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Note

Reversed-phase high-performance liquid chromatography of aluminium(III) and indium(III) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone

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Reversed-phase high-performance liquid chromatography (RP-HPLC) is a well known method for the separation and determination of organic compounds. In recent years, great interest has been shown in the potential of this method for metal ions and many research papers have been published. Metal ions are commonly separated and determined by RP-HPLC as their chelates. So far, many chelating agents, such as acetylacetone[1], benzoylacetone, quinolin-8-ol[2], dithiocarbamic acids[3] and 2-(5-bromopyridylazo)-5-diethylaminophenol[4], have been employed.

We now introduce 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) as a chelating agent for studies of the chromatographic behaviour of aluminium(III) and indium(III). PMBP has frequently been used as an extraction agent for various metals[5,6] and is known to have the ability to form stable chelates with most metals non-selectively at around pH 7. This suggests that it is possible to use PMBP for RP-HPLC studies of metals.

The purpose of this work is to search for the optimum conditions for the separation and determination of aluminium(III) and indium(III) in the form of PMBP chelates by RP-HPLC with spectrophotometric detection.

EXPERIMENTAL

Materials

PMBP was prepared and recrystallized as reported previously[5].

The PMBP chelates of aluminium(III) and indium(III) were synthesized as follows. About 1 g each of potassium aluminium sulphate and indium chloride were dissolved in water. The solutions were adjusted to about pH 7 with ammonium citrate and ammonia. Then the PMBP–methanol solution was added in a molar ratio of 1:3 (metals to PMBP). The mixture was allowed to react thoroughly in a water-bath at

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temperature of 70–80°C with agitation. The precipitates were washed with deionized water after filtration. The products were then dissolved and agitated in methanol by heating to remove the unreacted PMBP. After separation of the two phases, the refining process was repeated twice. The precipitates were then dried under vacuum and used as our testing chelates. The identities of the two PMBP chelates synthesized were confirmed by elemental analysis, as shown in Table I.

All other reagents and solvents were of analytical reagent grade, obtained from commercial sources. The solvents were degassed before use as the mobile phase.

Preparation of synthetic mixture

Sample solution containing 0.284 mg of aluminium and 5.23 mg of indium was taken in a 100-ml beaker, 10 ml of 0.1 *M* ammonium citrate solution and 10 ml of water were added and the mixture was adjusted to pH 5 with 1 *M* ammonia solution. Then 30 ml of 0.01 *M* PMBP solution in methanol were added with stirring and the beaker was placed in a water-bath at 70°C for at least 1 h to ensure complete precipitation of metal–PMBP complexes. The product (containing free PMBP) was separated by filtration and washed with water, then dissolved in 15 ml of dioxane. The solvent (containing a small amount of water) was then evaporated and the precipitate was dried completely at 70–75°C under vacuum, then dissolved in 50 ml of dioxane. A 5 μl aliquot of this dioxane solution was injected into the chromatograph. Acetonitrile was used as the mobile phase. The flow-rate was 1.0 ml/min. The amount of each metal was determined by measuring the peak heights.

Instrumentation

The high-performance liquid chromatograph consisted of a Japan Spectroscopic Model 880-PU pump, a Rheodyne injector and a Japan Spectroscopic Model 875-UV detector, together with a Rikadenki Multi Pen recorder. A Shim-Pack CLC-ODS(M) column 25 (250 mm × 4.6 mm I.D.) was used. The detector was operated at 290 nm, the mobile phase flow-rate was 1.0 ml/min and the recorder chart speed was 1.0 cm/min.

The PMBP chelates of aluminium(III) and indium(III) synthesized were dissolved in dioxane and were mixed to give suitable concentrations. An aliquot of the sample solution was injected into the chromatograph.

TABLE I

ELEMENTAL ANALYSIS OF THE CHELATES SYNTHESIZED

Complex	*Element*	*Calculated (%)*	*Found (%)*
$Al(PMBP)_3$	C	71.35	71.38
	H	4.54	4.37
	N	9.79	9.76
$In(PMBP)_3$	C	64.70	64.46
	H	4.16	4.01
	N	8.88	8.66

RESULTS AND DISCUSSION

The ultraviolet absorption spectra for PMBP chelates of aluminium(III) and indium(III) in dioxane at a concentration of $1.28 \cdot 10^{-6}$ M are shown in Fig. 1. Two maxima appear at 240 and 290 nm for each chelate. However, as at 240 nm the noise level was high due to absorption by the solvent (dioxane), 290 nm was chosen. The molar absorptivities for aluminium(III) and indium(III) chelates in dioxane at 290 nm calculated from the above spectra were found to be $6 \cdot 10^4$ and $5.5 \cdot 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$, respectively, indicating that an highly sensitive determination of aluminium(III) and indium(III) at 290 nm is feasible.

