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Comparison of ion exchange methods for lithium-7 isotopic enrichment for application in PWR reactors

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Abstract: ^{7}Li in the form of lithium hydroxide monohydrate ($LiOH \cdot H_2O$), remains liquid over a wide temperature range (180 to 1340ºC), making it an excellent pH controller on reactor coolant in Pressurized Water Reactors (PWRs). In contrast, ^{6}Li is a strong neutron absorber and unsuitable for PWRs, whereas ^{7}Li has a low neutron cross-section, making it ideal for reactor use. Enriching ^{7}Li to over 99.95% is essential but complex. The Colex method, involving mercury, was used for enrichment but was banned in the USA due to environmental concerns. Currently, Russia and China are the primary sources of enriched ^{7}Li. A mercury-free procedure to obtain this isotope is necessary, ion exchange techniques, including frontal analysis, elution, and displacement chromatography, offer alternative enrichment methods. This study evaluates these techniques to achieve the required ^{7}Li enrichment for PWR applications. Preliminary results showed an abundance of ^{7}Li at 95.65% after displacement of 830 cm.

Keywords: isotopic enrichment, ion exchange, displacement chromatography, isotopic analysis.

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Comparação de métodos de troca iônica para enriquecimento isotópico do Lítio 7 para aplicação em reatores PWR.

Resumo: ^{7}Li na forma de hidróxido de lítio monohidratado ($LiOH \cdot H_2O$), permanece líquido em uma ampla faixa de temperatura (180 a 1340 ºC), tornando-o um excelente controlador de pH no refrigerador em reatores de água pressurizada (PWRs). Em contraste, ^{6}Li é um forte absorvedor de nêutrons e inadequado para PWRs, enquanto ^{7}Li tem uma baixa seção de choque de nêutrons, tornando-o ideal para uso em reatores. Enriquecer ^{7}Li para mais de 99,95% é essencial, porém complexo. O método Colex, envolvendo mercúrio, foi usado para enriquecimento, mas foi proibido nos EUA devido a problemas de contaminação ambiental. Atualmente, Rússia e China são as principais fontes de ^{7}Li enriquecido. Um procedimento livre de mercúrio para obter este isótopo é necessário, técnicas de troca iônica, incluindo análise frontal, eluição e cromatografia de deslocamento, oferecem métodos alternativos de enriquecimento. Este estudo avalia essas técnicas para atingir o enriquecimento de ^{7}Li necessário para aplicações PWR. Resultados preliminares mostraram uma abundância de ^{7}Li em 95,65% após deslocamento de 830 cm.

Palavras-chave: enriquecimento isotópico, troca iônica, cromatografia de deslocamento, análise isotópica.

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1. INTRODUCTION

Lithium, the lightest alkali metal, has a density of 0.534 g cm^{-3}, atomic number 3, and atomic mass 6.94. Natural lithium consists of two stable isotopes: ^{6}Li (6.015 amu) and ^{7}Li (7.017 amu), with average abundances of 7.591% and 92.409%, respectively. This yields an isotopic ratio of $^{6}Li/^{7}Li = 0.08215$ [1]. The ^{7}Li isotope, in the chemical form of LiOH monohydrate, has a wide temperature range (between 180 to 1340ºC) in which it remains in the liquid state. Due to this property, it is currently used as pH stabilizer and helps to neutralize acidity caused by boric acid (containing boron-10), on primary coolant in PWR (Pressurized Water Reactor) nuclear reactors [2,5]. Additionally, it serves as an excellent pH stabilizer, helping to reduce corrosion of reactor primary circuit components.

The isotopes of a chemical element, specifically in the case of lithium, have very similar chemical and physical properties. However, for nuclear applications, these isotopes behave as completely different substances. ^{7}Li has a cross section of 0.045 barns, making it suitable for the purposes mentioned above. On the other hand, ^{6}Li has a cross section of 940 barns, which means that this isotope is a good neutron absorber and is used as a producer of tritium. Nevertheless, it is undesirable inside of a PWR. Consequently, the separation of its isotopes and the enrichment of ^{7}Li above 99.95% is necessary for this application, but there is a certain complexity in the separation of these isotopes [3-6].

