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Separation of Al(III), Cu(II), Ga(III), and Fe(III) as 8-Hydroxyquinoline-5-sulfonic Acid Complexes by High-performance Liquid Chromatography

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High-performance reversed-phase liquid chromatography with UV detection of 8-hydroxyquinoline-5-sulfonic acid (8-HQS) complexes is studied for the determination of Al(III), Cu(II), Ga(III), and Fe(III). After complexation with 8-HQS, these metals can be determined by direct aqueous injection onto a C 18 column in the range of 0.05 - 2 μg ml^{-1}, with a precision of 3.2 - 6.5%.

Recently, there has been increasing attention on the use of high-performance liquid chromatography (HPLC) for the separation and the determination of metal complexes. In particular, the reversed-phase HPLC method seems to offer excellent potential for the determination of many metals owing to its simplicity of operation and general convenience. In the HPLC studies on metal complexes, the chelating agents such as dithiocarbamic acids, dithizone, 8-hydroxyquinoline, β-diketones, pyridylazo compounds, schiff-bases, porphyrins and so forth have been commonly employed and a number of the reviews regarding the HPLC of such metal complexes have been published.[1-5)]

8-Hydroxyquinoline-5-sulfonic acid (8-HQS)[6)] which is a chelating agent similar to 8-hydroxyquinoline has several characteristics suitable for the HPLC studies. 8-HQS reacts with most metal ions to form water-soluble complexes. Although the molar absorptivities of the 8-HQS complexes at the absorption peaks which lie at the longer wavelength above 350 nm are not very large, but these have another absorption maxima with the large molar absorptivities around 254 nm. The latter absorption maxima have been not used so far in spectrophotometry of the metals because the wavelengths are close to the absorption maximum of 8-HQS. In HPLC, however, the large molar absorptivities of the complexes around 254 nm may be useful for the detection of trace metals after separation. The formation constants of most metal-8-HQS complexes are as large as those of 8-hydroxyquinoline complexes, suggesting that they would be stable under the HPLC conditions.

As is well-known, 8-HQS has been widely used for the spectrophotometric and the fluorometric determination of trace metals. However, only an investigation on the fluorescence properties and HPLC separation of metals[7)] has been reported about the metal-8-HQS complexes. The purpose of the present work is to examine the use of 8-HQS as a precolumn complexing reagent for the reversed-phase HPLC of trace metal ions. The method provides the basis for the HPLC determination of Al(III), Cu(II), Ga(III), and Fe(III) by direct aqueous injection.

The HPLC system consisting of a Hitachi 655 pump unit, a Hitachi 638-0410 UV detector, a Rheodyne 7125 loop injector (20 µl), and a Shimadzu C-R3A recorder was used with a Merck LiChroCART column (250 mm x 4 mm I.D., 7 µm). A Hitachi 200 - 20 recording spectrophotometer and a Hitachi-Horiba F-7 ss pH meter were also used.

Methanol and acetonitrile were distilled in all-glass apparatus. The distilled/deionized water was further purified by using the Millipore Milli-Q system. All solvents were filtered through a 0.45 - µm filters before use. Analytical-reagent grade 8-HQS was obtained from Kanto Chemicals Co. All metal salts and other reagents used were of guaranteed reagent grade. The mobile phase was an aqueous/methanol/acetonitrile (70:20:10) solution containing 10^{-4} mol l^{-1} of 8-HQS, 4 x 10^{-2} mol l^{-1} of hexylamine hydrochloride, and 4 x 10^{-2} mol l^{-1} of ammonium acetate buffer (pH 4.25). The flow-rate of the mobile phase was 1.0 ml min^{-1}, and the UV absorption detection was made at 254 nm.

The recommended procedure is as follows. A sample solution containing Al(III), Cu(II), Ga(III), and Fe(III) was taken in a 10 - ml volumetric flask, and 3 ml of 2 x 10^{-3} mol l^{-1} 8-HQS solution was added. The solution was adjusted to pH 4.25 by the addition of 1 ml of 0.1 mol l^{-1} ammonium acetate solution and diluted to 10 ml. An aliquot (usually 20 µl) of this solution was then injected into the chromatograph.

