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Short Communication

Simultaneous determination of molybdenum, vanadium, gallium, copper, iron and indium as 8-quinolinolate complexes by high-performance liquid chromatography

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ABSTRACT

8-Quinolinol (HQ) was used as a precolumn chelating reagent for the reversed-phase high-performance liquid chromatographic (HPLC) determination of Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III). The metal–HQ complexes were separated on a C_{18} column using a mobile phase of methanol–water (67:33, v/v) containing $1.25 \cdot 10^{-3}$ *M* HQ and 0.02 *M* chloroacetate (pH 3.5). The metal–HQ complexes were preconcentrated by solvent extraction, evaporation of the solvent and dissolution of the residue in methanol. After preconcentration, $\mu g\ l^{-1}$ levels of the metals can be determined by HPLC with satisfactory precision. The proposed method was applied to the simultaneous determination of Mo(VI), V(V), Cu(II) and Fe(III) in sea water.

INTRODUCTION

High-performance liquid chromatography (HPLC) of metal complexes is an attractive method for the simultaneous determination of trace metal ions. In particular, reversed-phase HPLC seems to offer excellent potential for the determination of many metals owing to its high efficiency and simplicity of operation. Several revies on the HPLC separation of metal complexes have been published [1–5].

8-Quinolinol (HQ) has been extensively used for the separation of metal ions by HPLC. HQ is an suitable reagent for this purpose as it forms stable complexes with many metal ions. A number of papers concerning the determination of metal ions as HQ complexes by HPLC have been published [6–19]. A variety of separation conditions, detectors and derivatization techniques have been used. Separations have been reported with the use of both normal-phase [6–11] and reversed-phase [10–19] HPLC. UV–VIS detection is the most frequently employed detection method in the HPLC of HQ complexes. Fluorescence detection [16] and electrochemical detection

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[14] have been evaluated. In addition, precolumn complexation, on-column complexation [9,14,15,18] and postcolumn complexation [16] have been used. However, their application to real samples is seldom found. A few applications [15] have included the analysis of bovine liver, waste water and river water.

This work involved the low-level determination of Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III) by reversed-phase HPLC of their HQ complexes. For the trace enrichment of metal ions, the complexes have typically been extracted into an organic solvent such as chloroform prior to the chromatographic separation. However, the direct injection of more than 10 μl of an organic extract onto the separation column is inadequate for reversed-phase HPLC. Therefore, after extraction of the HQ complexes into carbon tetrachloride, the solvent was evaporated and the residue was dissolved in methanol prior to injection. Trace levels of the metals can be determined by HPLC after this enrichment, and the simultaneous determination of Mo(VI), V(V), Cu(II), and Fe(III) in sea water by this method is possible.

EXPERIMENTAL

Instrumentation and reagents

The analytical column was a Tosoh (Tokyo, Japan) TSK-GEL ODS-80TM (25 cm × 4 mm I.D.) with a 5-μm particle size. A Rheodyne Model 7125 injector was used. The detector was a Japan Spectroscopic (Tokyo, Japan) Model 870 variable-wavelength UV detector, together with a Shimazu (Kyoto, Japan) Model U-125 MU recorder. The HPLC pump was a Nihon Seimitsu Kagaku (Tokyo, Japan) NP-DX pump with a hexane damper. The mobile phase was methanol–water (67:33, v/v) containing $1.25 \cdot 10^{-3}$ *M* HQ and 0.02 *M* chloroacetate (pH 3.5). The mobile phase flow-rate was 1.0 ml min^{-1} and the detector was operated at 370 nm.

HQ was obtained from Wako (Osaka, Japan) and used without further purification. Methanol and carbon tetrachloride were purified by distillation. Distilled, deionized water was purified with a Millipore Milli-Q system and was used for all solutions and dilutions. All solvents were filtered through a 0.45-μm filters before use.

Stock solutions (1000 mg l^{-1}) of metal ions were prepared from salts and metals purchased from the following sources: $CuSO_4 \cdot 5H_2O$, Ga, NH_4VO_3, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ and In from Wako and $Na_2Mo_0O_4 \cdot 2H_2O$ from Kanto Chemicals (Tokyo, Japan). All reagents were of analytical-reagent grade.