In the 1950s, some companies used the Colex method to enrich ^{7}Li, which consists of using mercury amalgam in separation by ion exchange. However, this method was banned in the USA in 1963 due to the significant environmental impact caused by the exposure of mercury as waste, leakage, and evaporation in the environment [1,6]. Currently, the market of enriched ^{7}Li are detained by Russia (80%) and China (20%). Russia obtains ^{7}Li by electrolysis of lithium chloride, which also involves the use of mercury [1].

To address environmental concerns, a new lithium isotope production method is required [7]. The ion exchange technique is a method where the separation of isotopes is carried out by balancing the fractionation of isotopes into two phases: stationary phase (ion exchange resin) and mobile phase (solution). Key benefits include resin regeneration and reusability. There are three main techniques in ion exchange: frontal analysis, elution and displacement [8].

In this work, three procedures were carried out to enrich ^{7}Li by ion exchange, frontal analysis, elution and displacement chromatography. The goal was to evaluate which technique is the most suitable for achieving ^{7}Li enrichment to 99.95% for application in a PWR reactor.

1.1. Chromatography by Frontal Analysis, Displacement and Elution

In ion exchange by frontal analysis, the solution containing the target ion is introduced into the column until the resin reaches its total retention capacity. With the continuous passage of the feed solution, the ion with the lowest affinity is desorbed by the resin and thus begins to displace and promote enrichment. In the elution technique, after loading the resin with the ion mixture, separation is promoted by adding a solution containing ions with less preference than the ions to be separated, but in excess. The ions are released from the resin according to their affinity for it [9,10].

In the displacement technique, one of the isotopes is adsorbed on the resin, forming an adsorption band that moves through the column by interacting with a displacement solution, containing ions with more affinity for the resin. The adsorption band maintains a constant and distinguishable length of the displacement solution, with rear and front edges well defined. The isotopes within the band are rearranged in the order of their distribution coefficients. This technique is widely used for isotopes of light elements due to its simplicity and achievement of satisfactory separation factors [8-11].

Among these cited techniques some advantages and disadvantges should be highlighted in respect of isotopic separation in specific. The disadvantage of elution technique is the limited amount of target solute that might be introduced in the colunm, dispersion of the adsorption band formed occurs during elution causing isotopic dilution and the bell-shaped elution curve is obtained. Conversely, once elution is complete, the resin will have been regenerated and ready to use again [12,13]. A large solution volume would be required to enrich the ^{7}Li isotope for frontal analysis technique, making it economically unfeasible.

Displacement chromatography offers the advantage of maintaining constant band length, facilitating isotopic separation with lighter isotopes at the rear and heavier isotopes at the front of adsorption band. However, enriching ^{7}Li from 92.5% to 99.95% requires extensive displacement, resulting in a prolonged process [8].

