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High-performance liquid chromatographic determination of aluminium and iron(III) in solar salt in the form of their 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone chelates

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ABSTRACT

Aluminium and iron(III) ions in solar salts were separated and simultaneously determined in the form of their 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) chelates by HPLC. Four imported solar salt samples were subjected to this investigation. The samples were dissolved in dilute nitric acid with heating. An aliquot of the solution was pipetted and adjusted to pH 3 with acetate buffer, then 10 ml of 0.02 M PMBP–methanol solution were added. The chelates obtained were dissolved in dioxane and 10 μl were injected and analysed by HPLC. The determinations were completed within 20 min and the recoveries of each metal were satisfactory. Divalent metal ions did not interfere under the same chromatographic conditions.

INTRODUCTION

A knowledge of the presence of various trace metals in sodium chloride samples is important for the quality control of salt. Therefore, the determination of trace metals in such samples is of great value [1–3]. Interference by NaCl is often troublesome in the analysis of solar salt for trace metals, and the latter are usually separated and concentrated by liquid–liquid extraction and by coprecipitation techniques and subsequently determined by a variety of methods. The major advantage of the coprecipitation technique is that a large volume of sample solution can be used in the concentration of desired elements. In this study we applied the coprecipitation technique to the concentration of aluminium and iron in solar salt samples.

The high-performance liquid chromatographic (HPLC) separation and determination of metals in the form of chelates is gaining increasing popularity and many chelating agents have been introduced

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[4–8]. The ligands used need to have such properties as a high reaction ability with most metals, formation of stable chelates over a wide pH range and formation of chelates with high molar absorptivities in the UV or visible region.

In previous studies, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was used for the group extraction and separation of trace metals with subsequent atomic absorption spectrometric analysis [9–11]. PMBP is an excellent complexing agent of metals owing to the high reactivity and stability of its complex. It satisfies well the conditions for the prederivatization of metal ions for HPLC determination. The chromatographic behaviour and simultaneous determination of Al and In have been published previously [12–14]. These methods would be of value especially for the selective separation of In in Al and Ga.

In this paper, the use of PMBP as a precolumn derivatizing agent for the mutual separation and determination of Al and Fe(III), which had been concentrated by PMBP coprecipitation, by HPLC in imported solar salt samples is reported.

EXPERIMENTAL

Apparatus and reagents

The analytical HPLC system consisted of a Japan Spectroscopic (JASCO) Model 880-PU pump and Model 875-UV spectrophotometric detector and a Rheodyne Model 7125 injector with a 20-μl injection loop. The recorder was a CR4A Chromatopak (Shimazu). A Chemcosorb 5-ODS-UH column (250 × 4.6 mm I.D.) was used throughout. The PMBP chelates of Al and Fe(III) were synthesized as described previously [12] and their composition was found by elemental analysis to be 1:3 (metal: PMBP). The purities were found to be *ca.* 94% for Al–PMBP and 100% for Fe–PMBP.

All solvents and reagents were of analytical-reagent grade.

Al and Fe(III) stock standard solutions were prepared by dissolving 21.5 and 22.2 mg of Al– and Fe(III)–PMBP, respectively, in dioxane and diluting to 25 ml with dioxane, giving a concentration of $1 \cdot 10^{-3}$ M for each metal. The solutions were mixed to make a $2.5 \cdot 10^{-5}$ M solution of Al or Fe by appropriate dilution with dioxane. Dioxane was chosen as the solvent for dissolution of the chelates because it is more efficient than other solvents such as acetonitrile and methanol.

Procedure

Chromatographic separations were carried out at room temperature using pure acetonitrile as the mobile phase at a flow-rate of 1.0 ml min^{-1}. An aliquot of the solution was injected with a 20-μl loop injection in all instances. The spectrophotometric detector was set at 245 nm.

Application

The proposed method was applied to the determination of Al and Fe(III) in solar salt samples imported from Australia and Mexico. A sample of about 40 g was dissolved on a thermostated hotplate (100°C) in 150 ml of water containing 5 ml of concentrated nitric acid, then the solution was diluted to 200 ml with distilled water. A 20-ml aliquot of the sample solution was pipetted into a 100-ml beaker and the pH was adjusted to about 3 with 1 M sodium acetate. A 10-ml volume of 0.02 M PMBP solution in methanol was then added, and the solution was heated to 90°C while being stirred

on a water-bath for about 1 h. The precipitate was filtered off, washed with water and finally dissolved in and diluted to 25 ml with dioxane. A 10-μl aliquot of the sample solution was injected into the chromatograph and the determination of the two metals was carried out with the dioxane solution of pure chelates as a standard. Then 1 ml of a standard solution containing 14 and 30 μg of Al and Fe, respectively, was added to the 20 ml of salt solution and treated as above. The recoveries of the two metals were calculated.

