



Removal of Mineral Salts by Heteropoly Acid-Crown ether Adduct for Quick Determination of Trace Amounts of Lithium in Natural Brines

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ABSTRACT

There is severe interference by a number of metallic ions found in brines in the determination of lithium by flame atomic absorption and emission spectroscopic methods. The formation of heteropoly acid-crown ether adduct was used for removing the interfering ions from the brine matrix. The appropriate crown ether was selected to make sure that essentially all lithium ions are left in the solution. Then, the experimental conditions, including the molar ratio of the crown to total cations, the molar ratio of the crown to heteropoly acid were optimized and the influence of acid addition and the stirring time on the measured lithium were investigated. This is a simple and quick method with adequate accuracy for the determination of lithium in highly concentrated solutions and natural brine samples, which contain trace amounts of lithium. The superiority of this method is that organic solvents are not used. This method has been applied to determine lithium and then to estimate the lithium reserves in the natural brine of the Iranian playa.

Key words: Trace amounts of lithium determination, Brine, Heteropoly acid, Crown ethers, Flame spectrometry.

INTRODUCTION

Lithium is one of the rare elements. During recent years, metallic lithium and various kinds of lithium compounds have become important materials in a wide variety of applications, particularly in the industrial, energy and pharmaceutical sectors. The lithium extraction from brines is completed in some countries in South America. The growing demand for lithium draws forth a particular interest for correct determination and identification of natural resources of this element.

Flame emission spectrometry has been widely used for lithium determination due to the low detection limit and the relative simplicity of instrumentation. However, it is subject to several interferences from alkaline and alkaline earth elements, particularly in brines and other geological samples, where the concentration of these elements is very high. A suppressing effect on the lithium determination is observed for Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions. These interferences are caused by scattering, ionization and overlapping spectral emissions. The spectral interferences incurred by calcium (CaOH)

and strontium (SrO) emissions around 670.8 nm are particularly severe.^{1,2} This interference is a systematic constant error that cannot be eliminated using the standard addition method.¹

The use of a platinum-loop atomizer has been proposed to eliminate interference from Ca and Sr, as salts of these elements remained as solid residues on the loop material where high contents of anions, particularly Cl⁻ reduces the lithium signal due to loss of lithium chloride.²

The use of atomic absorption spectrometry for determination of lithium is also subject to interference errors both in flame¹ and in flameless^{3,4} methods.

Some methods have been reported for minimizing interferences in determining lithium, particularly in brines by atomic absorption spectroscopy, including matching the matrix contents of standards with samples, the adoption of standard addition and bracketing standard methods and the use of a high temperature nitrous oxide-acetylene flame instead of an air-acetylene flame. All these methods proved to be effective but time-consuming or in some cases, inputs are not easily obtainable.^{1,5}

Brine is an aqueous solution of one or multiple salts whose TDS is normally above 50 g.L⁻¹. This amount exceeds 250 g.L⁻¹ in natural brines such as salt lake and oilfield brines. In many cases, the brine samples contain trace amounts of lithium ions compared with other components. It has been proven that the molar ratio of lithium to other cations in the brines can be as low as 10⁻⁴. Consequently, the determination of trace amounts of lithium in brines encounters significant interferences of other elements in both emission and absorption spectrometry. So, it is necessary to develop a quick and accurate method to remove the interfering mineral salts from the brine samples in order to determine its lithium content by flame spectrometry.

One method has recently been developed for the determination of trace amounts of lithium in brines by flame spectrometry. In this method, isopropanol is used for removing chloride salts first

after which the sulfate and magnesium ions were removed by precipitation.⁶

In this work, we have developed a method for removing of mineral salts in brines based on interactions of cations, crown ether and heteropoly acid in order to determine trace amounts of lithium by flame emission spectrometry.

EXPERIMENTAL

Reagents and apparatus

Merck lithium chloride standard solution was used. Merck analytical grade metallic chlorides were used in the preparation of the solutions of other salts. The standard solutions of other elements were prepared from analytical grade Merck chemicals as nitrates. Silicotungstic acid (STA), 15-crown-5 (15C5), 18-crown-6 (18C6) and Kryptofix 222 (K222) were purchased from Merck.