2. MATERIALS AND METHODS

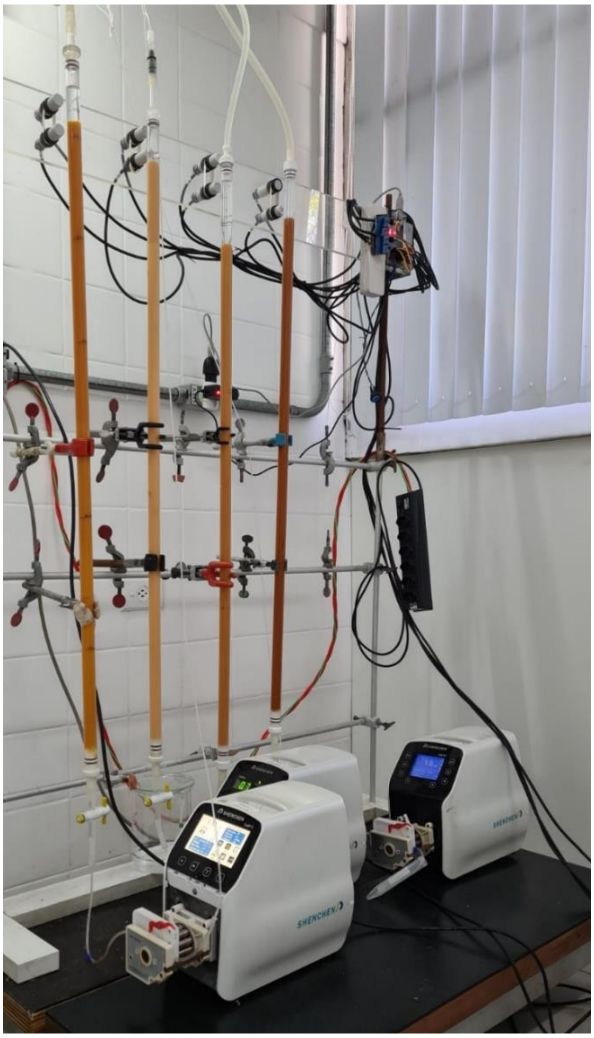
To carry out the experiments, glass columns of 120 cm lenght and 13 mm in diameter, as well as acrylic columns 100 cm lenght and 13 mm in diameter, were used. The resin employed was BioRad AG® 50w x16 with a mesh size of 200-400. LiOH and LiCl were employed as feed solutions. Samples collected from the columns underwent analysis using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy – ESPECTRO model ARCOS) to determine the concentration and ICP-MS (Inductively Coupled Plasma Optical Emission Mass Spectrometry – PERKINELMER model Elan 6000) to determine the isotopic ratio.

The experiment 1 was set for elution technique. It utilizes 400 mL of feed solution at 0.02 M LiOH in acidic medium and 30% methanol (MeOH), to adsorb onto the resin. The LiOH was recirculated over three glass columns, filed with AG 50W x16 resin with average lenght of 40 cm (totaling 460 mL of resin). The total length traveled was 744 cm. Subsequently, each column was eluted with 1.0 M HNO_3 solution containing 80% MeOH. From column 1, fourteen samples of 20 mL were collected, fifteen samples from column 2 and thirteen samples from column 3. All samples were analysed by ICP-OES and ICP-MS.

The experiment 2 was set for frontal analysis, employed the same columns as in Experiment 1, 4.5 L of 0.22 M LiOH solution in 0.5 M HCl and 30% MeOH until saturation of the 3 columns. The separation and enrichment of isotopes were then facilitated by circulating 1.0 L of LiOH solution in 0.5 M HCl and 60%, 70% and 80% MeOH. Each column was individually eluted with a solution of 1.0 M HCl containing 80% MeOH and 15 samples of 20 mL were collected from columns 1, 2 and 3.

And finally, the experiment 3 was set for displacement chromatography technique. It utilized 4 acrylic columns filled with resin to a length of 92.5 cm, as show in Figure 1. A 0.15 M LiCl solution was percolated through the first column until saturation. The resulting band was displaced with 0.15 M Calcium Acetate solution. After 829.5 cm length an aliquot of 10 mL was collected and subjected to analysis by ICP-OES and ICP-MS.

Figure 1: Experiment 3 employs displacement chromatography utilizing four acrylic columns in series for isotope enrichment. Peristaltic pumps facilitate solution circulation.



Source : Author's personnal archive.

Isotopic analysis were performed using ICP-MS ELAN DRC II (PerkinElmer). Daily optimization of nebulizer gas flow and autolens settings employed a certified lithium carbonate standard (LSVEC from International Atomic Energy Agency – IAEA), exhibiting a natural isotopic ratio of 0.08215 (6Li: 7.591%, 7Li: 92.409%). The reference material (0.5 g) was dissolved in 50 mL of 2% ultrapure HNO_3, yielding a 10,000 mg L^{-1} stock solution. This was diluted to prepare:

1. Intermediate solution: 0.25 mL stock + 50 mL 2% HNO_3 (concentration: 50 mg L^{-1}).

2. Working solution: 1 mL intermediate + 1,000 mL 2% HNO_3 (concentration: 50 μg L^{-1}).

Collected samples were analyzed for concentration using ICP-OES Spectro, employing a calibration curve in a range of 0.25-10.0 μg mL^{-1}. Samples were then diluted to 50 μg L^{-1} and assessed for isotopic ratio by ICP-MS. Table 1 presents the method parameters used in the ICP-MS analysis.

