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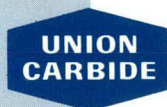
**MASTER**

DETERMINATION OF LITHIUM IN LITHIUM ALUMINATE

W. C. Dietrich

**UNION CARBIDE CORPORATION**  
**NUCLEAR DIVISION**  
**OAK RIDGE Y-12 PLANT**

operated for the **ATOMIC ENERGY COMMISSION** under **U. S. GOVERNMENT Contract W-7405 eng 26**



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### ABSTRACT

A method has been developed for determining the amount of lithium in the ceramic, lithium aluminate, and in other lithium compounds. Lithium is separated from any impurities by the cation exchange resin, Dowex 50-16X, and determined gravimetrically as the sulfate salt. The average recovery for lithium was 99.89 percent, and the  $LE_x (0.95)$  was  $\pm 0.65$  percent.

An interim flame photometric procedure that was established prior to the development of the ion exchange-gravimetric method is also discussed in this report.

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## SUMMARY

The ceramic material, lithium aluminate, was solubilized by fusing the material with a potassium carbonate-boric acid flux, then dissolving the cooled melt with a minimum of hydrochloric acid.

Lithium standards that closely approximated the sample concentrations were analyzed using an interim flame-photometric procedure. Standards that were made to contain 100.0-ppm lithium were analyzed and found to have an average value of 100.89 ppm, with an  $LE_x (0.95)$  of  $\pm 4.4$  ppm.

Solubilized lithium aluminate samples were added to a Dowex 50-8X, 50 - 100-mesh resin bed, and lithium was eluted through the bed in the presence of an 80 percent methanol-1 molar hydrochloric acid solution. Lithium was converted to the sulfate for gravimetric evaluation. The average lithium recovery as lithium sulfate showed 99.85 percent for the Set A samples and 97.16 percent for the Set B samples, and an  $LE_x (0.95)$  of  $\pm 2.32$  percent for the Set A samples and  $\pm 0.90$  percent for the B's.

Improved lithium purification was obtained by employing a Dowex 50-16X, 50 - 100-mesh resin bed and 0.5-molar hydrochloric acid as the elutriant for lithium. Lithium was converted to the sulfate for gravimetric evaluation. Results of the gravimetric analysis showed an average value of 97.67 percent for the A samples and 97.37 percent for the B samples; the  $LE_x (0.95)$  was  $\pm 0.59$  percent for the A's and  $\pm 0.37$  percent for the B's.

Estimates of the recovery of lithium from synthetic standards revealed 99.89 percent recovery and an  $LE_x (0.95)$  of  $\pm 0.65$  percent for the Dowex 50-16X-0.5 M hydrochloric acid-gravimetric sulfate procedure.

Lithium chloride solutions were spiked with various impurities and an estimate of the lithium recovery from a general sample was made, employing the ion exchange-0.5 M hydrochloric acid-gravimetric sulfate method. The average recovery was 99.56 percent and the  $LE_x (0.95)$  was  $\pm 0.49$  percent.

## INTRODUCTION

Determination of the lithium content of the ceramic material, lithium aluminate ( $\text{LiAlO}_2$ ), required a lithium analysis with a limit of error for a single determination at the 95 percent confidence level of  $\pm 2$  percent or better. Of the available procedures, a combination of ion-exchange chromatography followed by gravimetric determination of the purified lithium salt seemed most fruitful.

A preliminary investigation of careful flame photometry also appeared justified as an analytical aid during the developmental interim of the anticipated ion exchange-gravimetric procedure.

## ANALYTICAL PROCEDURE

### REAGENTS AND EQUIPMENT

#### Reagents

Hydrochloric Acid - Two solutions are required: 6 and 0.5 molar.

Hydrofluoric Acid - A dilute solution (1:1) is required.

Sulfuric Acid - A dilute solution (1:1) is required.

Dowex 50-16X, 50 - 100-Mesh Cation Exchange Resin - Condition the resin by the following procedure: Add about 100 grams of reagent-grade resin in the hydrogen form to a 500-milliliter beaker. Fill the beaker with distilled water, stir the resin briefly, permit the resin particulates to settle for about ten minutes, then remove the aqueous phase by decantation. Repeat this process two more times in order to remove the excessively fine particulates. Save the resin for the column preparation.

#### Equipment

Platinum Crucibles - Crucibles should have a volume of 25 milliliters.

