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The Preconcentration and Determination of a Trace Amount of Strontium in Fresh Water as Its 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone Chelate by Means of Solvent Extraction

Takaharu Honjo* and Takashi Nakata
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa 920

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Synopsis. The behavior of a trace amount of alkaline earth metals (magnesium, calcium, strontium, and barium) on solvent extraction has been examined with PMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) in benzyl alcohol; the results have also been applied to the preconcentration and determination of a trace amount of strontium in ppb order in fresh water as its PMBP chelate by means of solvent extraction.

The content of strontium in fresh water is generally known to be in ppb order, and it must be concentrated up to ppm order, prior to its determination by means of a usual atomic absorption method. Solvent extraction, especially chelate extraction, is a simple and highly selective convenient method for the preconcentration and determination of a trace amount of metals like heavy metals[1–6,8] and alkaline earth metals[3,6,7] in natural waters. Among the extractive chelating agents of 8-hydroxyquinoline, β-isopropyltropolone, 2-thenoyltrifluoroacetone, and PMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone), PMBP has been reported to be most useful for the extraction of alkaline earth metals.[3,6–8]

In this investigation, the behavior of a trace amount of alkaline earth metals (magnesium, calcium, strontium, and barium) in solvent extraction has been examined with PMBP in benzyl alcohol; the results have been applied to the preconcentration and determination of a trace amount of strontium in ppb order in fresh water as its PMBP chelate by means of solvent extraction for the subsequent atomic absorption analysis.

Experimental

Apparatus. A model 323 Hitachi Recording Spectrophotometer; a model 239 Hitachi Digital Spectrophotometer; a model 170—50 Hitachi Atomic Absorption/Flame Spectrophotometer; a Hitachi-Horiba glass electrode pH meter, model M-5; an Iwaki shaking machine, model KM; a Kubota centrifuge machine, and a Tomi-Seiko Swing Type centrifuge, model CD-50R, were used.

Materials. PMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) was synthesized by the condensation of 1-phenyl-3-methyl-5-pyrazolone with benzoyl chloride in dioxane, as described previously.[8] The PMBP was purified by recrystallization from a mixture of methanol and a dilute hydrochloric acid solution; it crystallizes in yellow plates (keto type) having the same reference value, melting point of 92 °C. The organic solvents used were all reagent-grade materials and if necessary were purified by an ordinary method. Benzyl alcohol was used within one week after opening the sealed bottle, because of its gradual degradation caused by air oxidation.

Distribution of PMBP. The distribution behavior of PMBP between various organic solvents and water was examined as follows: An equal volume (5 $\mathrm{cm^3}$) of 5×10^{-5}—10^{-3} M (1M=1 mol $\mathrm{dm^{-3}}$) each of various organic solutions of PMBP and buffer solutions of pH 1—12 adjusted to the desired value by mixing an appropriate amount of 0.1 M of hydrochloric acid, acetic acid, sodium acetate, boric acid, sodium borate, and sodium hydroxide, was equilibrated by shaking both phases for 30 min. After centrifugation at 2000 rpm for 15 min, the concentration of PMBP in the organic phase was determined spectrophotometrically by measuring its absorbance at 290—300 nm, around the absorption maxima of PMBP. The pH of the aqueous phase was checked again after the distribution.

Extraction of Alkaline Earth Metals. A 10 $\mathrm{cm^3}$ of 10^{-3} M alkaline earth metal ion solution adjusted to the desired pH with buffer solutions described above and a 10 $\mathrm{cm^3}$ of 10^{-2} M PMBP in organic solvent were placed in a 30 $\mathrm{cm^3}$ glass-stoppered centrifuge tube and agitated on a shaking machine for 30 min. After the separation of the two phases by centrifugation at 2000—3000 rpm for 15—30 min, a 5 $\mathrm{cm^3}$ of the organic phase was shaken with 0.1 M hydrochloric acid solution; the amount of metal ion stripped in the aqueous phase was determined by atomic absorption at 285.21 nm for magnesium, at 422.67 nm for calcium, and at 460.73 nm for strontium. The concentration of barium was determined by flame photometry at 553.6 nm. The pH of the aqueous phase was measured again after the extraction.