Table 1 : ICP-MS Method Parameter for isotopic analysis

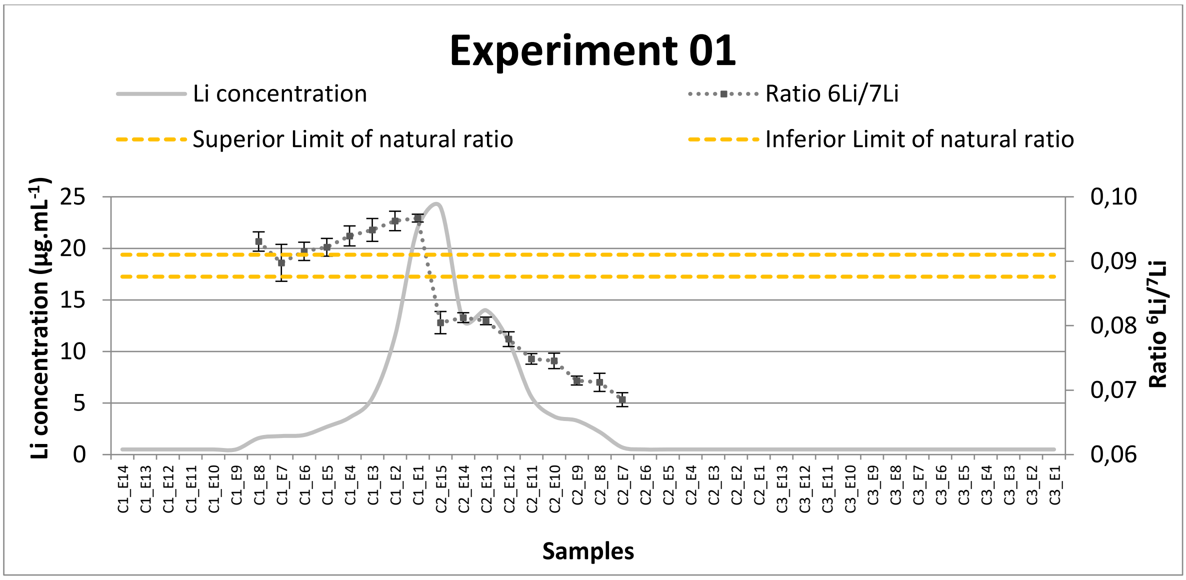
Parameter	HEAD
Nebulizer Gas Flow	1.1 L min^{-1}
Radio Frequency	600 W
Gas flow rate	1.2 L min^{-1}
Peak Hoping mode	-
Dwell time	480 ^{6}Li 80 ^{7}Li
Sweeps per reading	50

3. RESULTS AND DISCUSSIONS

Upon formation of a lithium adsorption band, continuous passage of Li solution or displacement solution causes isotopic separation, enriching ^{6}Li in the rear and ^{7}Li in the front [3,7,8,11].

