

SEPARATION AND DETERMINATION OF A TRACE AMOUNT OF LITHIUM AS ITS THENOYLTRIFLUOROACETONE COMPLEX WITH 12-CROWN-4 BY MEANS OF SYNERGIC EXTRACTION AND FLAME PHOTOMETRY

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Abstract - A new method for the separation and determination of a trace amount of lithium in ppb~ppm level in water as its thenoyltrifluoroacetone (TTA) complex with 12-crown-4 (12C4) has been established by means of synergic extraction and back extraction combined with flame photometry. The effect of various factors (pH, solvent, reagent concentration, shaking time, preconcentration factor, and foreign ions etc.) on the extraction and back extraction of lithium has been investigated.

Here the lithium TTA chelate in o-dichlorobenzene forms stable adducts with 12C4 ($\text{LiTTA} \cdot n12\text{C}_4$, $n=0\sim2$); the stability constants (β_n) of the adducts determined by means of curve fitting method being $\beta_1=4.46$ and $\beta_2=6.45$. The amount of lithium in sodium chloride of guaranteed reagent was found to be 9.5 ± 0.2 ppb by means of the proposed method.

Key words lithium, thenoyltrifluoroacetone, 12-crown-4, synergic extraction, flame photometry

The lithium content in natural waters and in analytical reagents of alkali metals is generally known to be in ppb~ppm level, and it must be separated and/or concentrated prior to its determination by means of an ordinary flame photometry. Moreover, it takes a long time to separate lithium from foreign ions, especially alkali metals, by ion exchange method to avoid their effect on flame photometry(1). It has been reported that the ion-pair extractability of lithium picrates with 12-crown-4 (12C4) in dichloromethane and o-dichlorobenzene (ascertained by the present authors) is about 0~1.7% (2). After preliminary experiments on the extraction behavior of lithium at about 7~8 with TTA (thenoyltrifluoroacetone) in various organic solvents such as benzene, benzene with 12C4, cyclohexane with 12C4, and o-dichlorobenzene with 12C4, it has been found that lithium can be extracted completely when using o-dichlorobenzene with TTA and 12C4; the synergic effect being larger than that with TTA and TBP (tributylphosphate) in benzene (3~5). On the basis of these results, the extraction behavior of TTA chelate of lithium in o-dichlorobenzene with 12C4 has been investigated in detail, and a new method for the preconcentration, separation, and determination of a trace amount of lithium has been established by means of extraction and back extraction combined with flame photometry.

EXPERIMENTAL

Apparatus A model Z-6100 Hitachi Polarized Zeeman Atomic Absorption/Flame Emission Spectrophotometer; a Taiyo Recipro Shaker, model SR-II, a Tomy Seiko Swing Type Centrifuge, model CD-50R, and a Hitachi-Horiba pH meter, model M-7II, were used.

Materials A 1000 mg/l of lithium standard stock solution ($f=1.01$) in 0.01 mol/l hydrochloric acid (obtained from Wako Pure Chemical Industries, Ltd.) was used by suitable dilution with water purified by ion-exchange treatment. Thenoyltrifluoroacetone (TTA) and 12-crown-4 (12C4) purchased from Dojindo Co., Ltd., and Kanto Chemical Co., Inc., were guaranteed-grade materials. All the other chemicals were reagent-grade materials.

Extraction of Lithium A 10 ml of 0.01~0.1 ppm lithium solution was adjusted to the desired pH with buffer solutions of pH 4~10 prepared by mixing an appropriate amount of the 0.1 M of hydrochloric acid and sodium borate buffer, and 1.0 M of hydrochloric acid and potassium hydroxide. When the buffer solutions of 0.5 M NH_4OH -0.5 M NH_4Cl and 0.1 M CH_3COONa -0.1 M CH_3COOH were used, the extractability of lithium at pH 7.5 was decreased as 91.0% and 43.9% respectively, and these buffer solutions were not used throughout this investigation.

