

Studies on Equilibria and Analytical Applications of Synergistic Solvent Extraction(II). Determination of Trace Lithium in Sea Water using TTA and TOPO

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An application of synergistic solvent extraction for the determination of trace lithium in sea water has been studied by forming an adduct complex of thenoyltrifluoroacetone (TTA) and trioctylphosphine oxide (TOPO) in a solvent. The interference by major constituents in sea water was eliminated by phosphate precipitation. Experimental conditions such as solution pH, concentrations of TTA and TOPO etc. were optimized in synthetic sea water with similar composition to its natural counterpart. To eliminate the interference, 1.38 g of ammonium dihydrogen phosphate and 2.5 mL of ammonia water were added into 100 mL of the diluted solution at 60 °C to form the phosphate precipitates of Ca²⁺ and Mg²⁺ ions. After the pH of this filtrate was adjusted to 8.0, 10.0 mL of *m*-xylene containing 0.1 M TTA and 0.05 M TOPO was added to the solution in a separatory funnel, and the solution was shaken vigorously for 20 minutes. The solvent was separated from the aqueous solution, and 20 μL of *m*-xylene solution was injected into a graphite tube to measure the absorbance by GF-AAS. The detection limit was 0.42 ng/mL. Lithium was determined within the range of 146 to 221 ng/mL in Korean coastal sea waters, and the recoveries in the spiked samples were 94 to 106%.

Introduction

Lithium is an important element widely used as a raw material for alloys, batteries, refrigerating agents, medicinal drugs and chemical products. Its use will increase drastically if fuel cells and power generation by nuclear fusion are perfected. At present, it is mainly obtained from a mining (spodumene), but the ocean can become a significant source of this element. Unfortunately, the concentration of lithium is very low (a few hundred ppb).

In the present work, an analytical method of determining lithium in sea water was developed based on an extraction method, using the formation of adduct complex with thenoyltrifluoroacetone (TTA) and trioctylphosphine oxide (TOPO). The TTA used here was one kind of β-Diketone. β-Diketone is widely used as a chelating agent for the solvent extraction of various metal ions. The important characteristics of such a β-diketone is tautomerism between enol- and keto- forms, but an enol-form is known to form stable complexes as an anion.¹



Tautomerism of β-diketone

For example, acetylacetone is widely used as one kind of β-diketone. The formula has methyl groups at R₁ and R₂ positions in the above structure, and it can form complexes with about 60 kinds of metals.² Benzoyltrifluoroacetone (BFA), pyrazolone, tropolone and so on are derivatives of β-diketone. Sekin and coworkers conducted fundamental studies on the synergistic extraction of lithium by using BFA^{3,4}

and tropolone derivative⁵ as well as Tba⁻ ion. And the use of 4-isopropyl tropolone and Tba⁺ ion was reported for the extraction of lanthanides.⁶ Umctani and coworkers studied the synergistic extraction of lithium, sodium and alkaline earth metals with pyrazolone derivatives and TOPO.^{7,8}

The thenoyltrifluoroacetone (TTA) used in this work is one kind of β-diketone in which the R₁ and R₂ positions are substituted with 2-thenoyl and trifluoromethyl group, respectively, and the acidity of the compound is stronger than the other β-diketone through the inductive effect of -CF₃ group. Since TTA was synthesized in 1944 by Calvin and Wilson, it has been used widely as a chelating agent for the extraction and spectroscopic determination of zirconium, hafnium, lanthanides and actinides.^{1,2}



Structure of thenoyltrifluoroacetone(TTA)

TTA used with TOPO or Tba⁻ is known to create a synergistic effect that can increase the extraction efficiencies of metallic ions as forms of adduct or ion-pair. Therefore, many researchers have utilized such characteristics.⁹⁻¹⁶ Recently, Sekin and coworkers^{17,18} conducted not only the fundamental research on the extraction of metallic ions using TTA and TOPO, but also the reaction kinetics of adduct complex formation between TTA, TOPO and metallic ion. Also, Takazawa *et al.*¹⁹ thermodynamically explained the synergistic function with an enthalpy change.

