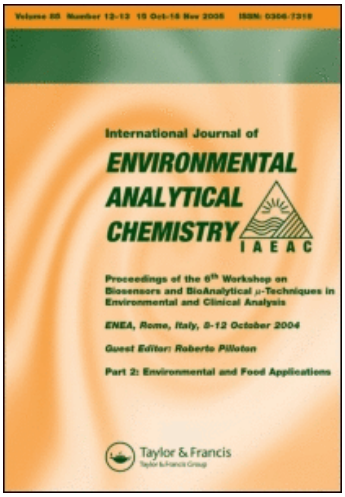

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Reversed-Phase High-Performance Liquid Chromatographic Determination of Molybdenum and Manganese in Sea Water as Chelates With 8-Hydroxyquinoline

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REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF MOLYBDENUM AND MANGANESE IN SEA WATER AS CHELATES WITH 8-HYDROXYQUINOLINE

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The chelates of Mo(VI) and Mn(II) with 8-hydroxyquinoline were separated on a C_{18} column by reversed-phase high-performance liquid chromatography (HPLC). The mobile phase was 1:1 acetonitrile/0.02 mol dm^{-3} acetate buffer (pH 4.1) containing the ligand at 10^{-3} mol dm^{-3}. The calibration curves were linear over the concentration range from 0.5 to 200 $\mu g\ dm^{-3}$ for both metals using spectrophotometric detection (390 nm). The detection limits were 0.2 μg for Mn(II) and 0.4 $\mu g\ dm^{-3}$ for Mo(VI) at a signal-to-noise ratio of 3, when the metal chelates were formed prior to injection onto a C_{18} column (pre-column chelation method). The method was applied to the analysis of coastal sea water samples.

KEY WORDS: HPLC determination, manganese, molybdenum, 8-hydroxyquinoline, sea water.

INTRODUCTION

A variety of chelating reagents have been employed for the separation and determination of metals as their chelates by high-performance liquid chromatography (HPLC)[1–4]. Of these, 8-hydroxyquinoline forms stable chelates with a large number of metal ions and therefore much interest has been paid to normal-phase and reversed-phase HPLC of its metal complexes[5,6]. Previously, we have found that simultaneous determination of Cu(II), Al(III), Fe(III) and Mn(II) by reversed-phase HPLC using 8-hydroxyquinoline is possible, but Mo(VI) can not be determined because it coelutes with Mn(II) and its complex decomposes in neutral aqueous phases[7]. Ohashi *et al.*[8] developed an HPLC procedure which involved the extraction of the Mo(VI) complex with 8-hydroxyquinoline into chloroform followed by injection onto a C_{18} column. This HPLC method seems to be time-consuming and tedious for routine analysis.

Recently, chromogenic reagents such as 2-(5-bromopyridylazo)-5-diethylaminophenol[9] and tetracycline[10] have been employed as a precolumn chelating agent for the reversed-phase HPLC determination of Mo(VI). These reagents, however, are very expensive and relatively difficult to obtain commercially.

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In this work we have developed a sensitive and rapid method for the reversed-phase HPLC determination of Mo(VI) and Mn(II) as their 8-hydroxyquinoline chelates. A C_{18} column (Tosoh) is very stable in moderately acidic media (pH 3~5), and therefore useful for this analytical purpose because the Mo(VI) chelate is rather stable and gives a sharp elution peak in such solutions. The proposed reversed-phase HPLC method has been successfully applied to analysis of sea water.

EXPERIMENTAL

Apparatus

Liquid chromatography was performed by use of a Tosoh CCPD pump, a Tosoh TSK gel ODS-80$_{TM}$ column (5 μm, 150 mm × 4.6 mm), and Rheodyne Model 7125 injector (0.100 cm^3). HPLC chromatograms were recorded with a Shimadzu Model SPD-6AV spectrophotometric detector (0.008 cm^3 flow cell) coupled to a Model R-101 laboratory recorder. A Toa Denpa Model HM-5A pH meter was used to measure the pH of the solution.

Reagents and solutions

Metal ion standards of the desired concentration were prepared by dilution of 1000 μg cm^{-3} standard solutions for atomic absorption spectrophotometry. 8-Hydroxyquinoline was purchased from Wako Junyaku Kogyo and used without further purification. The mobile phase was a 1:1 (v/v) acetonitrile/0.02 mol dm^{-3} acetate buffer (pH 4.1) containing 10^{-3} mol dm^{-3} 8-hydroxyquinoline. All other chemicals used were of analytical reagent grade.