Procedure

To 90 ml of sample solution containing Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III), 1.5 ml of 0.05 *M* HQ (0.05 *M* H_2SO_4) solution was added and the pH was adjusted to 4.0 by addition of 2 *M* sodium acetate solution. Then 2 ml of butanol were added and the mixture was heated at 60°C for 10 min. After cooling, the mixture was transferred to a separating funnel and the metal–HQ complexes were extracted into 10 ml of carbon tetrachloride by shaking for 10 min. The extracted organic phase was centrifuged for 2 min and 8-ml aliquots were transferred to eight test-tubes attached to a rotary evaporator. The solvent was evaporated and the residue was dissolved in 1 ml of methanol–water (4:1, pH 3.5) after cooling. Aliquots of 100 μl of this solution were then injected into the chromatograph.

RESULTS AND DISCUSSION

Chromatography and solvent extraction of the metal–HQ complexes

For the study of chromatographic behaviour, the HQ complexes of Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III) were prepared without a preconcentration step in the procedures described above as follows: to a sample solution containing 10 μg of each metal ion, 3 ml of methanol, 1 ml of 10^{-2} *M* HQ solution and 0.5 ml of 1 *M* ammonium acetate buffer solution were added. The mixture was diluted with water to 5 ml, then an aliquot of the solution was injected into the HPLC system.

The proportion of methanol in the methanol–water mobile phase was varied from 60 to 72.5 (v/v). The retention time of each complex increased with decreasing methanol content. Well resolved peaks suitable for the simultaneous determination of the six metal ions were obtained with methanol–water (67:33, v/v).

The effect of the mobile phase pH on the retention behaviour of the metal–HQ complexe was investigated in the pH range 2.5–4.0 and the results are shown in Fig. 1. The retention times of all the complexes were unchanged in the pH range 3–4, except for that time of the In(III) complex, which increased with increasing pH. It is known that In(III) is completely extracted into chloroform to form $In(HQ)_3$ with HQ above pH 4.0. The retention behaviour of the In(III) complex is considered to be due to an increase of the formation of $In(HQ)_3$ with increase in pH. The optimum chromato-

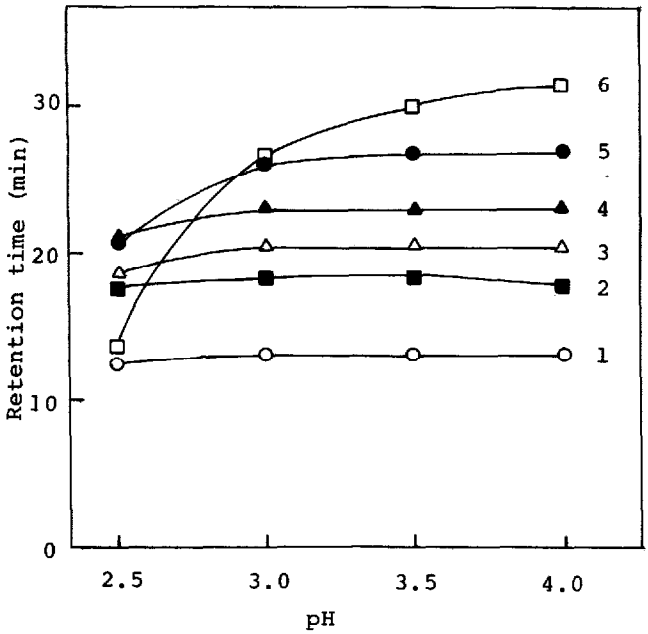

Fig. 1. Variation of retention time with pH of the mobile phase. Column, TSK-GEL ODS-80TM (25 cm × 4 mm I.D.; 5 μm); mobile phase, methanol–water (67:33, v/v) containing $1.25 \cdot 10^{-3}$ *M* HQ and $2 \cdot 10^{-2}$ *M* acetate buffer; flow-rate, 0.65 ml/min; detector wavelength, 370 nm; detector sensitivity, 0.02 a.u.f.s.; injection volume, 20 μl; metal, 20 ng. 1 = Mo(VI); 2 = V(V); 3 = Ga(III); 4 = Cu(II); 5 = Fe(III); 6 = In(III).

