Organic Ion-associate Phase Extraction / Back-microextraction for the Pre-concentration and Determination of Lithium Using 2,2,6,6-Tetramethyl-3,5-heptanedione by Liquid Electrode Plasma Atomic Emission Spectrometry and GF-AAS in Environmental Water

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Abstract

We developed an ion-associate phase (IAP)-extraction / acid back-extraction system for the pre-concentration and atomic spectrometric determination of lithium trace amounts in water. The chelating reagent for lithium works also as a constituent of the extraction phase.

The lithium in a 10 mL sample solution was converted through a chelate complex reaction with 2,2,6,6-tetramethyl-3,5-heptanedione (HDPM). Addition of a benzyldimethyltetradecylammonium ion caused the formation of an IAP suspension in the solution. Centrifugation of the solution led to the isolation of a liquid organic phase and the lithium complex was extracted as the upper phase from the centrifuge tube. After the aqueous phase was removed, lithium was back-extracted with a 400 µL nitric acid solution from the IAP. The acid phase was measured using liquid-electrode-plasma atomic-emission-spectrometry (LEP-AES) or graphite-furnace atomic-absorption spectroscopy (GF-AAS). The detection limits were 0.02 mg/L for LEP-AES and 0.02 µg/L for GF-AAS. This system was applied to the determination of environmental waters.

The HDPM in the organic phase was reusable.

Keywords: Ion-associate-phase extraction, back-microextraction, lithium, environmental water, 2,2,6,6-tetramethyl-3,5-heptanedione, LEP-AES, GF-AAS, reuse.
Introduction

Lithium is used in a wide range of fields, including lithium-ion batteries, glass ceramics, and metal alloys. In recent years, the use of lithium rechargeable batteries has been increasing. Over 90% of lithium worldwide originates from Australia, Chile, Argentina, and China. Lithium is unevenly distributed in the environment, and trace amounts are present in environmental water.

Liquid-electrode-plasma atomic-emission-spectrometry (LEP-AES) is an easy method for quantifying multiple elements simultaneously, since it requires only 40 μL of sample. With this method, lithium is preferably measured in an acid solution. On the other hand, graphite-furnace atomic-absorption spectroscopy (GF-AAS) is a highly sensitive method and requires only 20 μL of sample. Like many atomic spectroscopic methods, both LEP-AES and GF-AAS are affected by the matrix, so some pretreatment such as separation and concentration is required.

Separation and pre-concentration methods that take advantage of the small sample volume required by both LEP-AES and GF-AAS include cloud point extraction, dispersive liquid–liquid extraction, thermoresponsive polymer-mediated extraction, and homogeneous liquid–liquid extraction. These techniques are based on the dependence between equilibration temperature and time, the use of chloroform or chlorobenzene as an extraction solvent, the application of heat, or the use of a fluorine-based surfactant.

In this study, we develop an ion-associate phase extraction method with improved sensitivity and discerning ability against the matrix, and apply it to atomic spectroscopy. This technique converts the analyte in the environmental water into an appropriate form, if necessary, and adds an organic anion and an organic cation to form an ion-associate. The resulting ion-associate phase (IAP) is separated by centrifugation and the aqueous phase is discarded. The
IAP is dissolved in an organic solvent, and a mixed solution consisting of an organic solvent and acid, back-extracted with acid, and the analyte is then measured through atomic spectroscopic methods.

The hydrophobic chelating agent, DPM, acts as the organic anion in the developed IAP. The combination of IAP extraction and back extraction is the best combination for lithium pre-concentration and LEP-AES measurement. Therefore, we used this method to measure lithium in seawater by LEP-AES and in river water and spring water by GF-AAS. River water and spring water were measured by GF-AAS because the concentration of lithium is more than an order of magnitude lower than seawater and cannot be measured by LEP-AES.

**Experimental**

**Reagents and chemicals**

Lithium nitrate, 99.9 % (Wako Pure Chemical Industries Ltd.), was dissolved in 0.1 M nitric acid to make 1000 mg L$^{-1}$ solution.