General procedure

A sample aliquot (4 cm^3) of standard containing Mo(VI) and Mn(II) was transferred into a 10.0 cm^3 volumetric flask, and 1.0 cm^3 of 0.1 mol dm^{-3} acetate buffer and 5.0 cm^3 of 0.01 mol dm^{-3} 8-hydroxyquinoline solution in acetonitrile were added. The mixture was heated in a water-bath at 75°C for about 1 hr. After cooling, the volume was adjusted to 10.0 cm^3 with distilled water. The solution was filtered through a 0.45- μm membrane filter and an aliquot (100 mm^3) of the filtered solution was injected onto the analytical column. The metal chelates were eluted with the mobile phase described above at a flow rate of 1.0 cm^3 min^{-1} at 20°C and the absorbance at 390 nm was measured. The concentration of each metal ion was determined by measuring the peak height.

Pretreatment of sea water samples

Sea water was sampled off the Echizen Coast of the Fukui Prefecture, Japan. After sampling, it was filtered though 0.45- μm filter, and 6 mol dm^{-3} acetic acid was added to adjust the pH to 5.9 ± 0.2. The other procedures were the same as that described in general procedure.

RESULTS AND DICUSSION

Reversed-Phase HPLC of metal chelates with 8-hydroxyquinoline

The optimum chromatographic conditions for the separation of the metal chelates with 8-hydroxyquinoline were evaluated by changing the volume ratio of acetonitrile-to-water and the pH of mobile phases. Figure 1(A) shows a typical chromatogram obtained for Cu(II), Fe(III), Mo(VI) and Mn(II) as their 8-hydroxyquinoline chelates by the reversed-phase HPLC using a 3:2 acetonitrile/acetate buffer (pH 5.9).

Except for Mo(VI), the other metal chelates were separated very clearly under the conditions. The Mo(VI) chelate was retained and eluted from the C_{18} column with acidic mobile phases (pH 4.1), as shown in Figures 1(B) and (C). Figure 1(C) indicates that complete separation between Mn(II) and Mo(VI) could be achieved with 1:1 acetonitrile/acetate buffer (pH 4.1) containing 10^{-3} mol dm^{-3} 8-hydroxyquinoline as the mobile phase, whereas the Cu(II) peak was masked by the ligand. It was also found that