Spatter Shields - The shields are made of platinum screen welded with gold to a platinum wire ring that is one millimeter in diameter. Three platinum hooks, welded to the ring, support the lid which should be of such diameter as to permit a loose fit when inserted about 1/4 inch into the platinum crucible (see Figure 1).

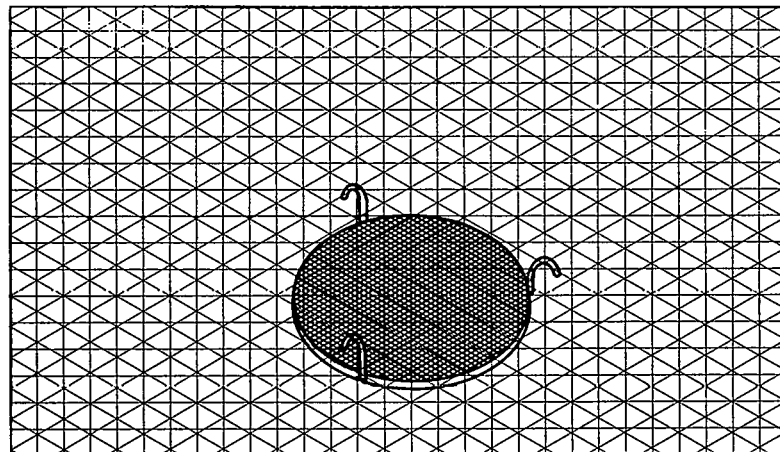


Figure 1. PLATINUM SPLATTER SCREEN.

Ion-Exchange Column - Prepare as follows: Insert a single-bore stopcock into a Size 5 1/2 rubber stopper and attach the stopper to the end of a glass tube having an inside diameter of 25 millimeters and a length of 12 inches. Add sufficient glass wool to the column to make a 1/2-inch pad at the bottom of the column when lightly tamped. Fill the tube halfway with distilled water. Slurry sufficient conditioned resin in water, adjust the stopcock to permit a rapid outflow of water, and immediately add slurried resin to the column. Permit this resin to settle and repeat the addition process until a resin bed has been produced that is 7 1/2 inches high. At no time must the inert resin lose contact with the aqueous phase, or the bed must be reconstructed. Add sufficient glass wool to the top of the bed to build a 1/2-inch pad. Adjust the stopcock to permit an effluent flow of three milliliters/minute and regenerate the bed for sample use by permitting 500 milliliters of six-molar hydrochloric acid to flow through the bed, then wash the bed with distilled water until the effluent has an acidity of about pH 4 - 6. The column is now ready for introducing the sample. During the acid regeneration cycle it is most convenient to introduce the six-molar hydrochloric acid elutriant to the column by a simple siphon system via a reservoir, line, and suitable stopper in the column.

## PROCEDURE

### General Considerations

The analyst must be fully aware of the resin-bed purity prior to analyzing a sample. It is strongly recommended that occasional blanks be determined. This analysis is achieved by eluting a clean resin bed with 0.5-molar hydrochloric acid only. The first 250-milliliter effluent fraction is discarded while the next 500-milliliter fraction is saved. A 200-milliliter aliquot is taken from the 500-milliliter fraction and spiked with 0.1668 gram of very pure lithium sulfate. The aliquot is evaporated to dryness and the sulfate residue submitted for a spectrographic analysis for impurities. The procedure outlined in the section that follows will explain the methodology for handling the ceramic material, lithium aluminate. Different sample material containing lithium may also be analyzed for its lithium content by adjusting sample aliquants on a lithium equivalency basis in order to process about the same amount of lithium. In this aliquant adjustment, caution is recommended in order not to exceed the exchange capacity of the resin bed by adverse component composition. For example, a small percentage value of the lithium in a given material would require excessively large samples to maintain the lithium equivalency found in a lithium aluminate material. Such large samples would overwhelm the exchange capacity and result in poor separations.