The aqueous solution and the same volume of an organic solution of 0.1 M TTA-0.2 M 12C4 in o-dichlorobenzene were placed in a 30 ml of glass-stoppered centrifuge tube, and were agitated on a shaking machine for 10 min. After the separation of the two phases by centrifugation at 2000 rpm for 5 min, and then by using separatory filter paper, a 10 ml

of the organic phase was shaken with 1 ml of 1.0 M hydrochloric acid solution for 1 min. The amount of lithium stripped from the organic phase was determined by flame photometry at 670.8 nm. The pH of the aqueous phase was determined again after the extraction. Another alkali (Na, K) and alkaline earth metals (Mg and Ca) were also extracted with 0.1 M TTA-0.2 M 12C4 in o-dichlorobenzene, and the concentration of metals was determined by atomic absorption spectrometry at 285.2 nm for magnesium and at 422.7 nm for calcium, and by flame photometry at 589.0 nm for sodium and at 766.5 nm for potassium after stripping their metals with 0.01~1.0 M hydrochloric acid solution.

RESULTS AND DISCUSSION

Effect of solvent The effect of organic solvent on the extractability of the lithium TTA chelate with or without 12C4 was investigated by varying organic solvents such as benzene, cyclohexane, and o-dichlorobenzene. The results are summarized in Table 1. The extractability of lithium as the lithium-TTA-12C4 chelate adduct (Fig. 1), $\text{Li(TTA)} \cdot 2(12\text{C}_4)$, in o-dichlorobenzene gave higher values of all solvent investigated.

TABLE 1. Effect of organic solvent on the extractability of lithium with 0.1 M TTA in various solvents with or without 0.2 M 12C4

Organic phase	Aqueous phase (pH)	% E
C_6H_6 (Benzene)	7.58	3.4
C_6H_6 with 0.2 M 12C4	8.05	57.2
C_6H_{12} (Cyclohexane) with 0.2 M 12C4	7.20	2.2
$\text{C}_6\text{H}_4\text{Cl}_2$ (o-Dichlorobenzene) with 0.2 M 12C4	7.81	99.0

Effect of pH The effect of pH on the extractability of the lithium-TTA-12C4 chelate adduct in o-dichlorobenzene was investigated. The result is shown in Fig. 2 along with those of sodium, potassium, magnesium, and calcium under the same conditions. The percent extraction (%E) of lithium rose steeply over the pH range 5.0~7.5, and reached a plateau (97.0~100%) in the pH-range 7.5~9.0.

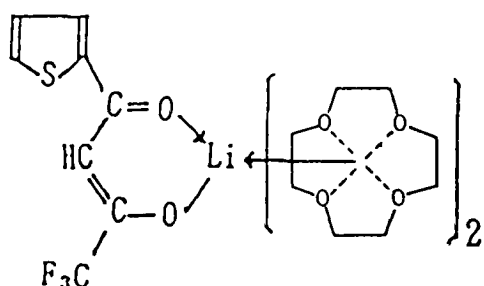


Fig. 1. Li-TTA-12C4 adduct

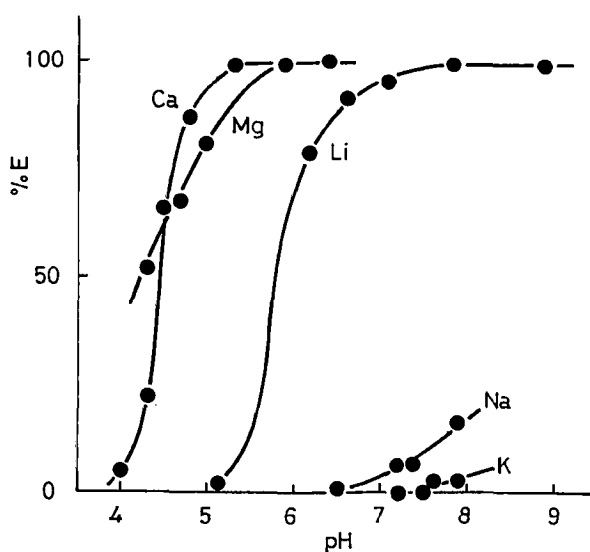


Fig. 2. Effect of pH on the extractability of lithium, sodium, potassium, calcium, and magnesium with 0.1 M TTA and 0.2 M 12C4 in o-dichlorobenzene