The atomic emission analysis was performed using a Jenway flame photometer PFP7 model. The magnesium and calcium remaining in solution were determined by complexometric titration (Vogel).

Preparation of synthetic brines

The synthetic solutions were prepared according to the compositions mentioned in Table 1, via dissolving of corresponding salts in distilled water. These solutions are similar to that of the initial brine to the ponds collected from the playa of Khor located in the central Kavir of Iran, and final brine remained after evaporating and separating of NaCl and KCl, having high calcium, magnesium, nitrate and chloride contents. Besides 5.0 or 20.0 mg.L⁻¹ of lithium ion was added to the synthetic solutions.

Procedure

2.5 mL of synthetic or natural brine was diluted to 100 mL with distilled water. To 10 mL of this solution, was added with constant agitation, various quantities of STA and crown ether corresponding to the different molar ratio of the crown to STA. After stirring for one hour, the precipitate was separated from the liquid by centrifugation. The filtrate was brought to the initial volume (2.5 mL) by evaporation. Finally, lithium or other elements contents were analyzed.

RESULTS AND DISCUSSION

Crown ethers have a specific property of selective complexation with cationic species.⁷⁻⁹ The complexing property of crown ether derivatives depends upon the relative size of ions, hole of the crown ether ring, number and variety of heteroatoms, the geometry of crown ether, etc., and these make them, particularly useful for separating alkali and alkaline earth metal ions.^{10,11} Furthermore, combining crown ether molecules with inorganic heteropoly acids produce organic-inorganic hybrid adduct precipitation that can act as ion exchanger.¹²⁻¹⁶ The crown ether-heteropoly acid precipitate has been used as sensor material in ion-selective

membrane electrodes¹⁷⁻¹⁹ and as adsorbents for adsorption of heavy metal ions.^{20,21}

In this work, it is used for removing interfering cations by precipitation from natural or synthetic brines so that lithium ions remain in solution and are determined without any noticeable interference.

Selection of appropriate crown ether

In order to select appropriate crown ether, three aliquots containing 20.0 mg.L⁻¹ of lithium ion was treated with STA and water soluble crowns, including 15C5, 18C6 and K222 (Scheme 1), individually. The obtained results have been shown

Table 1: Chemical composition of studied brines

Brine type	Concentration of ions (g.L ⁻¹)							Total
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
Initial brine	78.7	3.1	11.5	26.3	202.3	2.6	0.35	325
Final brine	2.4	2.6	61.3	154.9	452.9	10.0	-	684

Table 2: Lithium analysis in natural brines

Method	Concentration of lithium ^a (mg.L ⁻¹)	
	Initial brine	Final brine
Solvent extraction ^b	3.5	14.1
This work	3.6	13.1

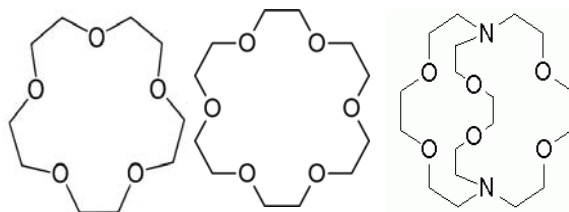
^aThe values represent the average of three experimental results with an error less than 5%. ^bThe reported method in reference 6

in Fig. 1. As it is seen, due to the formation of precipitates, 15C5 removes the majority of lithium ions but in the case of 18C6 and K222, all lithium ions remain in solution. The reason of this result is that 15C5 entraps the lithium ions (ionic diameter 1.56 Å²²) due to the smaller hole of the crown ring (1.84 Å²²) but neither of 18C6 and K222 interacts with lithium ions in solution due to the larger hole of the crown ring (2.9 Å for 18C6 and 2.8 Å for K222)²². Therefore, 15C5 was disregarded as an appropriate crown for precipitating other cations. The 18C6 was

selected for subsequent tests due to lower price and better availability than K222.