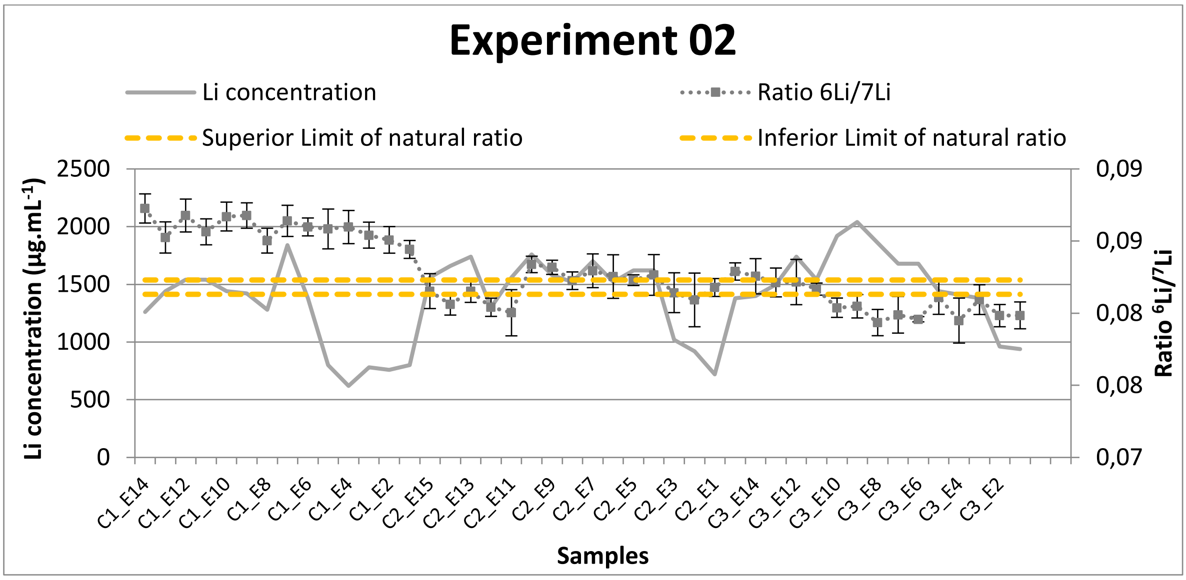
In experiment 1, 400 mL of LiOH were circulated through three columns for three times. After first and second rounds, a sample of 20 mL was collected for analysis. No Li was detected on those samples, which indicates that all Li ions were adsorbed on resin in the column. The Li band of 1.5 cm formed was displaced through approximately 744 cm of resin before the elution of each column. The lithium adsorption profile is presented in Figure 2.

Figure 2. Concentration and Isotopic Ratio Profiles of Eluted Samples from Experiment 1's Three-Column Configuration.



The concentration curve in the graph (Figure 2) reveals a split distribution of Li, with approximately half in Column 1 and half in Column 2. The elution curve's bell-shaped profile aligns with theoretical expectations of elution technique. Notably, Column 2 (C2_E7-C2_E15) exhibits enrichment of ^{7}Li in the front band, whereas Column 1 (C1_E2-C1_E15) shows ^{6}Li enrichment in the rear band. The transition from feed solution to HNO_3 elution solution alters the equilibrium constant, and potentially diluting enriched/depleted fractions.In experimente 2, after saturating three columns with 4.5 L of LiOH solution, samples of 20 mL were collected for analyisis. 1.76 L of 0.22 M LiOH in HCl/MeOH 30%, 1.0 L of 0.22 M LiOH in HCl/MeOH 60% and 1.0 L of 0.22 M LiOH in HCl/MeOH 80% were added to the columns. This experiment yielded 202 samples, which were analyzed, revealing no enrichment of Lithium isotopes. Subsequent individual column elution with 1.0 M HCl/MeOH (80%) produced 15 samples (20 mL each). The lithium adsorption profile from elution is presented in Figure 3.

Figure 3. Concentration and Isotopic Ratio Profiles of Eluted Samples from Experiment 2.



The elution curves exhibit near-bell-shaped profiles, suggesting incomplete Li desorption due to insufficient 1.0 M HCl concentration. Consistent with theoretical predictions, Experiment 2 showed that continuous charge solution input led to ^{7}Li accumulation at the band's front and ^{6}Li accumulation at the rear, with no band migration observed, unlike Experiments 1 and 3.In experiment 3, the first column was saturated with 0.15 M LiCl to form the Li adsorption band with a height of 92.5 cm. The Li band was displaced to the second column by introducing a solution of 0.15 Calcium Acetate. When the Li band was almost at the end of the second column, a third column was connected to receiv the band, followed by a fourth column. After the band left the column, the resin was regenerated with 3.0 M HCl and washed with ultrapure water until neutralized. Then the column was ready to receive the Li band again. Four samples were collected after the third time the Li band passed through the second column, moving 829.5 cm with displacement solution (Calcium Acetate). The results of concentration and isotopic ratio are presented in Table 2 in comparison with concentration and isotopic ratio of feed solution.