The combination with acetonitrile of several solvents, such as water, methanol and dioxane, as the dissolving solvent for PMBP chelates, was investigated as the mobile phase for chromatography of the two PMBP chelates of interest. The results of using acetonitrile–water system as the mobile phase for the separation of PMBP chelates of aluminium(III) and indium(III) are shown in Fig. 2. The retention time of the aluminium chelate increased with increasing content of water in acetonitrile, while the peak related to the indium chelate was at first very low and then disappeared abruptly. However, as the peak of indium chelate disappeared, a new broad peak was seen near the peak of dioxane, indicating that dissociation of indium chelate may occur during the chromatographic process. Noda *et al.*[7] think this may be due to the hydrolysis of indium chelate.

A similar result for the indium chelate was obtained by adding methanol to acetonitrile, which was used as the main component of the mobile phase. When increasing the methanol content, the peak of indium chelate became lower and gradu-

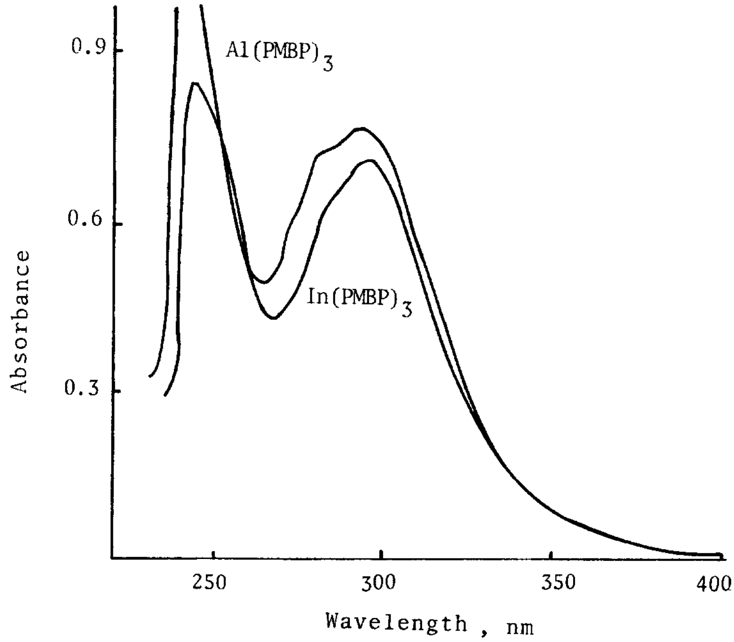

Fig. 1. Absorption spectra of $Al(PMBP)_3$ and $In(PMBP)_3$ ($1.28 \cdot 10^{-6}$ M) in dioxane.

