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HIGHLY SELECTIVE DETERMINATION OF TRACE METAL IONS WITH 2,2'-DIHYDROXYAZOBENZENE BY ION-PAIR REVERSED-PHASE PARTITION HPLC-SPECTROPHOTOMETRIC DETECTION SYSTEM

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The 2,2'-dihydroxyazobenzene (DHAB) chelates of Al^{III}, Co^{II}, V^{V}, and Fe^{III} ions give the well-resolved peaks on a Yanapak ODS-T column using an aqueous methanol mobile phase containing tetrabutylammonium bromide. The metal ions in the ng cm^{-3} to sub-μg cm^{-3} range are selectively determined with 0.01 absorbance unit full-scale at 510 nm. The versatility of DHAB derivatives in the HPLC system is demonstrated.

Growing attention has been currently focussed on high performance liquid chromatography (HPLC) of metal chelates with reversed-phase partition (RP) mode (including ion-pair RP systems) in combination with highly sensitive spectrophotometric detection.[1-12] It has been found recently that those metal chelates having the following features are suitable for the RPHPLC system, especially when no chromogenic reagent is added in the eluent: 1) stable and inert,[9] 2) water soluble, and 3) having a high molar absorption coefficient. The water soluble chelates are still more suitable than the neutral hydrophobic ones, because of the good solubility in a polar aqueous mobile phase and of the possibility of achieving more delicate resolution with a broad set of RP separation parameters (surface type of packing, pH, ionic strength, and organic modifiers). Spectral requirements of chromogenic reagents for RPHPLC system are expected to be different from those for the conventional colorimetry in the following points: a) neither the color change on complexation, nor the spectral difference among the metal chelates, is essential, because the chelates and the reagent are separated on the column and are eluted at different times, b) a molar absorption coefficient of the order of 10^4 dm^3 mol^{-1} cm^{-1} is sufficient for the determination of 10^{-7} mol dm^{-3} level (ppb level for the first transition metals) when they are detected at 0.005 absorbance unit full-scale (aufs) range.

Some of 2,2'-dihydroxyazobenzene (DHAB) chelates have been found to meet the above and other requirements, that is, they are highly colored, kinetically inert, and water soluble. They have the metal to ligand stoichiometries of 1 : 1 or 1 : 2.[13-15] The anionic DHAB chelates of Al^{III}, Co^{II}, Fe^{III}, and V^{V} ions are separated on a C_{18}-bonded silica packing by the ion-pair RP mode, while a number of other common cations give no elution peaks because of labile nature of their DHAB chelates.

In this paper, the elution behavior of those DHAB chelates in the ion-pair RPHPLC system is described, and the rapid and selective photometric method is established for the trace determination of Al, Co, Fe, and V.

The HPLC system used consisted of a TWINCLE pump unit, a UVIDEC 100-III spectrophotometric detector, and a VL-611 loop injector (100 mm^3) from Japan Spectroscopic Co. Ltd. The detector setting of 0.01 aufs range at 510 nm was used for 10 mV recorder out-put. A Yanapak ODS-T column (4 mm i.d. x 250 mm length from Yanaco) was used. The reagent, DHAB, was used as received from Dojindo Lab. and the stock solution (ca. 1.2 x 10^{-3} mol dm^{-3}) was prepared by dissolving it in a 10^{-3} mol dm^{-3} of sodium hydroxide solution containing 10 wt% PONPE-20 (4-(nonyl)-phenoxypolyoxyethyleneglycol with 20 oxyethylene units from Tokyo Kasei Kogyo Co. Ltd.) in a Teflon beaker and was stored in a polyethylene bottle. PONPE-20 was used for solubilization of DHAB. Metal ion stock solutions were prepared from the chlorides or the nitrates except vanadium(V) solution, which was prepared from ammonium metavanadate. Tetrabutylammonium bromide (TBABr) was used as obtained from Tokyo Kasei Kogyo Co. Ltd. All the other reagents and solvents used were of guaranteed reagent grade. As a mobile phase, an aqueous methanol (63.3 wt%) containing 6.9 x 10^{-3} mol kg^{-1} TBABr, 5 x 10^{-3} mol kg^{-1} sodium acetate, and 10^{-4} mol kg^{-1} disodium EDTA was used. An aqueous acetonitrile solution as an eluent gave the unsatisfactory resolution of the chelates.

Typical procedure is as follows: the acidic sample solution (less than 40 cm^3) containing less than 10 μg of each metal ions was taken into a Teflon beaker and was mixed with 4 cm^3 of the DHAB solution and 2.5 cm^3 of tris-HCl buffer solution (pH 7.8). The solution was heated for 10 to 20 min in a water bath at 90 °C and diluted to 50 cm^3 after cooling. An aliquot of the solution was injected with a 100 mm^3 loop injector.

Absorption spectra of DHAB and the metal chelates in neutral PONPE-20 solution are shown in Fig. 1. The detection wavelength was set at 510 nm, while the sensitivity for V^V and Fe^{III} ions may be increased when they are detected at their λ_{max} wavelengths.