As described above, there have been many studies on the extraction conditions and efficiencies for the solvent extraction of various metal ions using their complexes of β-diketone derivatives. But the application of this method to the

analysis of real samples have not been frequent. Furthermore, there have been few examples to which this method could be applied for the determination of trace lithium. The synergistic extraction procedure into *m*-xylene containing TTA and TOPO was studied to determine trace lithium in sea water. Various experimental conditions for the extraction and instrumental measurement were optimized, and the elimination of interference from coexisting ions in a sample was investigated for quantitative determination.

Experimental Section

Reagents and instruments. All reagents used were of analytical grade, and the distilled water was further purified by Millipore Milli-Q water system. The concentration of Li(I) in the standard solution (NIST, U.S.A.) is 100 $\mu\text{g/mL}$, and it was diluted to the proper concentration for use. The concentrations of thenoyltrifluoroacetone (TTA, Aldrich Co., U.S.A.) and trioctylphosphine oxide (TOPO, Aldrich Co., U.S.A.) were 0.1 and 0.05 M in *m*-xylene (Junsei Co., Japan). They were prepared whenever required for use. $\text{NH}_4\text{H}_2\text{PO}_4$ was a precipitant, and it was added directly to the sea water samples in solid state.

Perkin-Elmer model 2380 equipped with HGA-400 programmer was used with a hollow cathode lamp from Perkin-Elmer Co. The operating conditions for determining lithium extracted in *m*-xylene are shown in Table 1. Eysela pH meter PHM-2000 (Tokyo Rikakikai Co., Japan) and Ingold glass electrode were used after correction with a buffered solution.

Synthetic sea water. Synthetic sea water similar in composition to natural sea water²⁰ was prepared in our laboratory. In natural sea water, about 10 elements are present in concentrations above 1 $\mu\text{g/mL}$, comprising 99.58% of soluble materials. The synthetic water was prepared based on this composition as shown in Table 2.

Experimental procedure. 10 mL of a sea water sample taken accurately was diluted to 100 mL with synthetic sea water. 1.38 g of ammonium dihydrogen phosphate and 2.5 mL of concentrated ammonia water were added at 60 °C.

Table 1. Operating parameters of atomic absorption spectrophotometer

Instrumental parameter	
Wavelength	670.8 nm
Lamp current	15 mA
Bandwidth	2.0 nm
Signal mode	Absorbance
Heating program for graphite tube	
Inert gas	Argon
Tube Type	Un-coated tube
Drying	150 °C, [3], (5)
Charring	1000 °C, [8], (8)
Atomization	2700 °C, [3], (3)
Cleaning	2700 °C, [6]

Sample injection: 20 μL . | : Holding time, sec.; (): Ramping time, sec.

Table 2. Concentrations of major and minor constituents in real and synthetic sea waters

Element	Dissolved species	Sea water* mole/L	Synthetic sea water mole/L
Sodium	Na^+	3.7×10^{-1}	4.6×10^{-1}
Chlorine	Cl^-	5.5×10^{-1}	5.4×10^{-1}
Magnesium	Mg^{2+}	5.3×10^{-2}	5.2×10^{-2}
Potassium	K^+	9.72×10^{-3}	9.7×10^{-3}
Calcium	Ca^{2+}	1.03×10^{-2}	1.9×10^{-2}
Strontium	Sr^{2+}	9.13×10^{-5}	1.5×10^{-1}
Sulfur	SO_4^{2-}	2.82×10^{-2}	2.8×10^{-2}
Carbon	HCO_3^-	2.33×10^{-3}	2.3×10^{-3}
Bromine	Br^-	8.39×10^{-1}	8.3×10^{-1}
Boron	B(OH)_4^-	4.06×10^{-1}	4.3×10^{-1}

*Douglas A. Seagar, "Introduction to Ocean Sciences", Wadsworth, Belmont, USA, 1998.

and the solution was let stand for 3 hours to precipitate calcium and magnesium completely. The precipitates were filtered out with filter paper (*whatman* #2). The filtrate was placed in a separatory funnel, and 10 mL of *m*-xylene solution containing 0.1 M TTA and 0.05 M TOPO was added. The funnel was shaken vigorously for 20 minutes with a mechanical shaker (Kukje Scientific Co., Ltd.). The solution was let stand for 20 minutes, separating into two phases. The absorbance of lithium extracted in *m*-xylene was measured with a GF-AAS. Extraction conditions were optimized in synthetic sea water. A series of standard solutions were prepared with the synthetic sea water to make a calibration curve.