### Analysis of the Sample

Accurately weigh about 0.5 gram of lithium aluminate powder and pour it into a 50-milliliter platinum crucible. Add 1.5 grams of potassium carbonate and one gram

of boric acid crystals to the same crucible. (Eliminate this step if the sample material can be solubilized without a fusion and proceed to the next step, minimizing the amount of hydrochloric acid.) Thoroughly stir the mixture and place a solid platinum lid on the crucible. Place the crucible about eleven inches above a Fisher burner and permit the contents to heat about ten minutes. Lower the crucible halfway toward the flame and maintain this position about ten minutes. Finally, apply the full heat of the flame to the bottom of the crucible until the contents have fused. Permit the melt to cool, add about 15 milliliters of distilled water, and then add about ten milliliters of concentrated hydrochloric acid. Warm the mixture gently until the reaction subsides, then heat the solution no more than to the simmer point until a complete dissolution of the sample is effected. Transfer the solution with a minimum amount of water to a 250-milliliter beaker and slowly evaporate the solution until moist salts are obtained. (Caution must be exercised during the evaporation in order to prevent bumping.) Add about 40 milliliters of water to the salt residue and warm the mixture on a hot plate until the residue is dissolved. Transfer the sample to the ion-exchange column with a minimum amount of distilled water. Adjust the column's stopcock and permit the effluent to flow from the column until the sample solution comes within about 1/4 inch of the resin bed surface. Wash the inner side walls of the exposed resin column with about ten milliliters of water and again permit the solution to come within 1/4 inch of the resin bed surface. Repeat this wash step two more times then, by siphon arrangement, attach a feed line of 0.5-molar hydrochloric acid via a rubber stopper to the top of the column and adjust the effluent flow rate to about 3 milliliters/minute and permit the elution to progress. Collect 250 milliliters of effluent in a glass graduate, then collect the next 500 milliliters of effluent in a 500-milliliter volumetric flask. Save a portion of the 250-milliliter fraction to ascertain the absence of any significant lithium. Take a 200-milliliter aliquot from the 500-milliliter fraction and evaporate this aliquot to dryness. With a minimum amount of distilled water, dissolve and transfer the lithium chloride residue to a tared 25-milliliter platinum crucible. Attach the tared platinum screen lid to the crucible and carefully evaporate the solution to dryness under a 250-watt infrared lamp located about ten inches from the platinum lid. Permit the residue to cool and pipette one milliliter of dilute sulfuric acid onto the platinum screen. Now add about one milliliter of dilute hydrofluoric acid to the screen and place the crucible under the infrared lamp. Lower the lamp until it is about six inches above the lid and heat the mixture until the dense white fumes of sulfur trioxide begin to show. At this point, lower the lamp to within three inches of the lid and leave it at this position for about two hours. Transfer the crucible to a muffle that is set for 250° C and heat the mixture for about 40 minutes. Increase the muffle temperature to 350° C and heat the mixture until the white fumes disappear. Increase the muffle temperature to 600° C and heat the mixture until there is an absence of white fumes. Finally, increase the muffle temperature to 800° C and heat the mixture at this temperature for about 30 minutes. Cool and weigh the crucible. Return the sample to the 800° C muffle for 15 minutes, cool, reweigh, and compare the weight to the first value. Continue this step until successive weights remain constant within 0.2 milligram. Subtract the original crucible-lid tare from the final weight to obtain the weight for

lithium sulfate. During the calculations, do not forget that the lithium sulfate found represents only  $2/5$  of the original sample. Equate the quantity of lithium in the lithium sulfate found to the lithium in the original sample.

Save the lithium sulfate residue for the spectrographic analysis for impurities. Then, if necessary, apply an impurity correction to the gravimetric evaluation of the determined lithium sulfate.

## EXPERIMENTAL WORK AND RESULTS

The refractory nature of lithium aluminate requires a special solubilizing treatment involving a fusion and dissolution of the fusion residue. For this fusion, a 0.5-gram sample of lithium aluminate was mixed with 1.5 grams of potassium carbonate and one gram of boric acid crystals, and the mixture melted in a platinum crucible by flame. For the dissolution, the cooled fusion residue was treated with 6 M hydrochloric acid until dissolved, then the excess hydrochloric acid was removed by careful evaporation. Finally, the chloride salt residue was dissolved in about 40 milliliters of distilled water and designated the "prepared" sample.

Standards were prepared to evaluate the spectrophotometric flame analysis of lithium in "prepared" lithium aluminate samples. One standard was prepared by dissolving 0.6109 gram of lithium chloride, 1.92 grams of aluminum chloride, 1 gram of potassium chloride, and 2 grams of boric acid in one liter of distilled water to give a solution containing 100 micrograms of lithium/milliliter. The second standard was identical to the first with the exception that it contained 0.5499 gram of lithium chloride or 90 micrograms of lithium/milliliter.