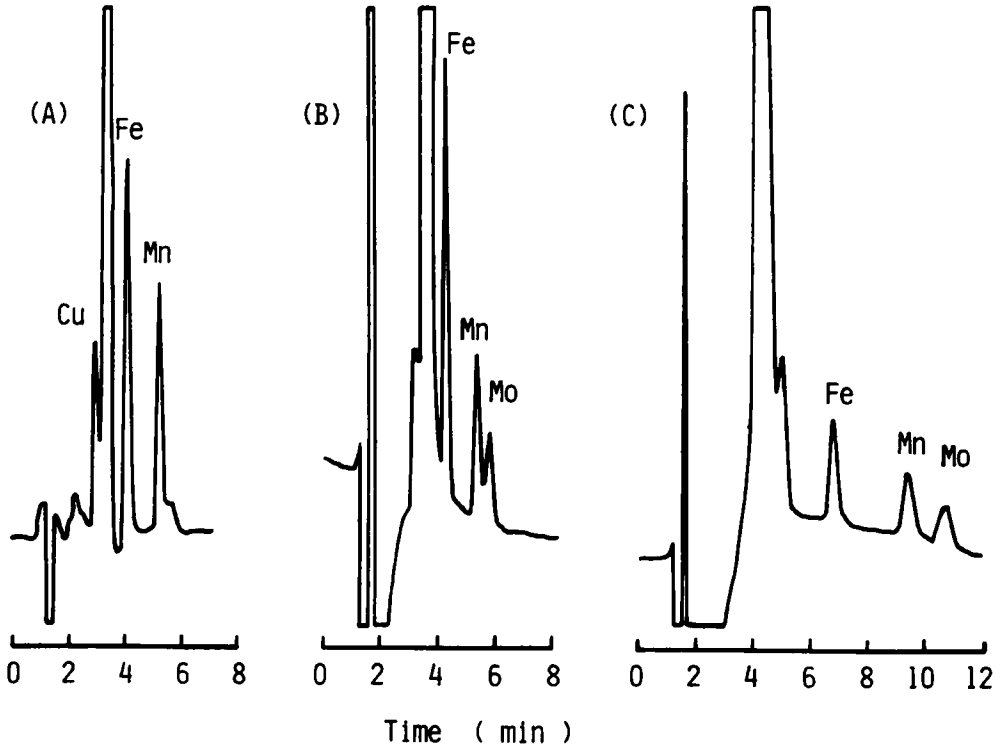

Figure 1 Chromatograms of metal chelates with 8-hydroxyquinoline with different mixtures of acetonitrile-acetate buffer as mobile phases.
(A) 3:2 acetonitrile/acetate buffer (pH 5.9); (B) 3:2 acetontrile/acetate buffer (pH 4.1); (C) 1:1 acetonitrile/acetate buffer (pH 4.1). The mobile phases contained 5×10^{-3} mol dm^{-3} 8-hydroxyquinoline at (A) and 1×10^{-1} mol dm^{-3} 8-hydroxyquinoline at (B) and (C). Chromatographic conditions: concentration of each metal ion, 20 μg dm^{-3}; Y-axis: recorder response; sensitivity: 0.01 AUFS (absorbance units full scale); wavelength: 390 nm; the other conditions are described in the text.

Mn(II) gave an elution peak when aqueous sample solutions were heated with the ligand solution in acetonitrile; in this process, Mn(II) was oxidized to Mn(III). From the results, the chromatographic conditions shown in Figure 1(C) are recommended for the simultaneous determination of Mo(VI) and Mn(II) by reversed-phase HPLC. On the other hand, a 3:2 acetonitrile/acetate buffer can also be used as the mobile phase for the sensitive HPLC determination of Mo(VI) or Mn(II) in aqueous media; the detection limits being 0.1 and 0.2 μg dm^{-3} for Mn(II) and Mo(VI), respectively.