Effect of shaking time The extraction was carried out for various time of shaking from 10 sec to 5 min at pH 7.2. The results are given in Table 2. Beyond 30 sec shaking, the extraction attained equilibrium. In order to ensure complete extraction, one min shaking was employed.

TABLE 2. Effect of shaking time on the extractability of lithium with 0.1 M TTA in o-dichlorobenzene with 0.2 M 12C4 at pH 7.2

Shaking time (min)	% E
0.17	93.8
0.50	97.0
1.50	97.0
2.00	97.1
3.00	96.7
3.50	97.0
4.00	97.1
4.50	97.1
5.00	97.1

Composition of extracted species The composition of the extracted species was ascertained by plotting a $\log D/D_0$ vs. $\log(12C4)_0$ at fixed pH 7.7 and by analyzing the data (Fig. 3) with curve fitting method (6). Judging from the partition coefficients of 12C4 between organic solvent of benzene derivative and water (2), it is assumed that most of 12C4 exist in o-dichlorobenzene after equilibrium. The $\log D$ vs. pH plots gave the straight line with a slope of unity. Where D and D_0 are the distribution ratios of lithium with or without 12C4. It has been found that the lithium TTA chelate in o-dichlorobenzene forms stable adducts with 12C4 ($LiTTA \cdot n12C4$, $n=0 \sim 2$); the stability constants (β_n) of the adducts being $\beta_1=4.46$ and $\beta_2=6.45$, β_2 of which was larger than that of $LiTTA \cdot 2TBP$ adduct in benzene ($\beta_2=5.96$) (3).

Effect of extraction volume When the volume of the organic phase of 0.1 M TTA with 0.2 M 12C4 in o-dichlorobenzene was kept at 10 ml, and when that of the aqueous phase was varied from 10 to 100 ml, the extractability of lithium at 7.2~7.7 decreased to about 50%. Therefore, the extraction of lithium was carried out with the same volume ratio of 1:1, after which the back extraction was carried out with 1.0 M hydrochloric acid solution with the volume ratio of 1:10; the preconcentration factor being 10, as in the case of the previous report (5).