Table 2. Results of concentration an isotopic ratio of a sample of Li band collected after displace 829.5 cm (Experiment 03).

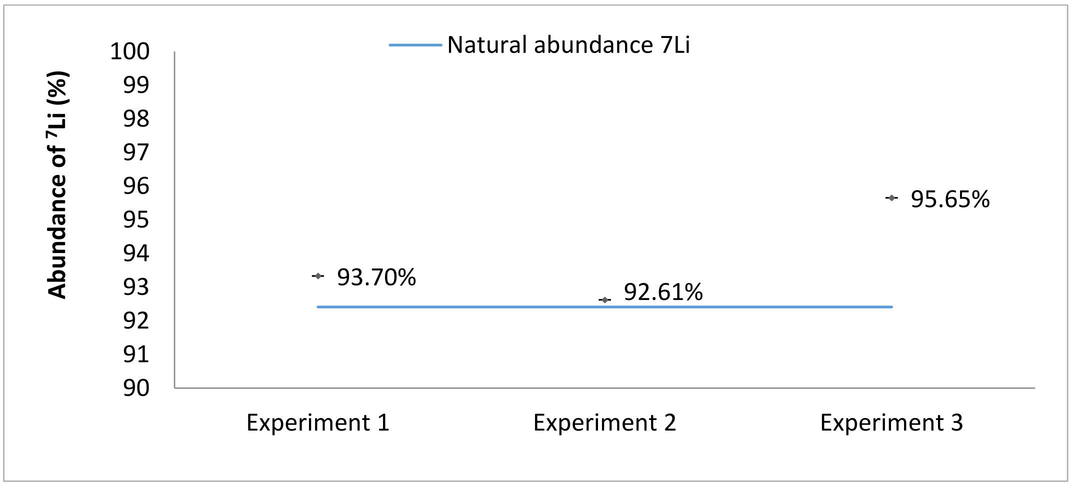
	Li Concentration (µg mL^{-1})	**Ratio ^{6}Li/^{7}Li**	**SD**
Feed Solution	1003.9	0.0807	0.0008
***P3C2-F4**	16.9	0.0482	0.0005

*Percolation 3 Column 2 – Fraction 4

Li detection in the fourth fraction indicated elution initiation. Experiment 3 sampling was halted at this point to facilitate sustained isotope enrichment through continuous Li band circulation. As the displacement solution remained unchanged, enriched and depleted fractions remained segregated, preserving the authentic enrichment results.

The ^{7}Li enrichment result from those three experiments are presented in the abundance of this isotope, as shown in Figure 4 below.

Figure 4: Abundance of ^{7}Li in each experiment. The standard deviation for each experiment was 0.095 (Experiment 1), 0.080 (Experiment 2) and 0.043 (Experiment 3).



Source : Author's data.

Results show Experiment 3 achieved greater enrichment than Experiment 1 and 2, despite comparable distances between experiment 1 and 3. Modifying the elution solution may have augmented this enrichment disparity due the changing in equilibrium constant resulting in dispersion of adsorption band. Frontal analysis proved ineffective for this study, as Experiment 2's high volume resulted in poor enrichment.

Displacement chromatography maintains adsorption band equilibrium throughout displacement, preventing enriched fraction mixing and yielding higher masses of enriched material due to column saturation. Unlike displacement chromatography, elution methods fail to leverage full column saturation, limiting utilization to approximately 5%.

4. CONCLUSIONS

This study demonstrates that displacement chromatography yields the most promising results for ^{7}Li enrichment among others ion exchange techniques such as elution and frontal analysis. However, achieving 99.95% enrichment requires displacement exceeding 900 cm, as supported by Hagiwara et al. [8]. Experiment 3 is ongoing to attain this target.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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