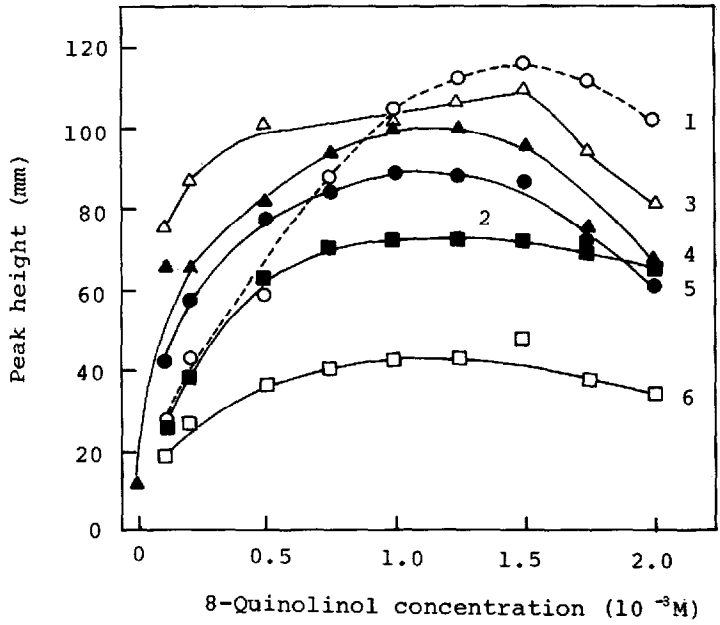

Fig. 2. Variation of peak height with HQ concentration in the mobile phase. Mobile phase, methanol–water (67:33, v/v). Other conditions as in Fig. 1. 1 = Mo(VI); 2 = V(V); 3 = Ga(III); 4 = Cu(II); 5 = Fe(III); 6 = In(III).

gram for the determination of six metal ions was obtained with a mobile phase pH of 3.5.

The peak height of the six complexes increased and the peak symmetry was improved with addition of HQ to the mobile phase. Fig. 2 shows the effect of HQ concentration in the mobile phase on the peak heights of the six complexes. The largest peak heights of the complexes were obtained at an HQ concentration of *ca.* $1.25 \cdot 10^{-3}$ *M*. The peak heights of the complexes decreased at HQ concentrations above $1.5 \cdot 10^{-3}$ *M* because the peaks became broadened. The retention times of the complexes, however, were approximately constant in the HQ concentration range $0.5 \cdot 10^{-3}$–$2.0 \cdot 10^{-3}$ *M*.

A typical chromatogram for the separation of the HQ complexes of Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III) is shown in Fig. 3. The six peaks are well resolved and separated from the peak of HQ.

Solvent extraction of metal complexes is an effective preconcentration method for the low-level determination of metal ions by HPLC. The solvent extraction of HQ complexes has been widely investigated. It has been reported [20] that the HQ complexes of Mo(VI), V(V), Ga(III), Cu(II), Fe(III) and In(III) can be extracted from acidic–neutral or acidic–basic media with various solvents. In this work, the effects of pH, HQ concentration and addition of butanol on the extraction of these complexes from 100 ml of aqueous phase into 10 ml of carbon tetrachloride were investigated according to the procedures previously described. The addition of an alcohol such as butanol is required for complete extraction of V(V) [21]. The aqueous phase was