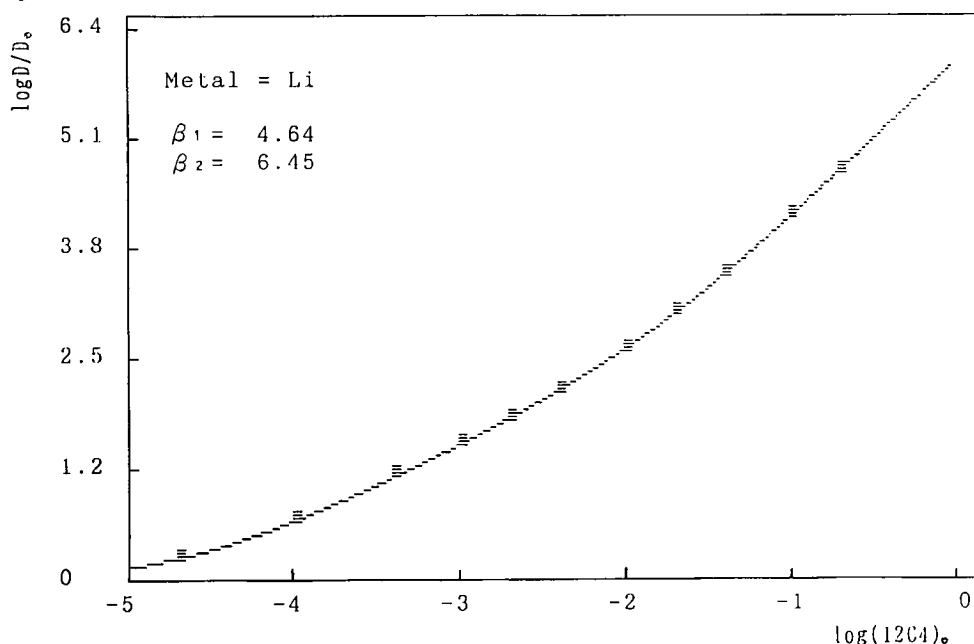


Fig. 3. Effect of 12C4 concentration on the extractability of lithium with 0.1 M TTA in o-dichlorobenzene at fixed pH 7.7

Calibration curve A calibration curve of lithium was prepared by measuring the absorption intensity with a flame photometer at 670.7 nm by varying the amounts of lithium in 0.01 M hydrochloric acid solution. Excellent linearity of the calibration curve of lithium was obtained in the range of 0.01~0.1 ppm. A 1 ppb of lithium can be determined by the present method, because the volume of the final aqueous solution has no effect on the back extraction recovery of lithium, even at a tenth volume of the organic phase. The recommended systematic experimental procedure is shown in Fig. 4.

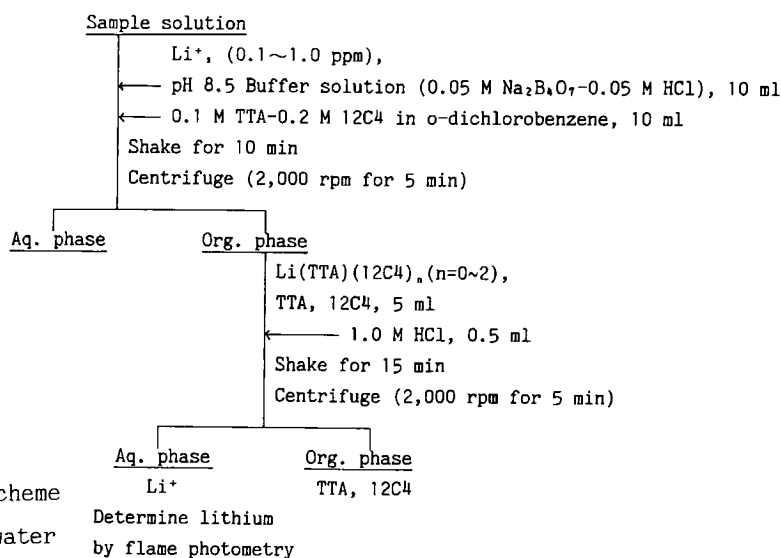


Fig. 4. Analytical scheme
of lithium in water

Effect of foreign ions The effect of the presence of foreign ions which may exist in fresh water, on the determination of a trace amount of lithium with the recommended method is given in Table 3.

These results indicate that none of the ions investigated interferes with the determination of lithium. Sodium and potassium co-extracted along with lithium can be pre-removed by back extraction at pH 7.0~8.0, and then lithium can be back extracted quantitatively at pH 5.0~6.0; magnesium and calcium being remained in organic phase without interference with the determination of lithium.

TABLE 3. Effect of foreign ions on the determination of a trace amount of lithium (0.1 ppm Li)

Foreign ions	Concentration (times that of Li)	Recovery of Li (%)
Na ⁺	11,500	99.8*
Mg ²⁺	1,000	108.7
Ca ²⁺	1,000	92.1
Cl ⁻	17,700	99.8*
CO ₃ ²⁻	1,000	98.3
SO ₄ ²⁻	1,000	98.4

1.0 ppm Li

Analysis of lithium in sodium chloride reagent The amount of lithium in 1g of sodium chloride of guaranteed grade reagent dissolved in water was found to be 9.5 ± 0.2 ppb by means of the proposed method. In this analysis, the extraction and back extraction were repeated twice times; the recovery of lithium being 74~76%.

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