ml in this instance). If the simultaneous determination of metal ions is not required, then by coupling the ion chromatographic column to a classical UV detector (at a fixed wavelength) instead of a diode-array UV detector, increased sensitivities can be obtained.

This method, however, has the following disadvantages: it is not a universal method but is restricted to the determination of Cu and Ni; 8-quinolinol-bonded silica has a tendency to decompose and may mask metal peaks; it is extremely difficult to remove the last traces of metal from the preconcentration column; and the use of a diode-array detector is a prerequisite as high cyanide concentrations hamper the determination of the metal cyano complexes at 214 nm.

Further efforts will be required to find silicas that are resistant to decomposition and have fast chelating kinetics and a more universal method for determining transition metal ions.

ACKNOWLEDGEMENTS

The authors are very grateful to Miss Caroline Haffner for laboratory work and to the translators, Mrs. Mary-Lou Pelapat and Nalini Parthasarathy.

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