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Separation Behaviors of Aluminum(III) and Indium(III) Complexes with 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone in High-performance Liquid Chromatography

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Aluminum- and indium-PMBP chelates were prepared and separated by liquid chromatography on an ODS column using acetonitrile as a mobile phase. The retention time of indium chelate varied significantly with a mobile phase of acetonitrile containing sodium chloride.

The separation of indium from aluminum has been of importance in analytical determinations, since indium is frequently encountered together with this metals. In this study, the separation and simultaneous determination of aluminum and indium in the form of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone(PMBP) chelates by high-performance liquid chromatography(HPLC) are described. The use of HPLC for separation of metal compounds, especially in the form of chelates, has increased rapidly.[1,2] PMBP is an unselective chelating agent that forms water-insoluble chelates with most common metals. These PMBP chelates are absorbed strongly in the UV, and thus may be quite amenable to chromatographic separation and analysis. Aluminum- and indium-PMBP chelates both exhibit maximum absorption at 290 nm, making them suitable for simultaneous detection at a fixed wavelength. These metal pyrazolonates were prepared by mixing PMBP dissolved in methanol and the appropriate amount of metal salts in water. The mixture was heated to 70 °C with stirring for about 1 h. The colored precipitate was filtered off, washed with water and methanol, and finally dried in a vacuum oven. The compositions of these chelates were found by elemental analysis to be metal:PMBP=1:3. Metal chelate solutions required for the chromatographic separation were prepared by dissolving the corresponding metal pyrazolonates in dioxane. The HPLC system consisted of an 880-PU pump, an 875-UV spectrophotometric detector(both from JASCO, Tokyo), and a Rheodyne injector(Model 7125). A Shim-pack CLC-ODS(M) column(250 x 4.6 mm I.D., 5 μm) was used. Chromatographic separations were carried out at room temperature, using a mobile phase flow-rate of 1.0 ml/min.

In the initial studies using acetonitrile as a mobile phase, good separation of aluminum and indium was obtained as shown in Fig.1. When a mobile phase of acetonitrile-water(100:5) mixture was used, the indium chelate did not appear on the chromatogram, owing to on-column dissociation. The dissociation of the chelate

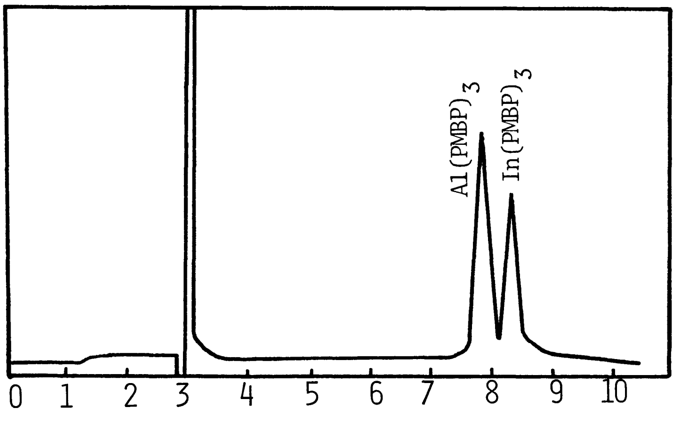

Fig.1. Separation of Al- and In-PMBP complexes on ODS column. Mobile phase: acetonitrile; flow rate: 1 ml/min; detector: UV detector at 290 nm; Al-, In-PMBP complexes: 8x10^{-6} M, 5 µl.

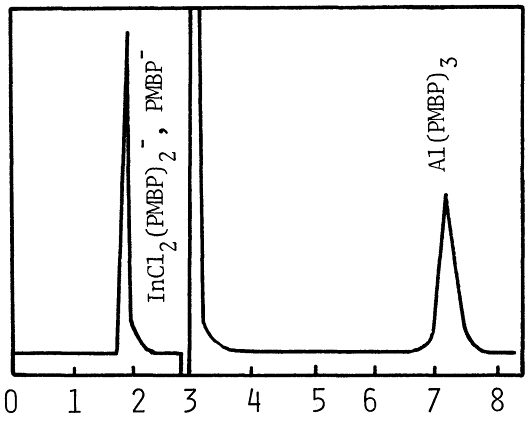

Fig.2. Separation of Al-, In-PMBP complexes. Mobile phase: acetonitrile saturated with NaCl. Other conditions were the same as in Fig.1.

likely occurred even if the mobile phase contained trace amounts of water. However, when the acetonitrile saturated with NaCl was used as the mobile phase, the separation of aluminum and indium chelates was dramatically improved, where the indium chelate showed no retention, as can be seen in Fig.2. On the other hand, the retention time of aluminum chelate was little affected by this eluent. Similar chromatographic behavior was also observed with acetonitrile saturated with LiCl as a mobile phase. The fraction of the first peak in Fig.2 was collected manually and the presence of indium in the fraction was confirmed by atomic absorption spectrophotometry.

It should be noted that the HPLC behavior of indium was strongly influenced by the NaCl or LiCl in acetonitrile. This phenomenon is probably related to the lability of the indium chelate.

In the synergic extraction study on indium with PMBP and aliquat($TOMA^+ \cdot Cl^-$), Brunette et al.$^{3)}$ have recently reported that the indium exists in the form of $InCl_2(PMBP)_2^- \cdot TOMA^+$ in the toluene solution. In a polar solvent such as acetonitrile, however, ionization of the indium chelate may occur to some extent. Thus, the charged species passed through the column without distribution for the stationary phase. Therefore, the chromatographic behavior of the indium chelate may be reasonably well explained by assuming that the chelate decomposes to the negatively charged species, as shown by the following equation:

$$In(PMBP)_3 + 2Cl^- = InCl_2(PMBP)_2^- + PMBP^-$$

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