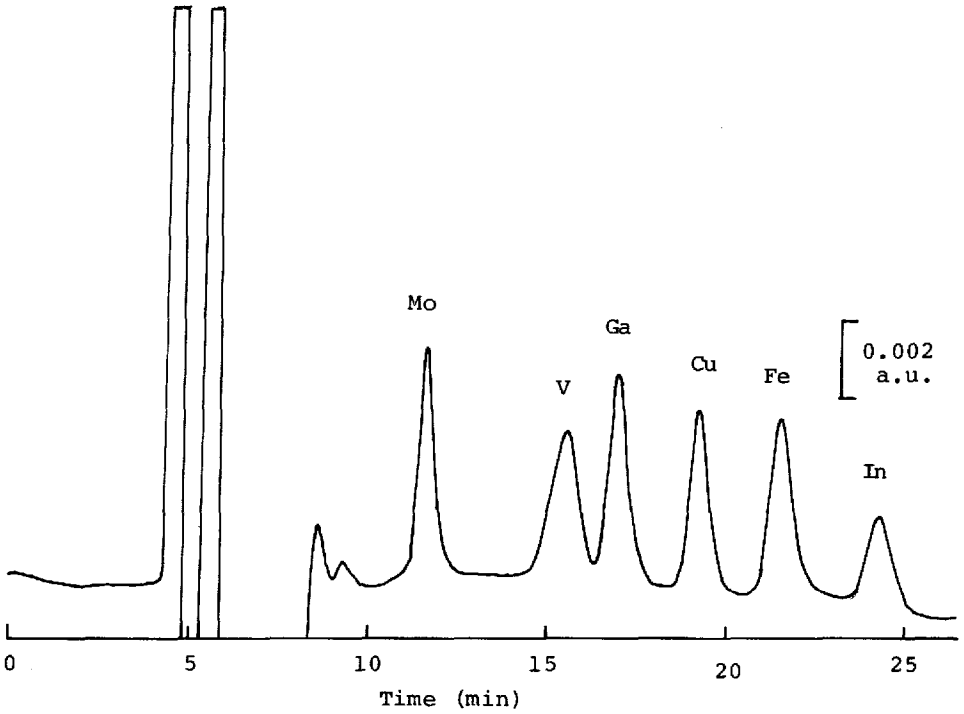

Fig. 3. HPLC separation of metal–HQ complexes. Mobile phase, methanol–water (67:33, v/v). Other conditions as in Fig. 1.

heated at 60°C in order to accelerate the complexation prior to solvent extraction. From the results, an HQ concentration of $7.5 \cdot 10^{-4}$ *M*, 2.5% (v/v) butanol and pH 4 were chosen for subsequent work. All complexes were completely extracted under these conditions. The extracted organic phase was evaporated to dryness and then the residue was dissolved in methanol prior to injection, because the direct injection of more than 10 μl of the organic extract is inadequate for reversed-phase HPLC.

Detection limits and precision

Aqueous solutions containing Mo(VI), V(V), Ga(III). Cu(II), Fe(III) and In(III) were analysed according to the above procedures. The calibration graphs obtained from 100-μl injections were linear for 0.5–50 μg l^{-1} Mo(VI), V(V) and Ga(III), 1–50 μg l^{-1} Cu(II), 4–60 μg l^{-1} Fe(III) and 0.5–60 μg l^{-1} In(III) when the peak heights (370 nm) were measured. The detection limits, defined as the metal ion concentration which gave a peak height three times larger than the background noise, were 0.04 μg l^{-1} for Mo(VI), 0.06 μg l^{-1} for V(V), 0.05 μg l^{-1} for Ga(III), 0.2 μg l^{-1} for Cu(II), 1.1 μg l^{-1} for Fe(III) and 0.1 μg l^{-1} for In(III). The detection limits could be significantly lowered through the use of large volume sample solution in the solvent extraction step. The relative standard deviations for the peak heights were 2.7, 7.0, 1.6, 2.7, 4.0 and 5.8% for 1.5 μg l^{-1} Mo(VI), 2.0 μg l^{-1} V(V), 1.5 μg l^{-1} Ga(III), 7.0 μg l^{-1} Cu(II), 15 μg l^{-1} Fe(III) and 3.5 μg l^{-1} In(III), respectively.

TABLE I

ANALYTICAL RESULTS FOR Mo(VI), V(V), Cu(II) AND Fe(III) IN SEA WATER

Injection volume, 100 μl; other conditions as in Fig. 1.