Results and Discussion

The distribution behavior of PMBP in various organic solvents was first studied in order to find the proper solvent having a higher distribution ratio and better phase separation in the basic region, where alkaline earth metals can be extracted quantitatively.[3,6–8] The preliminary experiments revealed that the distribution of PMBP expressed by percent extraction (%E) in an organic solution increased in the order of benzene, butyl acetate, isobutyl methyl ketone (0%) <chloroform (5%)<isopentyl alcohol, hexyl alcohol, decyl

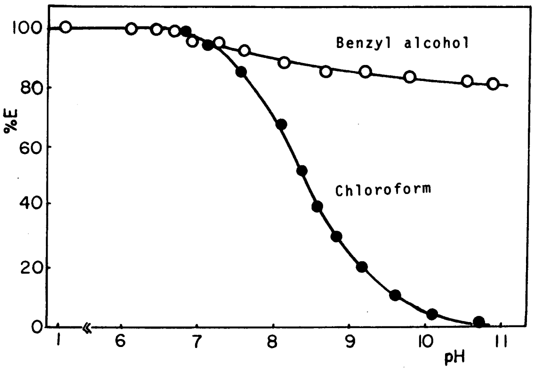

Fig. 1. Distribution of 5×10^{-5}—10^{-3}M PMBP in chloroform and benzyl alcohol as a function of pH.

alcohol, octyl alcohol (40—60%)<benzyl alcohol (83%) at pH 10 (Fig. 1). Judging from the higher distribution of PMBP in the organic phase and the better separation of the two phases by centrifugation at 2000 rpm for 15 min, it was evident that benzyl alcohol was most suitable for the extraction of alkaline earth metals with PMBP. Next, the pH dependence of the extractability of alkaline earth metals (magnesium, calcium, strontium, and barium) with 10^{-2} M PMBP in benzyl alcohol was examined in the region of pH 1.0 to 10.0. The results (Fig. 2) are shown in terms of percent extraction (%E) vs. pH plots of alkaline earth metals extracted in benzyl alcohol. The quantitative extraction of the PMBP chelate in benzyl alcohol was achieved in the pH region above 6 for magnesium, in the pH region above 7.0 for calcium, and in the pH region of 7.5—8.5 for strontium. Barium was not extracted completely in any pH region. The log D vs. pH plots gave straight lines having a slope of about 2, which gave the number of the PMBP molecule bound to alkaline earth metals. In general, the extractability of alkaline earth metals with PMBP in benzyl alcohol is better than in chloroform, benzene, and cyclohexane, without synergic extraction with the aid of TOPO (trioctylphosphine oxide).[3,6–8] On the basis of these results, it was decided that the extraction of strontium with 10^{-2} M PMBP in benzyl alcohol should be carried out at pH 8.0. Although the complete and quantitative extraction was achieved after 3 min of shaking, the two phases were shaken for 5—10 min. When the volume of the organic phase of 10^{-2} M PMBP in benzyl alcohol was kept at 10 cm³, and when that of the aqueous phase was varied from 10 to 100 cm³, almost the same extractability (100±1%) was obtained in each case. The effect of the presence of foreign ions, which exist in fresh water, on the extraction of strontium is given in Table

Table 1. Effect of Foreign Ions

Ion added		Sr^{2+} taken	Sr^{2+} found
	ppm	ppm	ppm
Ca^{2+}	50	0.20	0.21
Mg^{2+}	10	0.20	0.20
Al^{3+}	1	0.20	0.21
HCO_3^-	100	0.20	0.20
SO_4^{2-}	20	0.20	0.20
PO_4^{3-}	1	0.20	0.20