Lithium in the "prepared" lithium aluminate samples diluted to 500 milliliters was then directly compared against the two standards. Results from the flame analysis are presented in Tables 1 through 3. The overall average was 100.87 ppm of lithium with a limit of error at the 0.95 confidence level for a single determination of  $\pm 4.4$  ppm. The limit of error of the mean of four determinations was  $\pm 2.2$  percent.

Lithium in the "prepared" lithium aluminate samples was measured gravimetrically as the sulfate after attempting its purification by ion-exchange chromatography.

Results obtained from one resin system consisting of a Dowex 50-8X cation-exchange resin column (17 mm D x 2,790 mm L) in a medium of 80 percent methanol-1 molar hydrochloric acid are reported in Table 4. For this study, the lithium aluminate from two different sources was arbitrarily labeled A and B. The actual theoretical recovery of lithium as lithium sulfate was 99.85 percent for A and 97.16 percent for B, with a limit of error  $(0.95)_x$  of  $\pm 2.32$  percent for A and  $\pm 0.90$  percent for B. Spectrographic analysis of the impurities in the lithium sulfate residues is reported in Table 5.

Table 1  
 FLAME ANALYSIS OF LITHIUM STANDARDS  
 (Lithium Range: 90 - 100 ppm)

Standard (ppm Li)	Chart Reading
100	97
100	98
90	93
90	92
100	97
100	97
90	94
90	94
100	97
100	97
90	94
90	94
100	97
100	96
90	93
90	94
100	98
100	97
90	94
90	93
100	98
100	97
90	94
90	94

Results from the second resin system consisting of Dowex 50-16X cation exchange resin in 0.5 molar hydrochloric acid revealed improved lithium separation. Various column dimensions were employed to find an optimum bed geometry, Figures 2, 3, and 4. A bed geometry of 25 millimeters diameter and 1,840 millimeters length was selected as the desired operational unit (Figure 4). Several lithium aluminate samples were then analyzed for lithium using this column. As can be seen from Table 6, the average actual versus theoretical lithium recovered as lithium sulfate was 97.67 percent for Set A and 97.37 percent for Set B, with a limit of error  $(0.95)_x$  of  $\pm 0.59$  percent for Set A and  $\pm 0.37$  percent for Set B. Spectrographic analysis of impurities in the lithium sulfate residues is summarized in Table 7.

A standard 500-milliliter solution equivalent to 0.5 gram of "prepared" lithium aluminate/25 milliliters was made by adding known quantities of lithium, aluminum, and potassium chloride plus boric acid to distilled water. Replicate 10-milliliter aliquots were weighed out and lithium was separated by ion exchange in 0.5 molar hydrochloric acid and determined gravimetrically as the sulfate (Table 8). The average recovery was 99.89 percent with a limit of error  $(0.95)$  of  $\pm 0.64$  percent for a single determination.

Table 2  
FLAME PHOTOMETRIC DETERMINATION OF LITHIUM ALUMINATE

Sample Number	Standards (ppm Li)	Chart Reading
	100	93
	100	93
1		95
1		96
	100	95
	100	95
1		96
1		97
	100	96
	100	96
2		95
2		97
	100	97
	100	97
3		95
3		96
	100	96
	100	97
3		97
3		97
	100	95
	100	96
4		96
4		97
	100	95
	100	96
4		96
4		96
	100	96
	100	96
5		95
5		96
	100	95
	100	95
5		96
5		98
	100	97
	100	97
6		98
6		97
	100	97
	100	97
6		98
6		97
	100	97
	100	98

A general application of the proposed Dowex 50-16X resin-0.5 molar hydrochloric acid-gravimetric sulfate method for lithium in lithium salts was evaluated. Synthetic samples were prepared that contained known amounts of lithium (Table 9) plus added quantities of sodium, potassium, aluminum, manganese, iron, cobalt, nickel, and



Table 3  
 STATISTICAL SUMMARY FOR THE FLAME ANALYSIS OF  
 LITHIUM IN LITHIUM ALUMINATE

Sample Number	Average Lithium Concentration (ppm $\pm$ LE mean) <sup>(1)</sup>		Difference Between Days (ppm)
	First Day	Second Day	
1	101.38 $\pm$ 2.2	98.92 $\pm$ 2.2	2.5 $\pm$ 3.1
2	101.35 $\pm$ 3.1	101.70 $\pm$ 2.2	-0.4 $\pm$ 3.8
3	101.38 $\pm$ 2.2	101.00 $\pm$ 2.2	0.4 $\pm$ 3.1
4	100.70 $\pm$ 2.2	101.70 $\pm$ 2.2	-1.0 $\pm$ 3.1
5	102.08 $\pm$ 2.2	101.00 $\pm$ 2.2	1.1 $\pm$ 3.1
6	99.63 $\pm$ 2.2	99.62 $\pm$ 2.2	0.0 $\pm$ 3.1