Dipivaloylmethane (HDPM), which is liquid at room temperature, was used (2,2,6,6-tetramethyl-3,5-heptanedione; Aldrich, 98%) as received without dissolving.

Potassium hydroxide solution, 2 M, was prepared by dissolving 28 g KOH in 250 mL water. The solution was stored in a plastic bottle. For GF-AAS, the reagent for trace analysis (Kanto Chemical Co. Inc.) was used.

A benzyldimethyltetradecylammonium (C$\text{14}$BzBMA$^+$) solution, 0.1 M, was prepared by dissolving 4.04 g Zephiramine (benzyldimethyltetradecylammonium chloride dihydrate, Dojindo, Kumamoto, Japan) in 100 mL water.
A benzethonium (Ben⁺) solution, 0.1 M, was prepared by dissolving 4.5 g benzethonium chloride (diisobutylphenoxyethoxyethyl)-dimethylbenzylammonium chloride) (Kanto Chemical Co. Inc.) in 100 mL water.

A benzyldimethyldodecylammonium solution, 0.1 M, was prepared by dissolving 3.84 g benzyldimethyldodecylammonium bromide (Fluka, Buchs, Switzerland) in 100 mL water.

All reagents (e.g., nitric acid, hydrochloric acid, sulfuric acid, acetonitrile) were of analytical grade or better quality and used without further purification. The water in all experiments was ultrapure water (18.2 MΩ) produced by the ultrapure-water-production system Direct-Q3 UV (Millipore).

**Apparatus**

Measurements of trace lithium in the aqueous solutions were performed using a Micro Emission (Japan) Model MH-5000 liquid-electrode-plasma atomic-emission-spectrometer (LEP-AES) equipped with a LepiCuve-02 cuvette or using a Hitachi (Japan) Model Z-5010 polarized Zeeman GF-AAS with a pyro cuvette. The instrumental conditions for LEP-AES were as follows: analytical wavelength, 670 nm; injection volume, 40 μL; applied voltage, 950 V; pulse duration, 3 ms; pulse interval, 2 ms; and 10 integrations. The instrumental conditions for GF-AAS were as follows: analytical wavelength, 670.8 nm; sample volume, 20 μL; slit, 0.4 nm; drying, 80 to 140°C, 40 s; ashing, 600 °C, 20 s; atomization, 2400 °C, 5 s; cleaning, 2500-°C, 4 s.

Centrifugation was performed using a Kubota (Japan) centrifuge (Type 5420) or a Kokusan (Japan) centrifuge (Type H-80R). UV spectra were measured using a spectrophotometer by Shimadzu (Japan), Model UV-2450, with a 1 cm quartz cell.
Seawater was filtered using a mixed cellulose ester membrane filter (0.45 μm pore size) from Advantec Toyo (Japan). For the entire sample preparation process, a 50 mL plastic centrifuge tube (As One, Japan) was used.

Results and Discussion

Optimization of Extraction

In order to extract lithium from water, crown ethers\textsuperscript{1,17} and porphyrins\textsuperscript{18} have been used as chelating reagents in the past, apart from β-diketones\textsuperscript{1,19} such as 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, HDPM).\textsuperscript{20-22} In this study, HDPM was selected because it is relatively cheap and acts as an organic anion. We investigated the optimum amount of the chelating reagent HDPM to be used for the recovery of lithium (Figure 1-A). Recovery was obtained by double extraction. However, it was almost the same as the recommended procedure, but to the second extraction KOH was not added, and 0.4 mL of HDPM was added instead of 0.6 mL. Recovery (R) is

\[
R, \% = \frac{(I_1 - I_2)}{I_1} \times 100
\]

where \(I_1\) is the intensity of first extraction and \(I_2\) is the intensity of the second extraction. Different amounts of HDPM were added from 200 μL to 1000 μL. Recovery was almost maximal and constant above 600 μL, this is 2,000 times the molar ratio of lithium in this experiment. When the amount of HDPM is small, the ion associate phase will float, making it difficult to separate from the aqueous phase. The addition 600 μL HDPM was recommended because ease of handling and economic reasons.