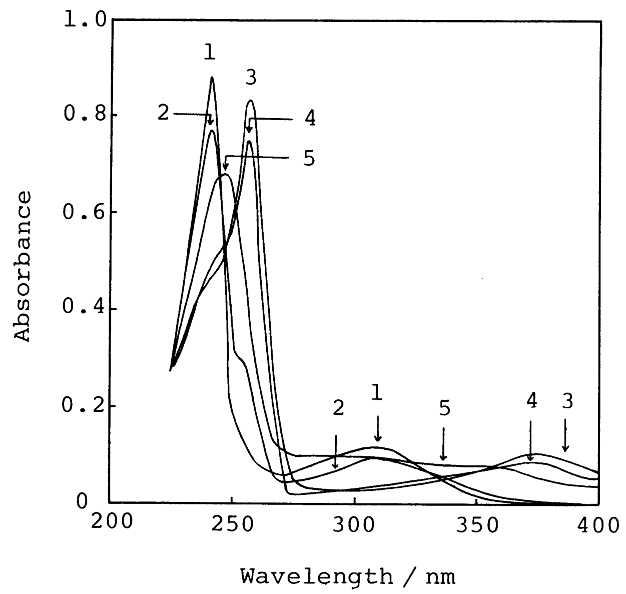

Fig.1. Absorption spectra of metal-8-HQS complexes.

1:8-HQS, 2:Al(III), 3:Cu(II), 4:Ga(III), 5:Fe(III). 8-HQS:3 x 10^{-5} mol l^{-1}, Al(III), Ga(III), Fe(III):1 x 10^{-5} mol l^{-1}, Cu(II): 1.5 x 10^{-5} mol l^{-1}. pH:4.25, reference:water/methanol/acetonitrile (70:20:10)

The absorption spectra of the 8-HQS complexes are shown in Fig. 1. The complexes have plural absorption peaks around 254 nm and above 350 nm. The molar absorptivities of the complexes around 254 nm are considerably large, but the absorption maxima are very close to each other and also to that of 8-HQS. Although this characteristics of the 8-HQS complexes is not preferable in conventional spectrophotometry, it is really desirable for the simultaneous detection of metal complexes at a fixed wavelength after HPLC separation.

The chromatographic behaviors of the 8-HQS complexes were investigated by using a Lichrosorb PR-18 (ODS, 7 µm) column with water/methanol/acetonitrile as the mobile phase. The hexylamine was added to the mobile phase as a counter cation, since the 8-HQS complexes are generally anionic species. Figure 2 shows a typical chromatogram for the separation of Al(III), Cu(II), Ga(III), and Fe(III) complexes. All four peaks are well resolved and separated from the peak of 8-HQS.

In order to establish the optimum experimental conditions, the effects of some variables on the chromatographic behaviors of Al(III), Cu(II), Ga(III), and Fe(III) complexes were examined. The content of methanol in the water/methanol mobile phase was varied from 60 to 20% V/V. Although the retention time of each complex increased with decreasing methanol content, adequate separation of the four complexes was not achieved. When acetonitrile was added to water/methanol system, the four peaks were reasonably separated. The well-resolved peaks suitable for the simultaneous determination of the four metal ions were obtained with water/methanol acetonitrile (70:20:10). The effect of the mobile phase pH on the retention behavior of the 8-HQS complexes were investigated in the pH range 3.5-5.5. The results are shown in Fig. 3. In the pH range 4.5 - 5.5, two peaks of the Al(III) complex appeared at the quite different retention times which might be corresponded to the different compositions. The condition of this pH range was unsuitable for the separation of four metals because the latter peak of Al(III) complex overlapped with the peaks of Cu(II) and Ga(III) complexes. The retention times of Cu(II), Ga(III), and Fe(III) complexes did not change so much in the pH range 3.5 - 4.25, but decreased significantly over pH 4.5. The optimum chromatogram for the determination of four metal ions was obtained with the mobile phase pH at 4.25.

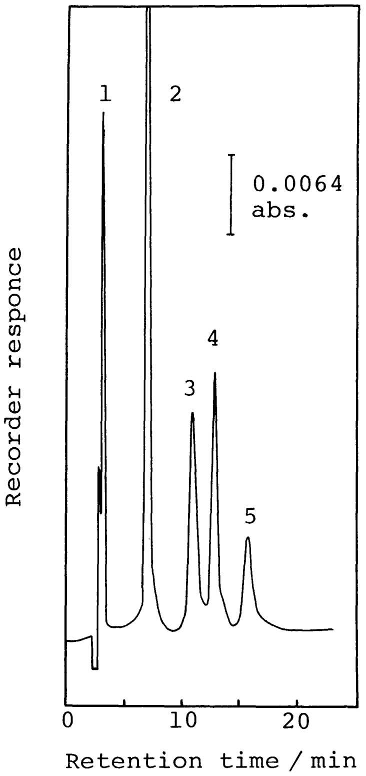

Fig.2. Chromatogram of metal-8-HQS complexes.