RESULTS AND DISCUSSION

The absorption spectra of Al– and Fe(III)–PMBP chelates were measured in dioxane solution. Both Al– and Fe(III)–PMBP chelates exhibit maximum absorption at 245 nm, as shown in Fig. 1. The molar absorptivities of Al– and Fe(III)–PMBP chelates in dioxane at 245 nm were found to be $5.4 \cdot 10^{4}$ and $7.4 \cdot 10^{4}$ dm^{3} mol^{-1} cm^{-1}, respectively, making them suitable for trace analysis by HPLC because of the excellent sensitivities. In this study, 245 nm was chosen as the detection wavelength.
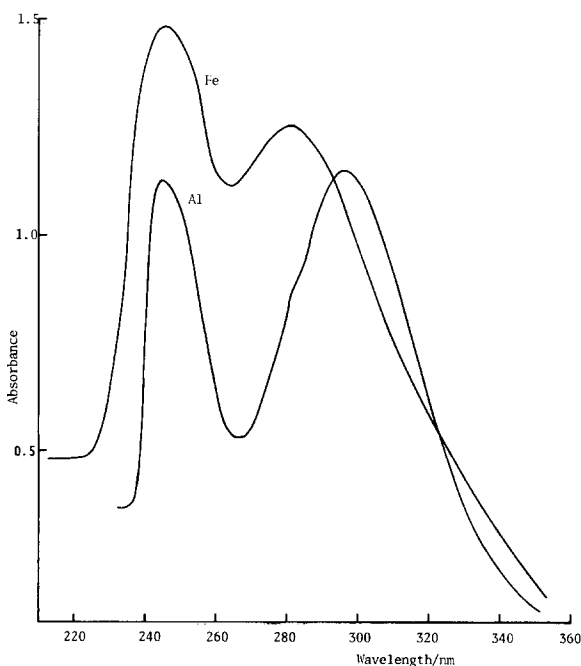

Fig. 1. UV spectra of PMBP chelates in dioxane. Al(PMBP)$_3$ and Fe(PMBP)$_3$ concentrations, $2.0 \cdot 10^{-5}$ M.
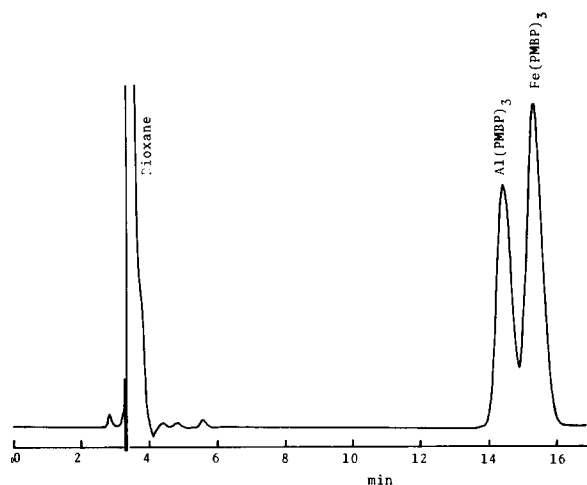
Fig. 2. Chromatograms of Al– and Fe–PMBP chelates with pure acetonitrile as the mobile phase. Al(PMBP)$_3$ and Fe(PMBP)$_3$ concentrations, 2.5 · 10^{-5} M.
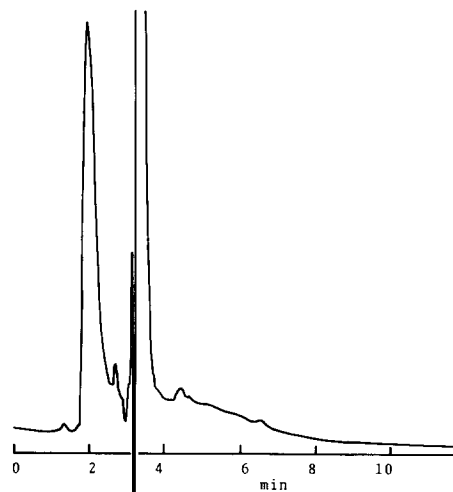

Fig. 3. Chromatogram of Al– and Fe–PMBP chelates with methanol as the mobile phase. Al(PMBP)$_3$ and Fe(PMBP)$_3$ concentrations 2.5 · 10^{-5} M.