The HDPM acid dissociation constant \(pK_a\) is 11.75.\textsuperscript{23} Since the chelating reagent HDPM forms a complex with lithium in a strongly basic solution, the pH was adjusted here with a KOH
solution. The results are shown in Figure 1-B. The reaction between lithium and DPM in strong alkaline solution follows Equations (2) and (3).

$$\text{HDPM} + \text{OH}^- \rightleftharpoons \text{DPM}^- + \text{H}_2\text{O} \quad (2)$$

$$\text{DPM}^- + \text{Li}^+ \rightleftharpoons [\text{Li}/\text{DPM}] \quad (3)$$

As the KOH concentration increases, the dissociated DPM\(^-\) increases and reacts with more organic cations. Lithium can be recovered more quantitatively by increasing the volume of the organic phase (IAP). However, when the KOH concentration exceeds 1.0 mol/L, the emission intensity of lithium decreases.

The standing time, that is the time from the addition of the KOH solution until the addition of organic cation, was investigated. The results are shown in Figure 1-C. When the cation was added immediately after the KOH solution, the LEP-AES intensity was slightly lower, but almost the same result was obtained for 10 - 60 min time difference between the two. From this result, the formation of the lithium complex was considered to reach equilibrium within 10 min after the addition of the KOH solution.

In this IAP extraction method, the DPM\(^-\) serves as the constituent ion (organic anion) of the IAP. For this reason, the IAP can be formed only by adding organic cations. Therefore, the types of reagents added can be reduced. Benzyldimethyltetradecylammonium ion (C\(_{14}\)BzDMA\(^+\)), benzyldimethyldodecylammonium ion (C\(_{12}\)BzDMA\(^+\)), and benzethonium ion (Ben\(^+\)) were investigated as the cations potentially constituting the IAP. C\(_{16}\)BzDMA\(^+\), the most hydrophobic of the three cations, showed the highest recovery of lithium. Therefore, C\(_{16}\)BzDMA\(^+\) was recommended as the organic cation for this study.
The amount of 0.1 M C₁₄BzDMA⁺ solution added as organic cation was investigated (Figure 1-D). By adding C₁₄BzDMA⁺, IAP was formed by Equation (4). When the amount of 0.1 M C₁₄BzDMA⁺ solution added was 2.0 mL, the lithium emission intensity was the highest. In this case, there is about 30 times more HDPM than C₁₄BzDMA⁺ in molar ratio. The addition of 3.0 mL of the C₁₄BzDMA⁺ solution led to solidification of the liquid organic phase when nitric acid was added for back extraction. This was probably due to the precipitation of the ion associate of the nitrate ion and the excess C₁₄BzDMA⁺ solution. Thus, the optimal addition amount of organic cation was 2.0 mL.

\[
\text{DPM}^- + \text{K}^+ + \text{C}_{14}\text{BzDMA}^+ \rightleftharpoons \text{C}_{14}\text{BzDMA}^+ \text{DPM}^- \quad (\text{KDPM})_m \quad (4)
\]

From the result of the UV measurement, the ratio of C₁₄BzDMA⁺ to DPM in the IAP before back-extraction was roughly 2 : 9. Schematic representation of the lithium complex formation, ion-associate extraction and back microextraction system is showed Figure 2.

When C₁₄BzDMA⁺ is added, an ion associate is formed with DPM⁻, and the complex is extracted into the ion associate phase. Lithium reacts with DPM⁻ to form a complex. Since the ratio of C₁₄BzDMA⁺ to DPM is 2 : 9, it is considered that the ion associate of K⁺ and DPM⁻, and HDPM also constitute the ion associate phase. Lithium is extracted into the aqueous phase by acid back extraction. When the organic phase (IAP) after the measurement was collected and allowed to stand, it was separated into two phases. The UV spectra of upper phase were consistent with that of HDPM. This suggests that the upper phase consists of pure HDPM and the lower phase consists of C₁₄BzDMA⁺ and DPM⁻ ion associate.