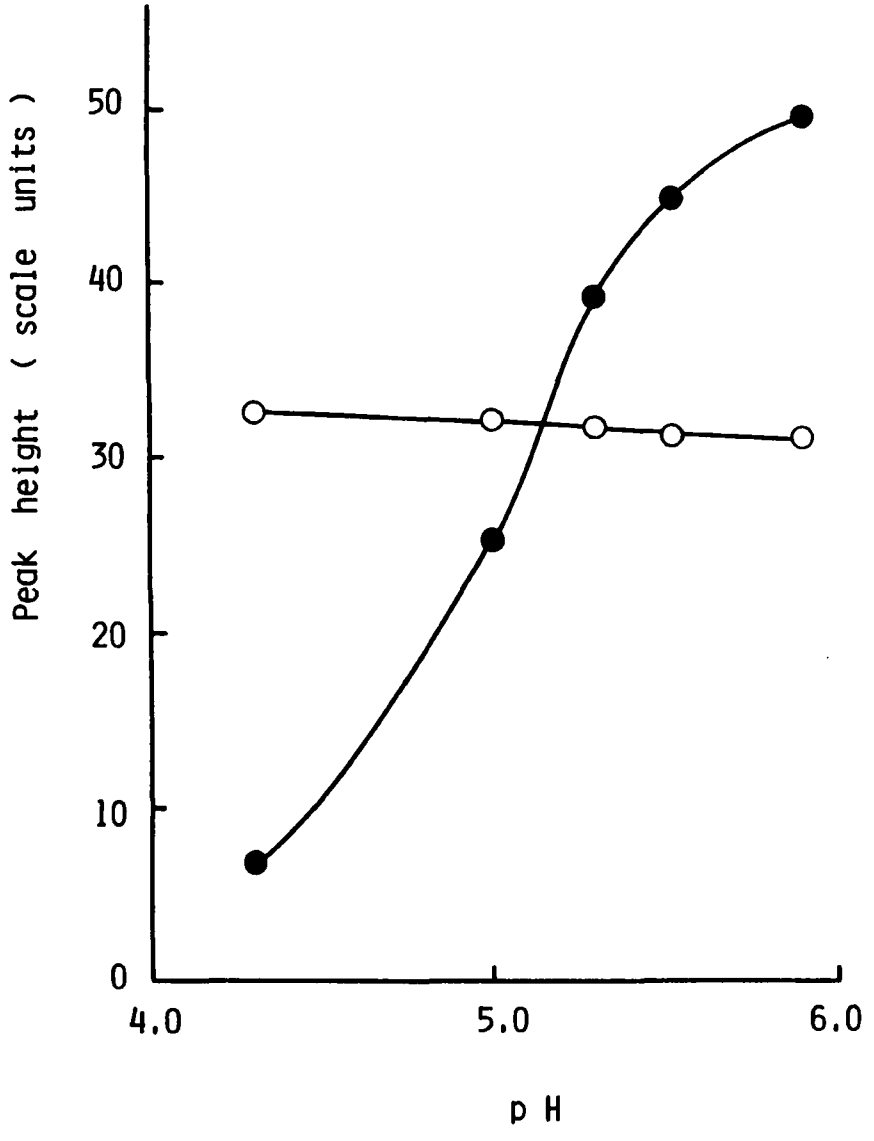

Figure 2 Effect of pH (sample solution) on peak heights.
○: Mo(VI); ●: Mn(II); the metal concentration was 20 μg dm^{-3}. The mobile phase was the same as those shown in Figure 1(C).

Choice of the optimum pH and temperature for the reversed-phase HPLC determination of Mo(VI) and Mn(II)

Chromatograms were recorded at various pH values of mobile phase and sample solution, and the relationships between pH and peak height of both metals were investigated. It was expected from the results described above that the Mo(VI) chelate was quite stable whereas the Mn(II) gradually decomposed in acidic media. In fact, the Mo(VI) peak increased but the Mn(II) decreased as the pH of the mobile phase decreased over the pH range 3.5–5.9. In this study, the pH of the mobile phase was kept at 4.1 ± 0.1. When the pH of sample solution was varied from 4.3 to 5.9 (Figure 2), the Mn(II) peak gradually decreased with decreasing pH, whereas the Mo(VI) peak was almost constant in height over the pH range. In order to obtain better precision and reproducibility, it was decided to buffer the aqueous sample solution at pH 5.9 ± 0.2.

The temperature of the analytical column was found to affect the retention time and peak height of both metal chelates. Therefore, the effect of temperature on retention time and peak height was investigated in the range 10–30°C (Figure 3). The results indicate that the increase in temperature resulted in decreased retention times and increased peak heights for both metals. Complete separation of the two metals was achieved at temperatures below 20°C. The temperature was kept at 20°C in all further experiments.

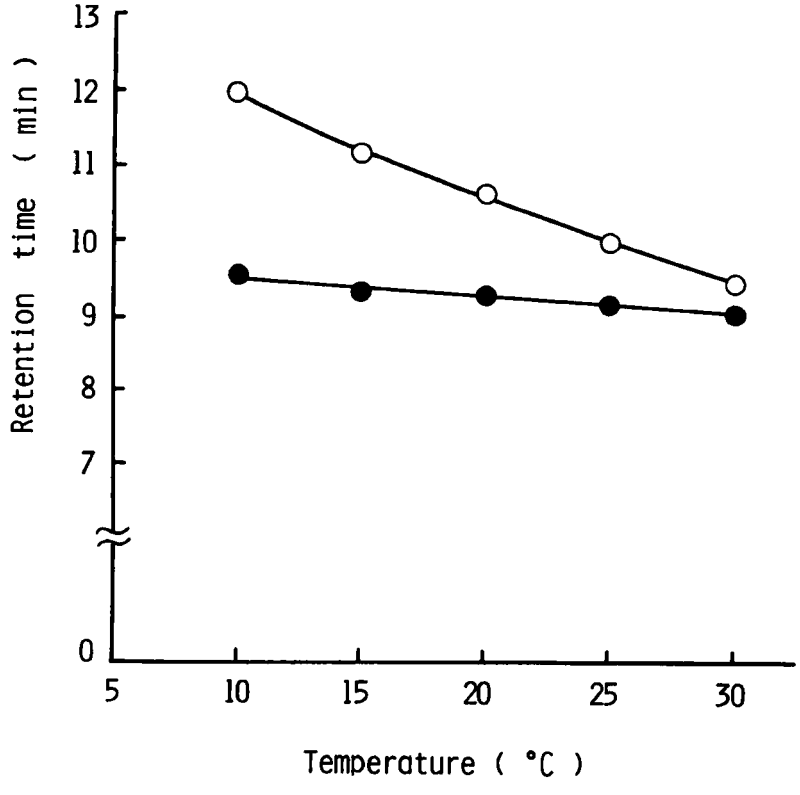

Figure 3 Effect of temperature on retention times.
The experimental conditions are the same as those shown in Figure 1(C).