Results and Discussion

Influence of coexisting ions. At first, the interference from major elements such as alkaline and alkaline earth elements was investigated to quantitatively extract trace lithium in sea water. That is, the lithium was extracted under given conditions from deionized water of 10 ng/mL lithium, with the concentration of alkaline and alkaline earth elements rising to twice the average concentration in sea water. The alkaline metals did not interfere with the extraction of lithium in the following results. The absorbance of lithium was nearly constant within the range of the alkaline metals' concentrations in sea water. But the presence of calcium and magnesium at low concentrations decreased lithium absorbance. Such a phenomenon could be explained as a result of the formation of their stable complexes with TTA. The interference was removed by the formation of their precipitates with ammonium dihydrogen phosphate in an ammonia solution of pH 9.

On the other hand, oxalate ion is known to be a good precipitant, but it could not simultaneously precipitate with calcium and magnesium. And the amount of 8-hydroxyquinoline(oxine) required, due to its large molecular weight, made it difficult to treat the precipitates.

The type of solvent. It was very important to select the

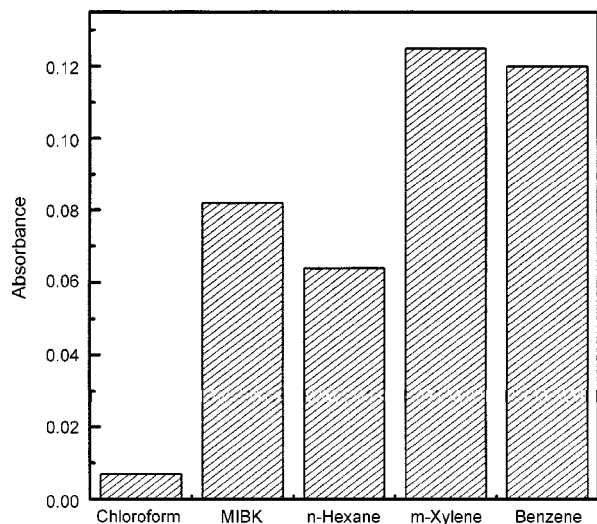


Figure 1. Comparison for the extraction efficiencies of Li-TTA-TOPO adduct by the type of solvent. Li: 10 ng/mL.

most proper solvent for the stabilization of the adduct complex of Li-TTA-TOPO as well as the best method of extraction. Therefore, the effect of the solvent on the extraction of Li⁺ was investigated before the optimization of other conditions for complex formation and extraction. That is, the extraction efficiency of lithium was compared with the absorbances of the extracted lithium in each of five different solvents: chloroform, methyl-isobutylketone (MIBK), *n*-hexane, *m*-xylene and benzene (Figure 1). The extraction with benzene or *m*-xylene showed much higher absorbance than the others. This contradicts the Machida study,²¹ in which he reported that greater efficiency was obtained in the extraction using TTA and TOPO with an aliphatic hydrocarbon such as *n*-hexane than with an aromatic hydrocarbon solvent. And the complex was nearly non-extractable in a polar solvent such as chloroform. This proves that Li-TTA-TOPO adduct was bulky and non-polar. But, MIBK is a solvent mainly used in solvent sublation because of its high extraction efficiency and low background in the measurement of AAS absorbance. But its solubility in an aqueous solution is inadequate for it to be used in this solvent extraction procedure and low efficiency was also shown in the extraction. Therefore, *m*-xylene was selected as an optimum solvent.