We examined the centrifugation conditions with respect to lithium recovery. The rotational speed was varied between 2500 and 4500 rpm and the centrifugation time was 15-30 min. Lithium was quantitatively recovered at the rotational speed from 3000 to 4500 rpm. The
higher the number of rotations, the shorter the centrifugation time required to achieve lithium recovery. However, the plastic centrifuge tubes were sometimes deformed due to the multiple use. Therefore, centrifugation for 30 min at 3000 rpm was adopted in this study.

**Back-extraction**

The IAP extracted the lithium-complex that was dissolved in an acetonitrile 0.36 mL and 2 M nitric acid 0.04 mL, and then measured it with a LEP-AES analyzer. Since the volume of the IAP was about 0.4 mL, the solution dissolved IAP is about 0.8 mL. The sensitivity by IAP extraction/organic solvent dissolution increased 12 times compared to the standard solution without concentration. In the dissolved IAP, the precision of the emission intensities of LEP-AES was poor without hydrogen normalization. This was due to the influence of coexisting organic substances during LEP-AES measurement, namely, the organic solvent used for IAP dissolution and IAP constituent ions.

With the LEP-AES measurement, Nakayama et al. reported that when the IAP was dissolved in methanol and nitric acid, copper and manganese were sensitized but lead and zinc were slightly desensitized.

By adding acid (HX), the lithium extracted into IAP can be back-extracted into acid solution by Equation (5).

\[
\{\text{Li/DPM, C}_{14}\text{BzDMA}^+\text{DPM}^-\} + \text{HX} \rightleftharpoons \text{HDPM} + \text{C}_{14}\text{BzDMA}^+\text{X}^- + \text{Li}^+ \tag{5}
\]

We tested the use of different acids, such as sulfuric acid and nitric acid, in the back-extraction of lithium. The results are shown in Figure 3. To extract lithium from IAP, a moderately large ion, such as nitrate ion, quantitatively extracts lithium. Large ions such as nitrate ions are considered to extract lithium ions more strongly into the aqueous phase than
chloride ions. However, if it is too large, such as perchlorate ion, it forms an insoluble aggregate. Nitric acid solution is preferred for GF-AAS measurement. Nitric acid was recommended as the optimal acid for back extraction from IAP.

In order to extract lithium quantitatively, the concentration of nitric acid and sulfuric acid were examined. The results are shown in Figure 4. In consideration of safety, the study was conducted at acid concentrations of up to 2.0 mol/L. The amount of back-extracted lithium varied with the acid concentration. At 2.0 mol/L, lithium was back-extracted quantitatively into the nitric acid solution. Therefore, the nitric acid concentration of 2.0 mol/L was recommended as the optimal back-extraction solvent.

In the LEP-AES measurement, when lithium was back-extracted from IAP with acid, the sensitivity was improved about 2 times compared to the case where IAP was dissolved in organic solvent (acetonitrile 360 μL and 2 M nitric acid 40 μL).

In the IAP extraction, since an ion associate was formed from the aqueous phase, the extraction of the analyte was performed instantaneously, so that shaking was not required. However, because back-extraction involves two phases, the IAP and the acid phase, shaking was sometimes required to provide sufficient partitioning. When the lithium concentration was high, that is, at the concentration level measured by LEP-AES, quantitative extraction was possible without using vortex. When the lithium concentration was low, that is, when measurement was performed using GF-AAS, shaking was considered because quantitative back-extraction was not performed. The maximum absorbance was obtained when the shaking time with vortex was 3 min. When the lithium concentration was low, that is, when measuring with GF-AAS, shaking was performed for 3 min using a vortex mixer.