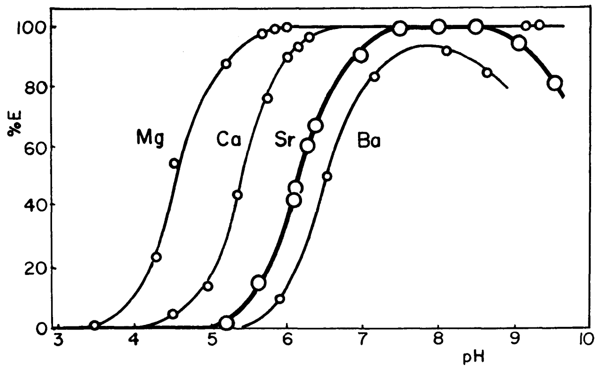

Fig. 2. Extraction of 10^{-3} M alkaline earth metals with 10^{-2} M PMBP in benzyl alcohol as a function of pH.

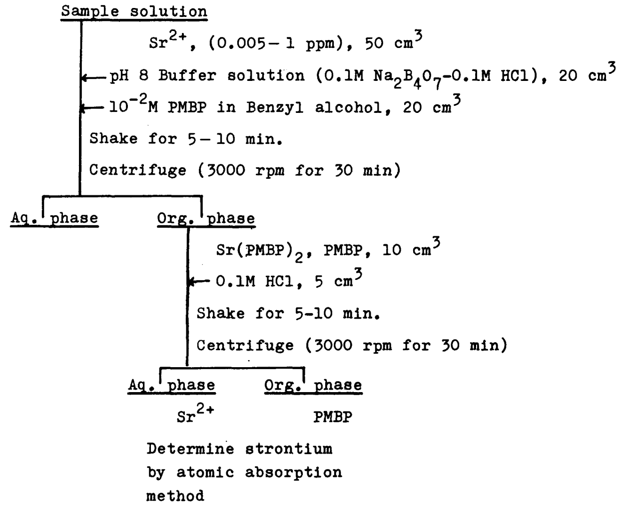

Fig. 3. Analytical scheme for the preconcentration and determination of a trace amount of strontium in fresh water.

Table 2. Content of Strontium, Calcium, and Magnesium Ions in Fresh Water near Kanazawa University

Sample	Solution volume	Sr^{2+} added	Sr^{2+} found	Sr^{2+} content[a]	Ca^{2+} content[b]	Mg^{2+} content[b]
	cm³	μg	μg	ppb	ppm	ppm
Tap water	50	0	3.55	71±1	14.4	6.2
		0	3.65	73±1	14.4	6.2
		1.0	4.60	72±1	14.4	6.2
OHTEBORI moat water	50	0	3.65	73±1	14.1	5.5
Thawing water	50	1.0	1.35	7±1	1.6	1.2

a) Mean and relative standard deviation for at least three determinations. The experimental results obtained by adding a definite amount of strontium to fresh water revealed that the recovery of strontium was about 100±1%. In the case of thawing water, the absortance of atomic absorption of strontium gave very small value, and the result obtained by adding a definite amount of strontium to fresh water was shown in Table 2. b) The experimental results obtained by direct determinations of magnesium and calcium in fresh water with atomic absorption method without preconcentration.

1. The concentration of these ions was prepared so as to be somewhat larger than that of general fresh water as river water and underground water. None of the ions investigated interfered with the extractability of strontium with PMBP in benzyl alcohol. Finally, the systematic experimental procedures (Fig. 3) for the determination of strontium in natural waters based on the extraction and atomic absorption spectrophotometric determination of strontium with 10^{-2} M PMBP in benzyl alcohol have been applied to the preconcentration and determination of a trace amount of strontium in ppb order in fresh water in the vicinity of Kanazawa University.

The results are given in Table 2 together with the values obtained for calcium and magnesium in ppm order without preconcentration, showing that the proposed method was useful for the preconcentration and determination of strontium in ppb order (7—73±1 ppb) in fresh water.

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