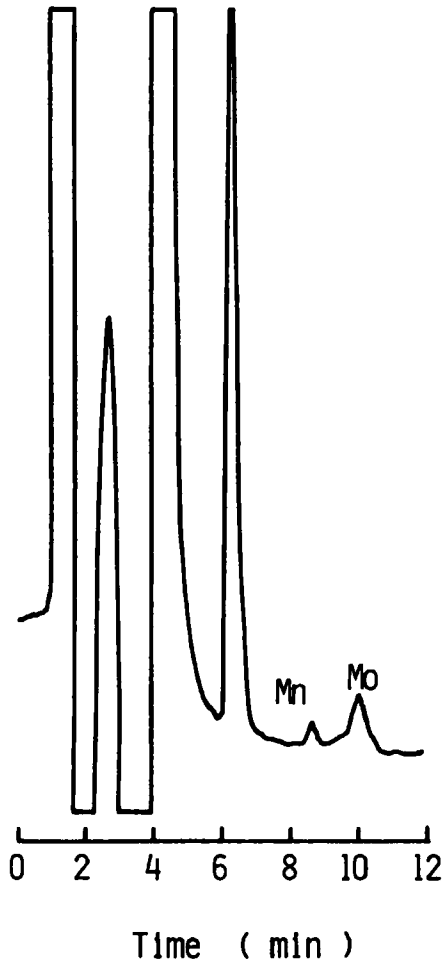

Figure 4 Simultaneous determination of molybdenum(VI) and manganese(II) in a coastal sea water sample. Detection was made at 0.002 AUFS (390 nm); Y-axis recorder response; the other chromatographic conditions are the same as those shown in Figure 1(C).

The Mn(II) peak-height of the chromatogram depends on both the reaction time and pH as Mn(II) oxidizes to Mn(III) very slowly. The initial reaction time was therefore varied from 10 min to 2 hrs at 75°C. It was found that the height of the Mn(II) peak increased gradually in time for the initial 1 hr after which it became almost constant. In this study, a reaction time of 1 hr was chosen as being the most suitable.

Calibration curves and interferences

Calibration curves were constructed for the simultaneous determination of Mo(VI) and Mn(II) by the present HPLC method. Good linearity was obtained for the two metals over the concentration range of 0.5~200 μg dm^{-3}; correlation coefficients of more than 0.9990 (0.002 absorbance unit full scale, AUFS) being obtained.

The detection limits (S/N = 3) were found to be 0.2 μg dm^{-3} for Mn(II) and 0.4 μg dm^{-3} for Mo(VI) for the sample solution (10 cm^3) prepared according to *General procedure*, respectively. The relative standard deviations for five determinations of 20 μg dm^{-3} Mn(II) and Mo(VI) were 4.7 and 2.8%, respectively.

Effect of foreign ions on the chromatographic determination of 10.0 μg dm^{-3} Mo(VI) and Mn(II) was studied. The presence of 1 mg of each Cu(II), Fe(III), Al(III), Pb(II), Bi(III), Zn(II), Ti(IV), W(VI) and V(V) showed no interference. Only Ni(II) interfered with the determination of both metal ions, but 100 μg of the metal could be tolerated.

Analytical application

The coastal sea water was taken from the Echnizen Coast at Fukui (Japan) and was analyzed according to the procedure described in the experimental section (Figure 4). The analytical results for replicate five determinations were 1.5 ± 0.3 μg dm^{-3} for Mn(II) and 9.6 ± 1.4 μg dm^{-3} for Mo(VI), respectively. The data are in good agreement with those obtained by graphite furnace atomic absorption spectrometry following solvent extraction of metal pyrrolydinedithiocarbamates (1.4 ± 0.2 μg dm^{-3} Mn and 9.5 ± 0.1 μg dm^{-3} Mo)[11,12]. We have already determined the concentration of mangenese in the sea water to be 1.4 ± 0.4 in the previous work[7]; in this work, 1.48 μg dm^{-3} Mn being obtained by standard addition method in which 2.0 and 4.0 μg dm^{-3} Mn(II) were spiked in the sample. When the concentration of manganese in sea water is below 1.0 μg dm^{-3}, we recommend to use a 3:2 acetonitrile/acetate buffer (pH 5.9) containing 5×10^{-3} mol dm^{-3} 8-hydroxyquinoline as the mobile phase because of better sensitivity.

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