When the organic phase (IAP) after acid back-extraction was collected, it was separated into two phases (Figure 2). In order to investigate the composition of the two phases, the absorption spectra were measured with a spectrophotometer.
The absorption spectra showed that the upper phase consisted only of the chelating reagent HDPM and the lower phase consisted of IAP (DPM$^-\text{C}_{14}\text{BzDMA}^+$). It was presumed that DPM$^-$, which was once ion-associated, did not complex with lithium again.

The upper phase of the recovered organic phase could be reused as a chelating reagent, but the lower phase could not be used as it was. Therefore, to reuse the reagent of the lower phase, as a result of trial and error, the organic cation (C$_{14}$BzDMA$^+$) of IAP (C$_{14}$BzDMA$^+$DPM$^-$) was replaced with potassium by washing with a saturated solution of potassium chloride (3.33 M), and then the acid was added. As a result, it was recovered as the chelating reagent HDPM. Using the recovered HDPM as the chelating reagent, the recovery of lithium was 93%, which was slightly higher than the recovery achieved by using a commercially available chelating reagent.

We compared the performance of nitric acid and hydrochloric acid in washing the lower phase. Washing with hydrochloric acid, contrary to washing with nitric acid, we were able to extract lithium in the same manner as with a commercially available chelating reagent.

**Optimized analytical procedure**

The procedure of scheme of the ion-associate phase extraction / acid back-microextraction method for atomic spectrometry are illustrated in Figure 5.

Place 10 mL portion of the sample water into a 50-mL poly centrifuge tube and add 600 µL HDPM (liquid). Then, add 10 mL 2 M KOH solution and stand for 10 min to form a lithium complex (Li/DPM). In the case of seawater, mix the investigated seawater with 2 M KOH in a 50-mL poly-centrifuge tube at a ratio of 1: 1, and then perform centrifugation (3500 rpm for 10 min) to precipitate hydroxide. Thereafter, dispense 20 mL of the supernatant accurately into another poly-centrifuge tube and add 600 µL HDPM and stand for 10 min to form a lithium complex (Li / DPM). Subsequently, add 2 mL 0.1 M C$_{14}$BzDMA$^+$ (Zeph$^+$) solution to form the
IAP ({C₄BzDMA⁺ DPM⁻ (KDPM)m})ₙ, and extract the chelate complex. Thereafter, perform centrifugation at 3000 rpm for 30 min and remove the aqueous phase with a pipette, and when the water is low, aspirate the aqueous phase with a micro syringe.

Add 400 µL of 2 M nitric acid to the IAP after extraction of the lithium chelate complex, and the lithium ion is back-extracted into the nitric acid phase (lower phase). If the concentration to be measured is low, that is if GF-AAS is employed, then shake the solution with a vortex mixer for 3 min. After that, the lithium in nitric acid phase can be measured by LEP-AES or GF-AAS. Concentration is 25-fold.

Yamamoto et al.⁵ reported that normalization with an emission line from the atomic hydrogen improves the precision of the emission intensities of LEP-AES. In our study, when the IAP was measured after dissolving it in an organic solvent and nitric acid, the linearity of the calibration curve was improved by normalization.⁵ However, in the case of back-extraction, the linearity of the calibration curve was good without normalization. The concentration factor was 25 times, and the quantification range was 0.1 to 1.0 mg/L. The detection limit (3σ) was 0.02 mg/L.

In the GF-AAS measurement, the quantification range was 0.1 to 0.4 µg/L and the detection limit was 0.02 µg/L.

This IAP / back-microextraction can be applied to measuring instruments with three orders of different sensitivity, and is a concentration method applicable to a wide concentration range. As a guide, after IAP / back-microextraction, saline water such as seawater should be measured with LEP-AES and fresh water should be measured with GF-AAS.