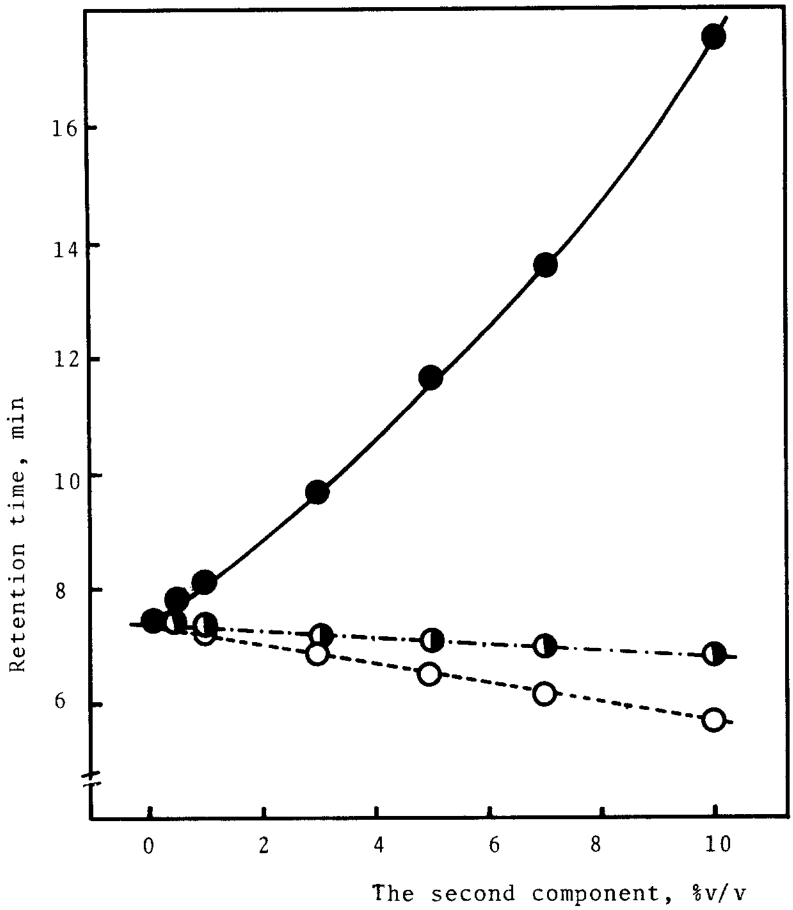

Fig. 2. Effect of the second component in acetonitrile on the retention time of Al(PMBP)$_3$ (8.0 · 10^{-6} *M*). ○, Acetonitrile–dioxane; ●, acetonitrile–water; ◑, acetonitrile–methanol.

ally disapppeared. On the other hand, when methanol was added to the mobile phase, the retention time of the aluminium chelate decreased slightly on increasing the methanol content and the elution peaks were sharp and symmetric, indicating that the PMBP chelate of aluminium was stable enough for the RP-HPLC determination.

Both aluminium(III) and indium(III) chelates can be dissolved in dioxane more easily than in acetonitrile or in methanol; thus the disappearance of the indium chelate peak may be suppressed by adding dioxane to acetronitrile. The effects of the dioxane content in the mobile phase on the retention of aluminium and indium chelates are shown in Fig. 2. The retention time of the two metal chelates decreased on increasing the dioxane content and the phenomenon of the disappearance of the indium chelate peak was no longer observed. However, the retention times of the two chelates became closer and their separation became worse when the content of dioxane increased. The optimum separation condition was obtained when the mobile phase was dioxane–acetonitrile (0.1:100).

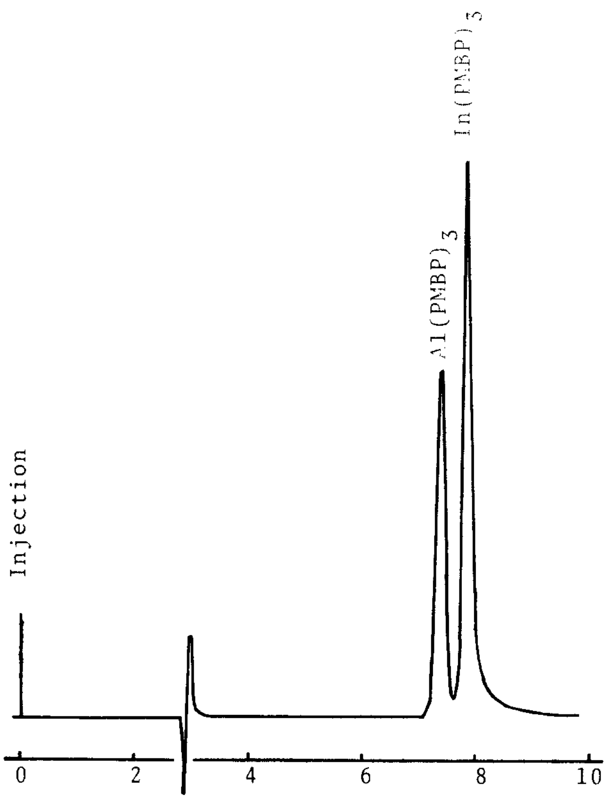

Fig. 3. Separation of $Al(PMBP)_3$ ($2.0 \cdot 10^{-4}$ *M*) and $In(PMBP)_3$ ($6 \cdot 10^{-4}$ *M*) with acetonitrile as the mobile phase. Volume injected: 5 μl.

TABLE II

ANALYTICAL RESULTS FOR ALUMINIUM AND INDIUM IN A SYNTHESIZED SAMPLE

Standard values: Al, 0.284 mg; In, 5.23 mg.