In the initial studies using acetonitrile as the mobile phase, a good separation of Al– and Fe(III)–PMBP chelates (eluted in that order) was obtained, as shown in Fig. 2. Pure acetonitrile was found to be the most suitable mobile phase for the separation of these two chelates in the investigated organic solvents (methanol, ethanol and water–actonitrile).

When pure methanol was used as the mobile phase, the peaks of the Al– and Fe(III)–PMBP chelates disappeared and a new peak was observed before the dioxane peak, as shown in Fig. 3. With ethanol, the two elements were also not separated and co-eluted with dioxane. This appearance of a new peak before the dioxane peak and lack of retention are due to ionization in the column, the charged species of the chelates passing through the column without distribution to the stationary phase. We did not pursue this point further because the aim of this study was to determine the Al and Fe under optimum conditions.

The effect of the water content in acetonitrile on the separation of the chelates was investigated in the range of 0–10% (v/v). The retention time of each chelate increased with increasing of water content in the acetonitrile, and some dissociation of the Fe–PMBP chelate was also observed. The elution of the two chelates took longer than 1 h and no peaks were observed for the Al– and Fe(III)–PMBP che-

lates; some new peaks, most of which overlapped with the dioxane peak, were observed before and after the dioxane peak when acetonitrile containing > 10% (v/v) of water was used as the mobile phase. These results suggest that the complexes were decomposed in the column by water. Dissociation of the chelate is presumably due to the hydrolysis of these chelates in the chromatographic process.

Fig. 4 shows the results of an attempt to separate PMPB chelates of Al, Fe(III), Mn(II), Zn, Ni, Co (II) and Pb using pure acetonitrile as the mobile phase. The peaks for the Al and Fe(III) chelates were well resolved, whereas for the other chelates co-eluted immediately behind the dioxane peak, indicating that the other metals do not interfere in the presence of a tenfold molar excess. The retentions of the chelates mainly depend on the charge of the central metal ion and on the molecular size of the chelate; hence there would be no difficulty in the mutual separation of di- and trivalent cations.

Fig. 5 shows the calibration graphs obtained for the Al– and Fe(III)–PMBP chelates. The linearity of both graphs is good in the metal concentration ranges 0–5 · 0^{-5} M with a 10-μl injection. The detection limits, defined as the concentrations where the peak height was three times the background, were ca. 13 and 28 μg/l for Al and Fe, respectively when the injection volume was 20 μl. The precision
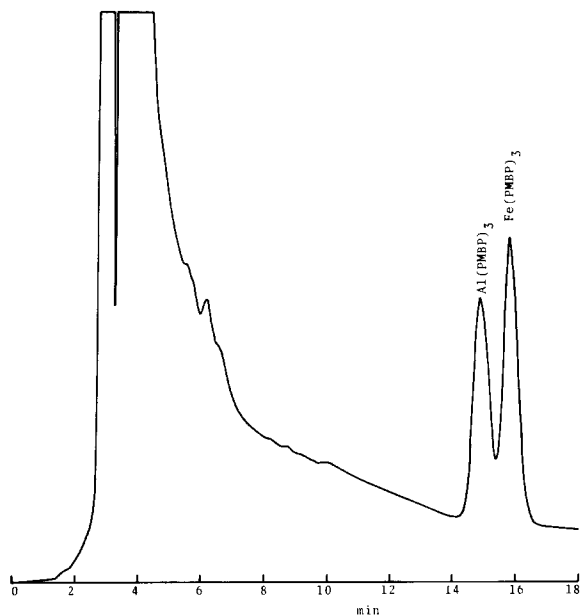
Fig. 4. Chromatogram of metal–PMBP chelates with acetonitrile as the mobile phase. Al– and Fe–PMBP chelate concentrations, $2.5 \cdot 10^{-5}$ M; Mn–, Co–, Ni–, Pb– and Zn–PMNB chelate concentrations, $2.5 \cdot 10^{-4}$ M.
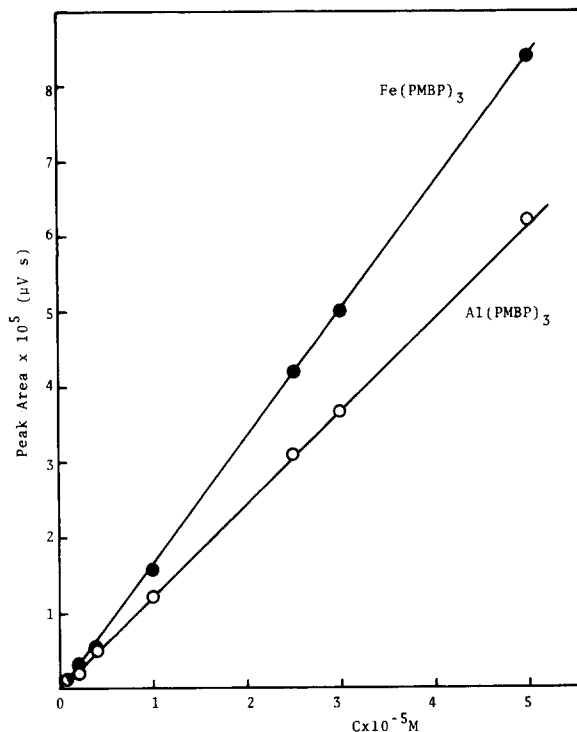