**Application to real water samples**

All four real sample waters were collected in Toyama Prefecture, Japan. The seawater sample was filtered through a membrane filter, placed in a plastic bottle, and stored in a
refrigerator. According to the optimized analytical procedure, IAP extraction / acid back-extraction was performed. As a result, lithium was recovered quantitatively without its co-precipitation due to hydroxide formation and precipitation. Addition recovery experiments were conducted on seawater samples at concentrations of 0.1 mg/L, 0.5 mg/L, and 1.0 mg/L (Table 1). Lithium sub mg/L level in seawater could be recovered quantitatively. When comparing the results obtained with seawater (slope $2.0 \times 10^3$) to the calibration curve prepared using the standard solution (slope: $2.0 \times 10^3$), a calibration curve with almost the same slope was obtained. Therefore, we clarified that lithium can be extracted efficiently without being affected by coexisting components in seawater.

For GF-AAS measurement, lithium in fresh water samples was measured. The lithium concentration in Oyabe River water was 0.038 μg/L, and Sho River water was 0.428 μg/L. For the spring water (Uriwari-syozu) sample, a spike recovery test was performed at concentration of 0.2 μg/L (Table 1). Lithium sub μg/L level in the spring water could be recovered quantitatively.

**Conclusions**

A method for the pre-concentration of lithium from environmental water by IAP extraction / acid back-extraction was developed and applied to measurements by LEP-AES and GF-AAS.

Dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione), which is a chelating reagent and an organic anion, can be reused by collecting the IAP after acid back-extraction and phase separation or washing.

Since the lithium was recovered quantitatively from seawater, this IAP extraction/acid back-extraction method has the potential for lithium recovery.
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Table 1  Recovery tests for lithium (Li) added to seawater and spring water samples

| Sample        | Li added / mg L\(^{-1}\) | Li found / mg L\(^{-1}\) mean ± sd\(^a\) | Recovery of added Li mg L\(^{-1}\) mean ± sd\(^a\) | RSD,\(^b\) % of mean ± sd\(^a\) | No. | Instrument |
|---------------|--------------------------|------------------------------------------|---------------------------------|---------------------------------|-----|------------|
| Seawater \(^c\) |                           |                                          |                                 |                                 |     |            |
| 0             | 0.27                     | —                                        | —                               | —                               |     |            |
| 0.10          | 0.37 ± 0.03              | 0.10 ± 0.03                              | 100 ± 30                        | 3                               |     | LEP-AES    |
| 0.50          | 0.78 ± 0.07              | 0.51 ± 0.07                              | 102 ± 14                        |                                 |     |            |
| 1.00          | 1.25 ± 0.06              | 0.98 ± 0.06                              | 96 ± 6                          |                                 |     |            |
| Spring water \(^d\) |                         |                                          |                                 |                                 |     |            |
| 0             | 0.00037 ± 0.00003        | —                                        | —                               | 5                               |     | GF-AAS     |
| 0.00020       | 0.00058 ± 0.00004        | 0.00021 ± 0.00007                        | 104 ± 34                        | 4                               |     |            |

a. mean ± sd: mean ± standard deviation.

b. RSD: relative standard deviation.

c. About 16 km from the mouth of the Jinzu River, in Toyama Bay.

d. Uriwari-syozu, in Tonami City, Toyama Prefecture, Japan.
**Figure Captions**

Fig. 1  Optimization of extraction conditions with (A) effect of the addition of 2,2,6,6-tetramethyl-3,5-heptanedione (HDPM) on the recovery of lithium as a chelating reagent and an organic anion, atomic spectrometer; LEP-AES, [Li⁺]; 1.0 mg/L, see section on optimization for the recovery, (B) effect of concentration of potassium hydroxide in the sample solution on the LEP-AES intensity, [Li⁺]; 1.0 mg/L, the same as the optimized analytical procedure, except for the concentration of potassium hydroxide, (C) standing time for the chelate formation, that is, the time from adding HDPM to adding C₁₄BzDMA⁺ soln., [Li⁺]; 0.5 mg/L, see section on optimization for the recovery, (D) effect of 0.1 M C₁₄BzDMA⁺ soln. added on the LEP-AES intensity, [Li⁺]; 1.0 mg/L, the same as the optimized analytical procedure, except for the concentration of potassium hydroxide. Error bars are standard deviation.