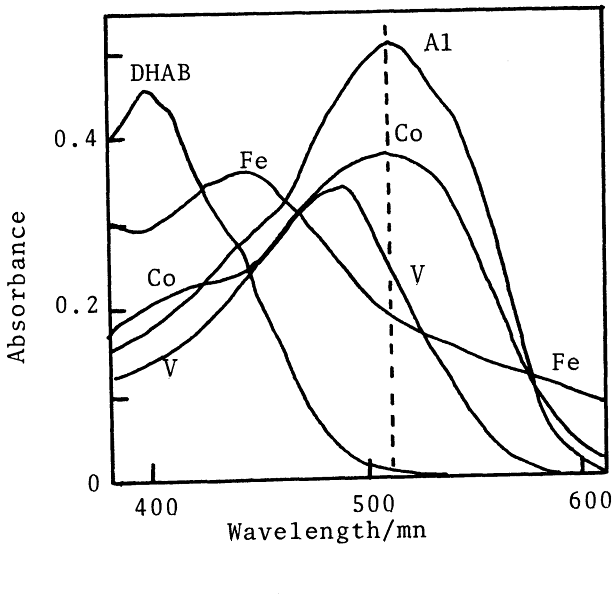
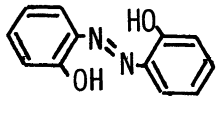


Fig. 1. Absorption spectra of DHAB and the metal chelates in neutral PONPE-20 solution with 1 cm cells.

C_M = 4.0 x 10^{-5} mol dm^{-3}, C_{DHAB} = 4.8 x 10^{-5} mol dm^{-3}, pH 7.1. PONPE-20, 0.8 wt%.



DHAB

The color development of the DHAB chelates is generally slow even in slightly alkaline solutions (pH 7.8), hence the reaction mixture was heated to 90 °C for saving analysis time. The typical chromatogram is shown in Fig. 2. The mobile phase was buffered at pH 7.5 ± 0.5 with sodium acetate and disodium EDTA, and the latter acts also as a masking agent for the metal ion contaminants from the wetted wall of the HPLC system. The DHAB chelates of V^{V}, Co^{II}, Al^{III}, and Fe^{III} ions can not be destroyed by EDTA along the HPLC column at room temperature.

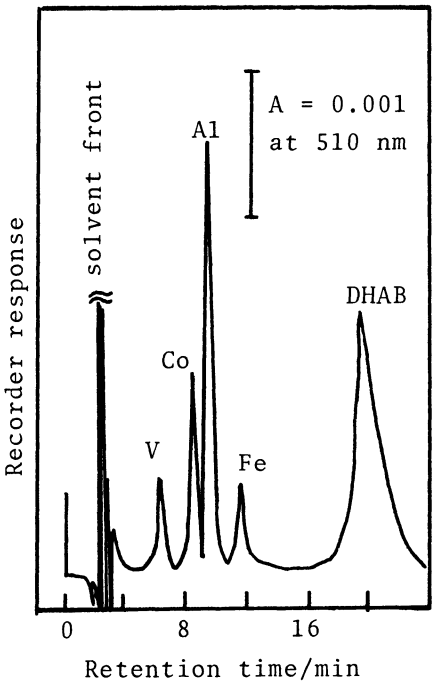


Fig. 2. Ion-pair RPHPLC separation of the DHAB chelates on a Yanapak ODS-T column.

$C_M/10^{-7}$ mol dm^{-3}: V,4.00; Co,4.35; Al,4.01; Fe,3.96; Cu,4.13; Ni,3.96; Mn,3.98.

$C_{DHAB} = 9.6 \times 10^{-5}$ mol dm^{-3}; pH 7.8 (tris-HCl buffer 8×10^{-3} mol dm^{-3}).

PONPE-20, 0.8 wt%.

Mobile phase: given in the text.

Flow rate, 1 $cm^3 min^{-1}$.

Regardless of the presence of EDTA in the eluent, Cr^{III}, Mn^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, and alkaline earth metal ions gave no elution peaks on the chromatogram. Up to 4×10^{-5} mol dm^{-3} in their total concentration, these metal ions gave no significant effects on the signals of the four metal ions to be analyzed. In fact, the somewhat tedious off-line separation prior to injection would be avoided in many cases. Cobalt and aluminium tend to interfere with each other at higher concentrations owing to relatively low resolution of their elution peaks. The linear ranges of the peak-height calibration curves for the metal ions at 0.01 aufs are summarized in Table 1. The proposed method is highly sensitive to Al^{III} ion whose detection limit is 0.4 ng cm^{-3} (0.4 ppb). The other metal ions in ng cm^{-3} to sub-μg cm^{-3} range are also readily determined with the ion-pair RPHPLC method. The relative standard deviations for the metal ions at 4×10^{-7} mol dm^{-3} obtained with the four sample determinations are V,3.5%; Co,2.1%; Al,1.3%; and Fe, 3.6%. Teflon or polyethylene wares should be used because serious aluminium contamination, most likely from glass beakers, was observed (about 5×10^{-9} mol in a 50 cm^3 final solution).

It is quite striking that even the simplest compound among 2,2'-dihyroxyazo derivatives, DHAB, serves as an excellent RPHPLC reagent for trace metal analysis. In this regard, other substituted 2,2'-dihydroxyazo analogues are also expected to have unique and attractive features in the RPHPLC-spectrophotometric detection systems.

The determination of trace aluminium in ground water by the method described here is now in progress.

Table 1. Linear ranges of the peak-height calibration curves at 0.01 aufs. Experimental conditions are the same as in Fig. 2.

Metal ion	Linear range[a)] $C_M/10^{-8}$ mol dm^{-3} [C_M/ng cm^{-3}]	Metal ion	Linear range[a)] $C_M/10^{-8}$ mol dm^{-3} [C_M/ng cm^{-3}]
V^V	4.0 - 200 [2.0 - 100]	Fe^{III}	6.5 - 200 [3.5 - 112]
Co^{II}	2.0 - 120 [1.2 - 71]	Al^{III}	1.4 - 80 [0.4 - 22]

a) Lower limits are corresponding to the signals twice the peak-to-peak base-line noise.

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