1:Al(III), 2:8-HQS,
3:Cu(II), 4:Ga(III),
5:Fe(III).
Metals : 1 μg ml^{-1} (20μl)

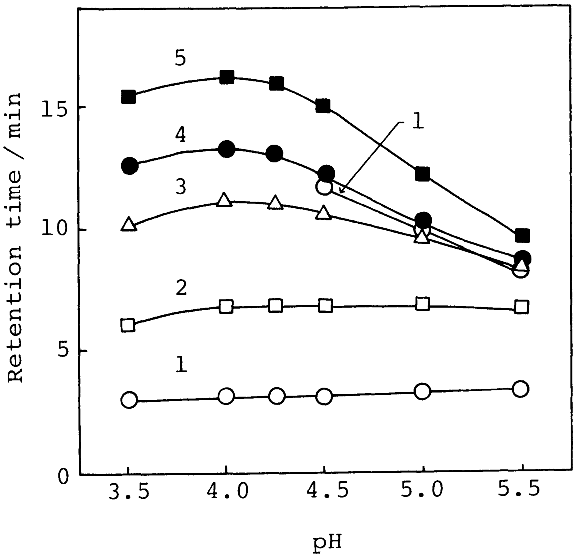

Fig.3. Variation of retention time with pH of mobile phase.

1:Al(III), 2:8-HQS, 3:Cu(II),
4:Ga(III), 5:Fe(III).

The chromatographic separation of Al(III), Cu(II), Ga(III), and Fe(III) complexes was also investigated by using the ion-pairing reagents, such as ethylamine, propylamine, butylamine, and hexylamine. The well-resolved peaks of the four complexes and 8-HQS were obtained only by the use of hexylamine. Figure 4 shows the effect of hexylamine hydrochloride concentration in the mobile-phase on the retention time of the four complexes and 8-HQS. The retention time of Al(III) complex was independent of the hexylamine hydrochloride concentration. On the other hand, the retention times of the Cu(II), Ga(III), and Fe(III) complexes increased with increasing the hexylamine hydrochloride concentration, and then gradually decreased. From these retention behaviors, it may be considered that Al(III) complex is a neutral or cationic species, while the Cu(II), Ga(III) and Fe(III) complexes are of the negative charge. The optimum concentration of hexylamine hydrochloride in the mobile phase was 4 x 10^{-2} mol l^{-1}. The peak heights of the four complexes became larger, and the peak symmetry was improved with the addition of 8-HQS in the mobile phase. The background noise of the chromatogram, however, increased with increasing the 8-HQS concentration. Then, the concentration of 8-HQS in the mobile phase was taken to be 1 x 10^{-4} mol l^{-1} for the optimum condition.

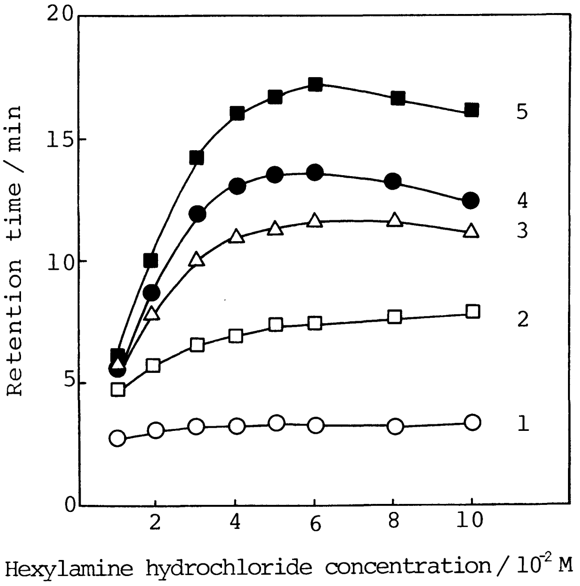

Fig.4. Variation of retention time with hexylamine hydrochloride concentration in mobile phase.

1:Al(III), 2:8-HQS, 3:Cu(II), 4:Ga(III), 5:Fe(III).

The peak height calibration curves obtained for 20 - µl injections were linear over the concentration range of 0.05 - 2 µg ml^{-1} for Al(III), 0.1 - 2 µg ml^{-1} for Cu(II) and Ga(III), and 0.2 - 2 µg ml^{-1} for Fe(III) at 0.064 a.u.f.s. The detection limits were 15 ng ml^{-1} for Al(III), 20 ng ml^{-1} for Cu(II), 15 ng ml^{-1} for Ga(III), and 50 ng ml^{-1} for Fe(III) at a signal-to-noise ratio of 3. The reproducibility of the present method was investigated for 0.2 µg ml^{-1} of each metal ion. The relative standard deviation was 3.2% for Al(III), 4.5% for Cu(II), 3.9% for Ga(III) and 7.6% for Fe(III) in the five replicate determinations.

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