Fig. 2 Schematic representation of the lithium complex formation, ion-associate extraction and back microextraction system. HDPM (DPM⁻): 2,2,6,6-tetramethyl-3,5-heptanedione (anion type), C₁₄BzDMA⁺: benzyldimethyltetradecylammonium ion, IAP and iap: ion-associate phase, aq.: aqueous phase. A: IAP extraction, B and B’: back-extraction, C and C’: organic phase (IAP) collected for recovery.

Fig. 3 Testing lithium back-extraction using different acids. The acid volume was 400 µL, the concentration of acid, 2.0 mol/L; the concentrations of lithium, 1.0 mg/L for LEP-AES (white bar, left axis), 400 ng/L for GF-AAS (black bar, right axis). The same as the optimized analytical procedure, except for the type of acid for back extraction.

Fig. 4 Effect of acid concentration on lithium measurement. The acid volume was 400 µL, the concentrations of lithium, 1.0 mg/L for LEP-AES (white circle and white triangle, left axis), 400
ng/L for GF-AAS (black circle, right axis). Acid; sulfuric acid (triangle), nitric acid (circle). The same as the optimized analytical procedure, except for description.

Fig. 5 Scheme of the ion-associate phase extraction / acid back-microextraction method for atomic spectrometry.

HDPM : 2,2,6,6-tetramethyl-3,5-heptanedione, C\textsubscript{14}BzDMA\(^+:\)

benzyldimethyltetradecylammonium ion, aq.: aqueous phase, iap: ion associate phase.
Fig. 1  Optimization of extraction conditions with (A) effect of the addition of 2,2,6,6-tetramethyl-3,5-heptanedione (HDPM) on the recovery of lithium as a chelating reagent and an organic anion, (B) effect of concentration of potassium hydroxide in the sample solution on the LEP-AES intensity, (C) standing time for the chelate formation, that is, the time from adding HDPM to adding C_{14}BzDMA^{+} soln., (D) effect of 0.1 M C_{14}BzDMA^{+} soln. added on the LEP-AES intensity.
Fig. 2  Schematic representation of the lithium complex formation, ion-associate extraction and back microextraction system. HDPM (DPM⁻): 2,2,6,6-tetramethyl-3,5-heptanedione (anion type), C₁₄BzDMA⁺: benzylidimethyltetradecylammonium ion, iap: ion-associate phase, aq.: aqueous phase. A: IAP extraction, B: back-extraction, C: organic phase (IAP) collected for recovery.
Fig. 3 Testing lithium back-extraction using different acids. The acid volume was 400 µL, the concentration of acid, 2.0 mol/L; the concentrations of lithium, 1.0 mg/L for LEP-AES (white bar, left axis), 400 ng/L for GF-AAS (black bar, right axis). The same as the optimized analytical procedure, except for the type of acid for back extraction.
Fig. 4 Effect of acid concentration on lithium measurement. The acid volume was 400 µL, the concentrations of lithium, 1.0 mg/L for LEP-AES (white circle and white triangle, left axis), 400 ng/L for GF-AAS (black circle, right axis). Acid; sulfuric acid (triangle), nitric acid (circle). The same as the optimized analytical procedure, except for description.
Figure 5  Scheme of the ion-associate phase extraction / acid back-microextraction method for atomic spectrometry.

HDPM : 2,2,6,6-tetramethyl-3,5-heptanedione, C\textsubscript{14}BzDMA\textsuperscript{+}:

benzyldimethyltetradecylammonium ion, aq.: aqueous phase, iap: ion associate phase.
Graphical Index

Measurement of Li⁺
Recovery of Li⁺

Recovery of HDPM

HDPM (Chelate, Organic anion)
KOH
C14BzDMA⁺ (Organic cation)
HNO₃
400 μL

Sample 10 mL
Chelation
Ion associate formation
Centrifuge
Remove aq. phase
Stand
Collect

Acid phase (Li⁺)
40 μL 20 μL
LEP-AES  GF-AAS

Reusable

Washing

Reusable as HDPM