(1) Overall Mean = 100.87 ppm  
 $LE_x = \pm 4.4$  ppm  
 $LE_x$  of 4 =  $\pm 2.2$  ppm

Table 4  
 ION EXCHANGE AND GRAVIMETRIC DETERMINATION  
 OF LITHIUM AS THE SULFATE  
 (Dowex 50-8X Resin - 80% CH<sub>3</sub>OH-1 M HCl System)

Sample	LiAlO <sub>2</sub> (gm)	Effluent Aliquot as Li <sub>2</sub> SO <sub>4</sub> (gm)		Recovery (%)
		Theoretical	Found	
A-1	0.5003	0.1669	0.1675	100.36
A-2	0.5024	0.1676	0.1688	100.72
A-3	0.5003	0.1669	0.1655	99.16
A-4	0.5003	0.1669	0.1640	98.26
A-5	0.5001	0.1668	0.1670	100.12
A-6	0.5011	0.1672	0.1680	100.48
B-1	0.5025	0.1676	0.1626	97.02
B-2	0.5019	0.1674	0.1619	96.71
B-3	0.5003	0.1669	0.1622	97.18
B-4	0.5011	0.1672	0.1620	96.89
B-5	0.5003	0.1669	0.1631	97.72
B-6	0.5000	0.1668	0.1625	97.42

Statistical Analysis

Set A - Average Recovery = 99.85%  
 $LE_x = \pm 2.32\%$

Set B - Average Recovery = 97.16%  
 $LE_x = \pm 0.90\%$

Table 5  
SPECTROGRAPHIC ANALYSIS OF LITHIUM SULFATE RESIDUES  
(Dowex 50-8X - 80% CH<sub>3</sub>OH-1 M HCl)