Expt. No.	*Al (mg)*	*In (mg)*
1	0.27	5.28
2	0.28	5.22
3	0.27	5.22
4	0.28	5.31
$\bar{x}$	0.28	5.26
σ	$5.8 \cdot 10^{-3}$	0.045
Recovery (%)	98.6	100.6

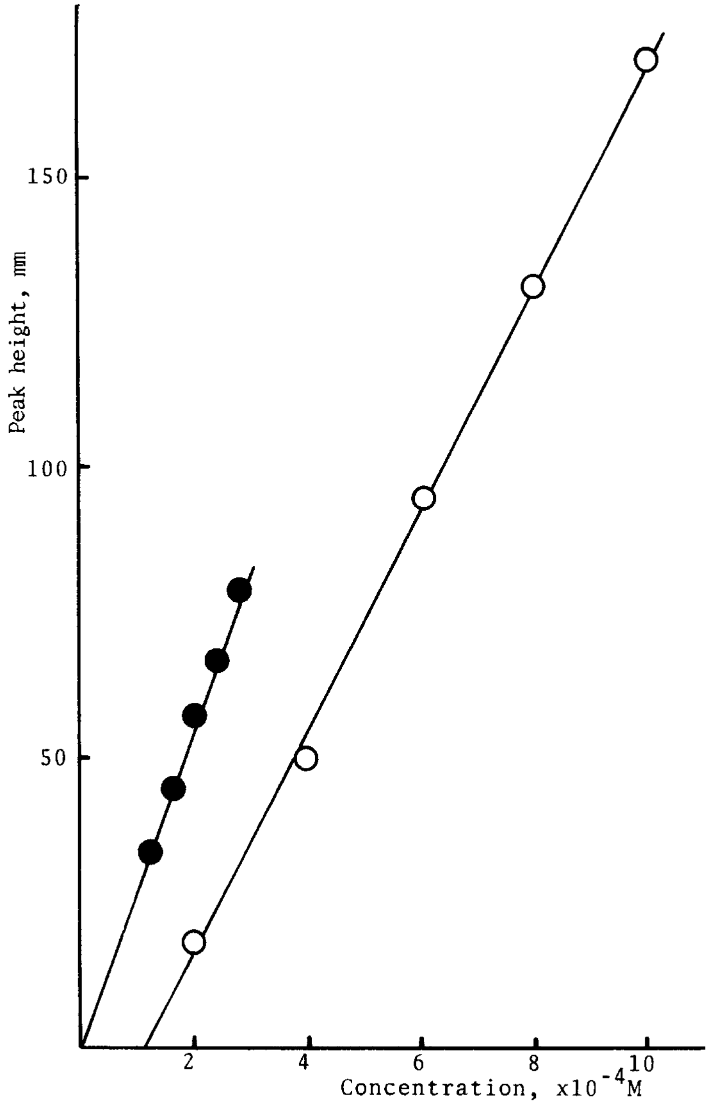

Fig. 4. Calibration graphs for Al(PMBP)$_3$ (●) and In(PMBP)$_3$ (○). Mobile phase: acetonitrile. Flow-rate: 1.0 ml/min. Volume injected: 5 μl.

An attempt was also made to separate the chelates simply by using acetonitrile as the mobile phase. A typical chromatogram is shown in Fig. 3 and it is clear that a similar result has been achieved.

The calibration graphs of peak height *versus* metal concentration injected were linear in concentration ranges 0–2.8 · 10^{-4} *M* for aluminium(III) and 2 · 10^{-4}–10 · 10^{-4} *M* for indium(III), as shown in Fig. 4. In the case of the indium chelate, the line does not pass through the origin, which may be due to the interference from trace amounts of water contained in acetonitrile, or from the silanol groups remaining in the stationary phase.

Finally, the method developed was applied to the separation and determination of aluminium and indium in synthetic mixtures. The results showed good agreement with the certified values (Table II).

CONCLUSION

The separation of aluminium(III) and indium(III) PMBP chelates has been achieved simply by using acetonitrile or by adding a smalll amount of dioxane to acetonitrile as the mobile phase. However, because of the lability of the indium(III) PMBP chelate, its peak can easily be destroyed by adding only a small amount of water to the mobile phase. It is therefore possible to determine aluminium(III) in samples containing indium(III) selectively by the proposed method.

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