The effect of pH. The extraction efficiency of lithium into *m*-xylene solution containing TTA and TOPO was investigated, changing the pH from 5 to 9 (Figure 2). It was found that the quantitative extraction of lithium was possible above pH 7, but the best extraction was done at pH 8. The extraction efficiencies of lanthanides and actinides by TTA increased in an acidic solution, but lithium could be effectively extracted in a weak basic solution as shown. This was considered to be a result of excess TTA being partitioned to an aqueous layer at high pH as in the following equations:

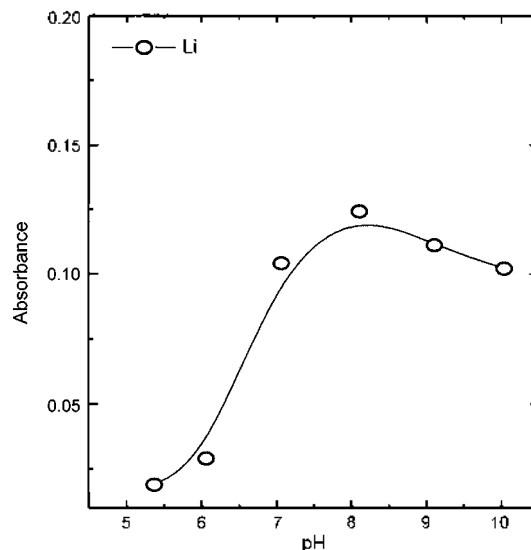
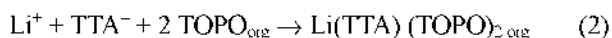
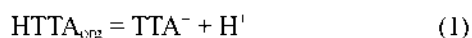


Figure 2. Effect of solution pH on the formation and extraction of Li-TTA-TOPO adduct complex. Li: 10 ng/mL.

As shown in the above equations, HTTA provides H⁺ ion to an aqueous solution if it is partitioned to an aqueous layer from the organic solvent. Therefore, the pH of the aqueous solution should fall, but the pH did not change because of the buffer action of the phosphate salt added.

The effect of TTA concentration. The concentration of TTA in *m*-xylene was investigated for the effective extraction, changing the concentration from 1.0×10^{-3} to 0.2 M under the same conditions. The absorbances of the extracted lithium were plotted against the TTA concentration (Figure 3). The figure shows that the absorbance increased up to 0.1 M and remained constant at more than 0.1 M. It is known that lithium can be quantitatively extracted with *m*-xylene of 0.1 M TTA. The amount of chelating agent, TTA, was equivalent to about 6.700 times the lithium in mole

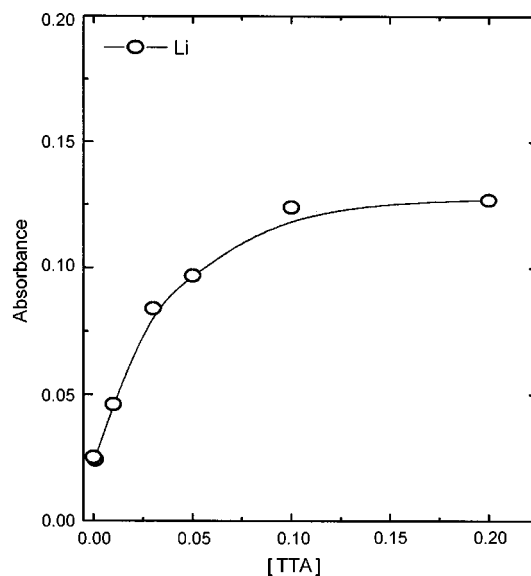


Figure 3. Optimum concentration of TTA for adduct complex formation of Li-TTA-TOPO.

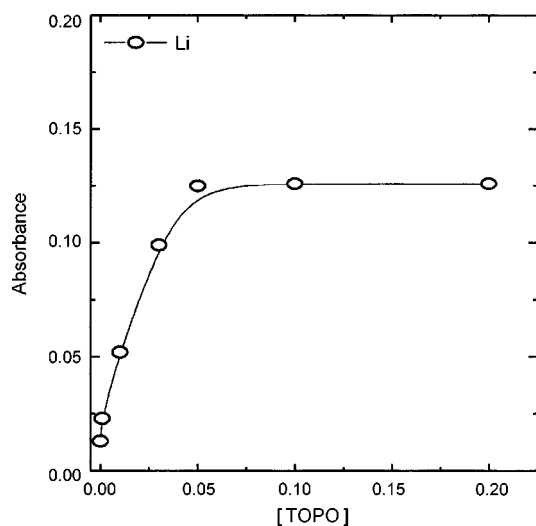


Figure 4. The effect of TOPO concentration on the adduct complex formation of Li-TTA-TOPO.

ratio.