Location	Amount found (μg l^{-1})[c]			
	Mo(VI)	V(V)	Cu(II)	Fe(III)
Isozaki coast[a]	7.8 ± 0.5	1.4 ± 0.09	1.4 ± 0.13	16.9 ± 1.4
Hitachi harbour[b]	7.9 ± 0.2	1.6 ± 0.06	0.72 ± 0.08	66.6 ± 4.3

[a] 36°22′40″N, 140°37′56″E.
[b] 36°28′27″N, 140°37′50″E.
[c] Mean ± standard deviation (n = 4).

Determination of Mo(VI), V(V), Cu(II), and Fe(III) in sea water

The possibility of interferences from other metals was investigated for the determination of Mo(IV), V(V), Cu(II) and Fe(III) in sea water. To an artificial sea water containing Al(III), Cr(VI), Mn(II), Ni(II), Sn(IV), Ti(IV), U(VI) and Zn(II) at the natural levels in real sea water, the four metals were added and determined by the above procedures. The chromatogram of the resulting solution showed no interferences from these metals with the peak of Mo(VI), V(V), Cu(II) and Fe(III).

The concentrations of Mo(VI), V(V), Cu(II) and Fe(III) in surface sea water from the Isozaki coast and Hitachi harbour of Ibaraki (Pacific coast of Japan) were determined using the above procedures and the results are given in Table I. All the values, except for Fe(III) in the Hitachi harbour sample, are similar to those reported by Kimura *et al.* [22] for sea water from the Pacific coast of Japan. The high level of Fe(III) in the Hitachi harbour sample is believed to be due to the dissolution of iron from ships' hulls. No Ga(III) or In(III) was detectable because their concentrations in sea water are very low.

REFERENCES

1 N. Suzuki and K. Saitoh, *Kagaku No Ryoiki, Zokan*, No. 138 (1983) 127.
2 T. Yotsuyanagi and H. Hoshino, *Bunseki*, (1983) 566.
3 B. R. Willeford and H. Veening, *J. Chromatogr.*, 251 (1983) 61.
4 J. W. OLaughlin, *J. Liq. Chromatogr.*, 7 (1984) 127.
5 G. Nickless, *J. Chromatogr.*, 313 (1985) 129.
6 C. S. Hambali and P. R. Haddad, *Chromatographia*, 13 (1980) 633.
7 B. Wenclawiak, *Fresenius' Z. Anal. Chem.*, 308 (1981) 120.
8 B. Wenclawiak, *Fresenius' Z. Anal. Chem.*, 310 (1982) 144.
9 B. W. Hoffman and G. Schwedt, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 439.
10 L. H. J. Lajunen, E. Eijarvi and T. Kenakkala, *Analyst (London)*, 109 (1984) 699.
11 B. Wenclawiak and F. Bickman, *Bunseki Kagaku*, 33 (1984) E67.
12 H. Hoshino and T. Yotsuyanagi, *Bunseki Kagaku*, 29 (1980) 807.
13 P. R. Haddad and S. Valeenuwat, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 127.
14 A. M. Bond and Y. Nagaosa, *Anal. Chim. Acta*, 178 (1985) 197.
15 C. W. Whang, L. C. Wu and L. C. Chou, *Proc. Natl. Sci. Counc., Repub. China, Part A, Phys. Sci. Eng.*, 11 (1987) 363.
16 B. D. Karcher and I. S. Krul, *J. Chromatogr. Sci.*, 25 (1987) 472.
17 A. Y. Malykhin, T. A. Bol'shova, A. S. N. Lanin and Y. S. Nikitin, *Zh. Anal. Khim.*, 42 (1987) 1773.

18 Y. Wu and G. Schwedt, *Fresenius' Z. Anal. Chem.*, 329 (1987) 39.
19 C. Baiocchi, G. Saini, P. Bertolo, G. P. Cartoni and G. Pettiti, *Analyst (London)*, 113 (1988) 805.
20 K. L. Cheng, K. Ueno and T. Imamura, *Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, p. 253.
21 A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinhold, London, 1970, p. 82.
22 A. Kimura, H. Tao and K. Bansho, *Bunseki Kagaku*, 34 (1985) 515.