Removing of interfering mineral salts

The removal of interfering cations in initial synthetic brine was studied by precipitation formation of STA-18C6 adduct. The results, shown in Fig. 2, indicate that this method can remove approximately 100% calcium, 83% potassium, 77% sodium, and 67% magnesium. For more removal of Mg²⁺, it can be precipitated with potassium or



Scheme 1: Structures of 15-crown-5 (15C5), 18-crown-6 (18C6) and Kryptofix 222 (K222) from left to right, respectively

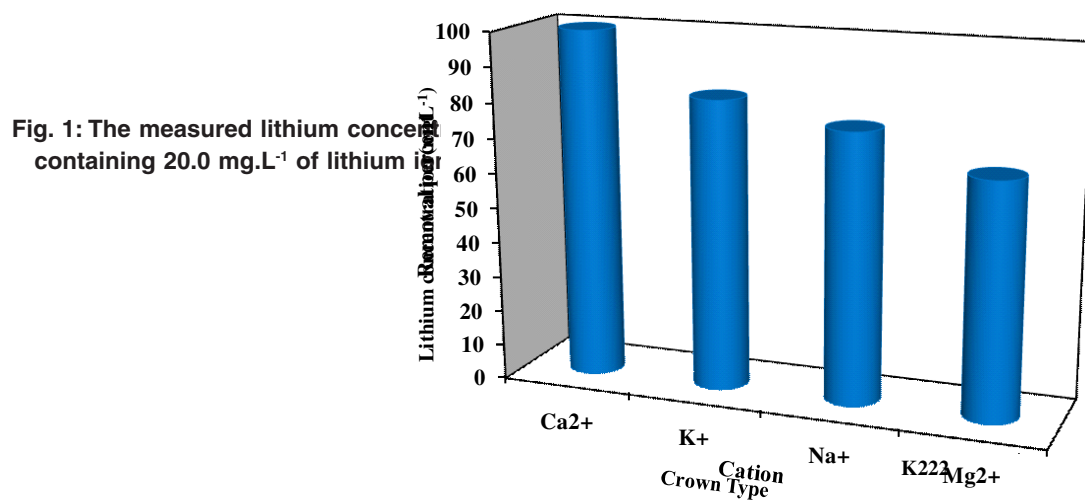


Fig. 2: The removal percent of interfering cations in initial synthetic brine by precipitation formation of STA-18C6 adduct

sodium carbonate. Hence, Mg^{2+} is replaced with K^+ or Na^+ cations that are removed more efficiently with STA-18C6. In an aqueous solution containing alkali and alkaline earth metal ions, 18C6 forms 1:1 complexes with Ca^{2+} , Na^+ and K^+ strongly, Mg^{2+} slightly less, but leaves Li^+ completely uncomplexed.²² Therefore, STA-18C6 precipitation decreases the content of the interfering ions without any remarkable effect on the lithium content.

Optimization of 18C6 concentration

In order to investigate of excess 18C6 on the measured lithium, the molar ratio of 18C6 to total cations was varied. The obtained results are shown in Fig. 3. The larger amounts of crown relative to total of cations don't create deviations in the measured lithium. It is obvious that the molar ratio of 18C6 to total of cations must be at least equal to one because lower amounts can not remove completely interfering cations present in brine.