Because the absorbance was directly measured by GF-AAS in the *m*-xylene, some fog was observed in the graphite furnace. This fog came from the burned product of the solvent containing TTA and TOPO at about 700 °C in the charring step. Therefore, the time for the charring step was extended up to 15 seconds to decrease the high background due to the fog.

The effect of TOPO concentration. TOPO coexisting with TTA in *m*-xylene was studied as an auxiliary ligand to extract the lithium. The extraction efficiencies were evaluated by the measurement of lithium absorbance, changing the TOPO concentration in *m*-xylene from 1.0×10^{-3} to 0.2 M (Figure 4). The absorbance did not increase at concentrations of more than 0.05 M. It was found that the trace lithium was quantitatively extracted into *m*-xylene containing more than 0.05 M TOPO. As in the case of TTA described above, the neutral ligand also caused an increase in the background of the absorbance measurement by generating fog at about 700 °C and the extent was greater. Such a cause was considered to be due to the fact that TOPO used in this experiment had a larger molecular weight than TTA. The same moles of TTA and TOPO have been used for such general solvent extraction, but a low concentration of the TOPO was used compared with 0.1 M TTA in this work. This concentration of 0.05 M TOPO induced the decrease of the background in the absorbance measurement as well as the increase in the dynamic range in the calibration curve.

Shaking time. 100 mL of the diluted sample and 10 mL of *m*-xylene containing 0.1 M TTA and 0.05 M TOPO were taken in a 250 mL separatory funnel. As in the experimental section, interfering ions of Ca^{2+} and Mg^{2+} were removed and the pH was also adjusted to 8 in the sample solution before taken. Under the consideration of a clean phase separation, the extraction of lithium complex was investigated by changing the shaking time from 1 to 60 minutes. Such a the complex can be quantitatively extracted by shaking with a

Table 3. Analytical results of lithium in real samples

Sample	Li added ng/ml	Li found ng/ml	RSD* %	Real concentration** ng/ml	Recovery %
Tae-jong-dae	0.0	20.1	1.9	204	98
	20.0	39.6 (recovered 19.5)			
Choo-am	0.0	17.3	1.6	190	105
	20.0	38.3 (recovered 21.0)			
Muk-ho	0.0	14.9	1.6	150	
Ul-jin	0.0	21.1	1.8	221	
Dae-chon	0.0	14.7	1.6	147	

*Values about 5 analytical data. **The concentrations of lithium in the original sea water.

mechanical shaker for more than 20 minutes. But the time was minimized to 20 minutes to shorten the experimental duration. Even though adduct complexes of other ions were known to be extracted into a solvent over a short period of time according to the previous works, such co-extractions could be suppressed by using a relatively low concentration of 0.05 M TOPO.

Analysis of natural sea water. The optimized conditions and procedure in this work have been applied to the determination of trace lithium in natural sea water samples. The samples were taken at 5 places along the Korean coastal ocean. But the content was so high above the dynamic range of this procedure that the samples were diluted to one tenth with synthetic sea water. Fortunately, this dilution provided the advantage of matching the matrixes between sample and standards more closely.

A series of lithium standard solutions, 1 to 50 ng/mL, was prepared by adding given amounts of a NIST standard solution of 100 ng/mL lithium to synthetic sea water. And a calibration curve was made using the measured absorbances of standard solutions treated with the same extraction procedure as for sample solutions. The linearity of curve was 0.996 and the detection limit equivalent to three times standard deviation of the blank absorbances was 0.42 ng/mL. The analytical results of 5 samples are given in Table 3. The recoveries in two spiked samples were 94 to 106%.

From above results, it can be concluded that trace lithium in a sea water was accurately determined by the synergistic extraction procedure after the large interference from major calcium and magnesium were eliminated by adding ammonium dihydrogen phosphate and ammonia water. The extraction was performed with *m*-xylene containing 0.1 M TTA and 0.05 M TOPO at pH 8 of the samples. Finally, this procedure is expected to be applied to the determination of trace lithium in any other materials and environmental samples with the correction of matrix effects.

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