Fig. 5. Calibration graphs for Al– and Fe–PMBP chelates.

of the peak height was excellent for five determinations of $2.5 \cdot 10^{-5}$ M Al and Fe, with relative standard deviations of 1.5% for Al and 1.0% for Fe.

A solar salt sample was dissolved (as described in the *Application* section) and the proposed method was applied to the determination of Al and Fe(III). The contamination of the solar salt with Al and Fe may be mainly caused by traces of soil and rust from the chemical tanker. The Al and Fe(III) levels in the soil probably vary with the method used for the dissociation of the salt; however, in this study, the salt sample was dissociated as described above. Fig. 6 shows a chromatogram for the solar salt sample. The larger peak preceding the Al– and Fe(III)–PMBP chelate peaks is due to the excess of PMBP; this peak did not affect the separation of these chelates.

The results for the determination of Al and Fe (III) in four solar salt samples by the proposed method are given in Table I. The results of recovery tests are also given. The recoveries of Al and Fe(III) added to the sample were 88.0–95.3 and 92.0–99.7%, respectively.
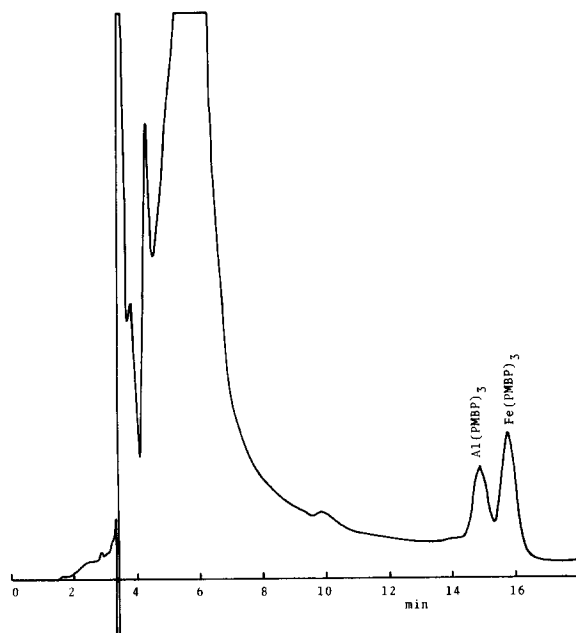

Fig. 6. Chromatogram obtained for solar salt sample.

TABLE I

ANALYTICAL RESULTS FOR Al AND Fe IN SOLAR SALTS

Results are averages of two determinations.

Sample[a]	Taken (g)	Element	Added (µg)	Found (µg)	Found in salt (ppm)	Recovery (%)
SA1	3.85	Al	0.0	6.3	1.6	
		Fe	0.0	17.6	4.6	
		Al	15.0	20.3		93.3
		Fe	30.0	47.5		99.7
SA2	3.93	Al	0.0	4.8	1.2	
		Fe	0.0	9.5	2.4	
		Al	15.0	18.0		88.0
		Fe	30.0	38.3		96.0
SA3	3.91	Al	0.0	5.1	1.3	
		Fe	0.0	7.1	1.8	
		Al	15.0	19.4		95.3
		Fe	30.0	37.0		99.6
SM	3.93	Al	0.0	4.7	1.2	
		Fe	0.0	13.8	3.5	
		Al	15.0	18.0		88.7
		Fe	30.0	41.4		92.0

[a] SA1 = Australian salt (date of sampling, July 1988); SA2 = Australian salt (date of sampling, April 1989); SA3 = Australian salt (date of sampling, January 1989); SM = Mexican salt (date of sampling, December 1989).

CONCLUSIONS

Al– and Fe(III)–PMBP chelates can be well separated on an ODS column with pure acetonitrile as the mobile phase. Divalent metals did not interfere under the same chromatographic conditions. The proposed method was applied to the determination of the two metals in imported solar salts. The recoveries and the precision of the determination were satisfactory, indicating that the method would be capable of the simultaneous determination of Al and Fe(III) in samples containing some divalent elements.

ACKNOWLEDGEMENT

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