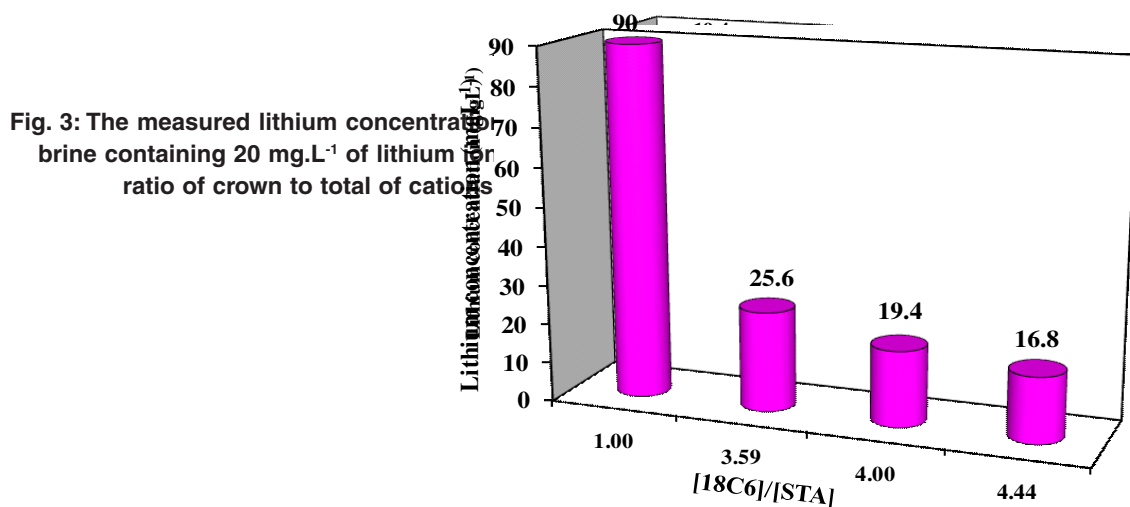


Fig. 4: The measured lithium concentration after treatment of initial synthetic brine containing 20.0 mg.L^{-1} of lithium ion with STA and 18C6 at various molar ratio of 18C6 to STA

Optimization of the molar ratio of 18C6 to STA

The obtained results due to the variation of the molar ratio of 18C6 to STA on the measured lithium in the synthetic brine containing 20.0 mg.L⁻¹ of lithium, shown in Fig. 4, indicate that there is the least deviation at the molar ratio of 4. This molar ratio was also tested on the synthetic brine containing 5.0 mg.L⁻¹ of lithium and the measured lithium was 4.9±0.1 mg.L⁻¹. The stoichiometric composition of crowns with silicotungstic acid has been reported between 2 to 4, where these form precipitates with metal ions.²³⁻²⁶

Influence of acid addition

In the literature,²³⁻²⁶ the precipitation formation of crown and heteropoly acid has been reported in the presence of nitric acid. Therefore, the influence of acid addition on the measured lithium was investigated by diluting of synthetic brine containing 20.0 mg.L⁻¹ of lithium with 1 M nitric acid instead of distilled water. The other steps were similar to the previous procedure. The measured lithium content (50.0 mg.L⁻¹) indicates a severe positive deviation from the added lithium content. Probably, the oxonium ions (H₃O⁺) form precipitation and inhibit from precipitation of other cations, particularly Na⁺ ions.¹⁶ Therefore, the remaining cations interfere in the lithium determination.

Influence of the stirring time

In order to study of lithium retention by STA-18C6 precipitation, the stirring time of solution after the precipitation formation was increased to 24 hours. The comparison of the result with that of the one hour stirring time indicated 11.3% loss of lithium. Therefore, STA-18C6 solid phase doesn't retain lithium in short times contrary to inorganic salt precipitation.^{6,27}

Application of the procedure to natural brines

The procedure was applied to trace lithium determination in natural brines of Khoran playa

located in the central Kavir of Iran. The composition of brines has been previously mentioned in Table 1. In the case of the strongly magnesian brine (final brine), firstly, Mg²⁺ ions were precipitated as Mg(OH)₂ by adding KOH solution. Therefore, the K⁺ ions replaced Mg²⁺ ions, which were essentially removed in the precipitation step with formation step with STA-18C6 (Fig. 2). The results obtained by this method and organic solvent extraction method,⁶ are tabulated in Table 2. As it is seen, the results conform well indicate our method presents accurate results. However, our procedure has advantages as follows: 1) It does not use any toxic organic solvent. 2) This method is simpler and quicker because it has one step and does not need to apply and then remove organic solvent through a distillation step. 3) The precipitation formation process does not add the other interfering ions to the solution. 4) The STA-18C6 precipitation does not incur lithium losses and therefore, the solid-liquid separation can be carried out shortly after the dosing.

CONCLUSION

In the present study, trace amounts of lithium have been determined in complex chemical composition of highly concentrated solutions and natural brines using a flame photometer. The interfering mineral salts were removed by a heteropoly acid-crown ether adduct. This is a simple and quick method with adequate accuracy and is free from toxic organic solvents. This procedure can be applied to the lithium determination in brines and hence evaluation of the lithium reserves in them.

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