Element	µgs Element/gm Li
Iron	9,600
Aluminum	1,350
Potassium	400
Boron	75

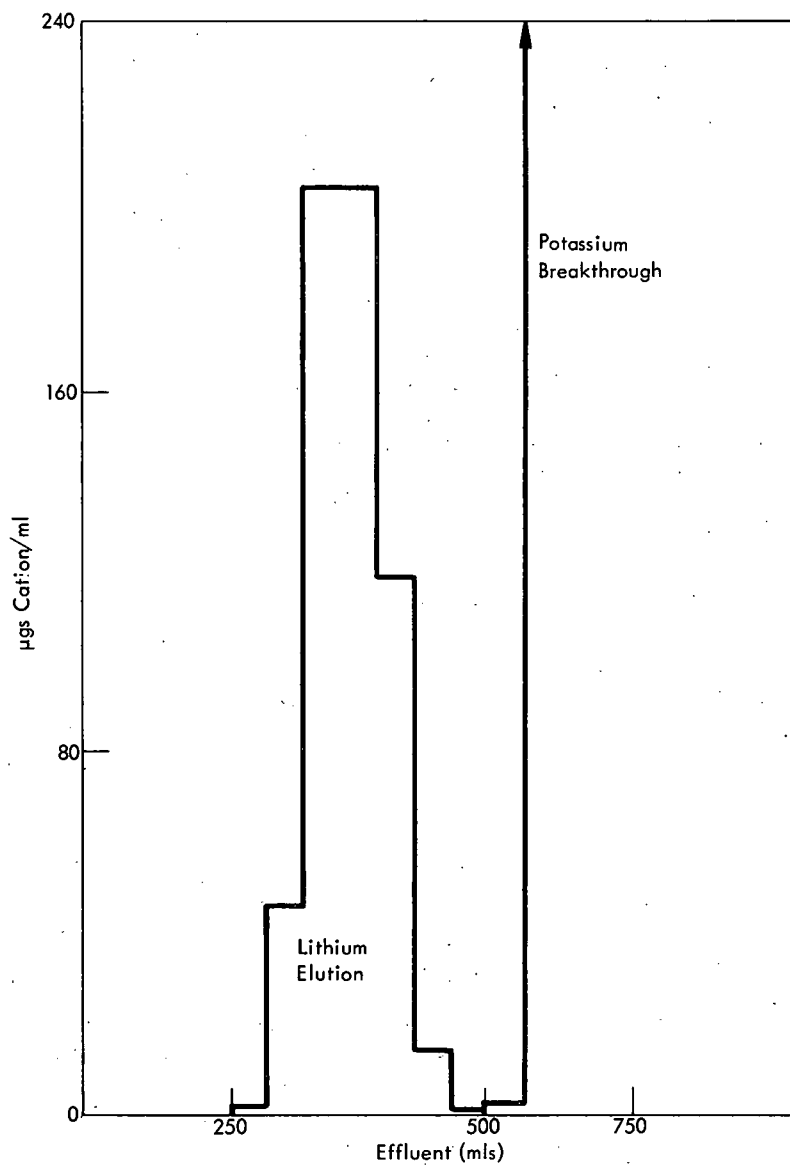


Figure 2. ELUTION CURVE FOR LITHIUM AND POTASSIUM. (Employing the 17-mm-D × 2,790-mm-L Dowex 50-16X Resin Bed and 0.5 Molar HCl)

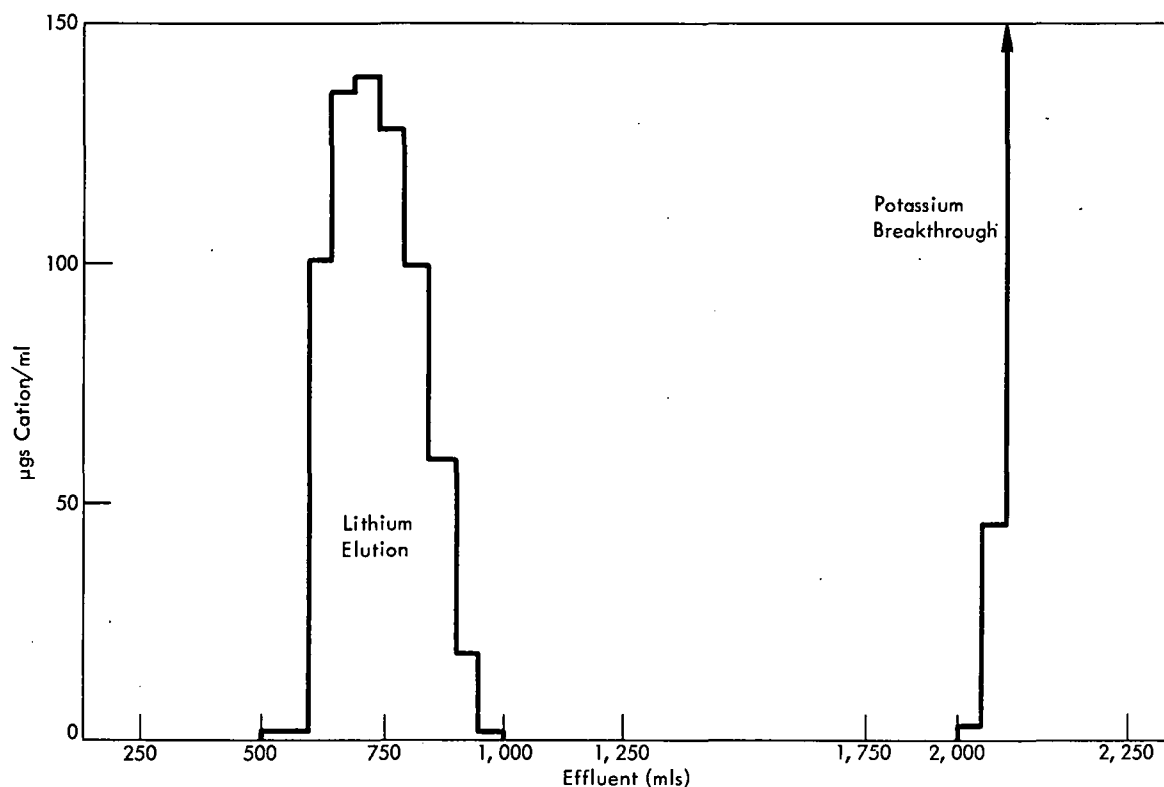


Figure 3. ELUTION CURVE FOR LITHIUM AND POTASSIUM. (Employing the 25-mm-D × 2,790-mm-L Dowex 50-16X Resin Bed and 0.5 Molar HCl)

copper (Table 10). The average recovery for lithium was 99.56 percent with an  $LE_x$  (0.95) of  $\pm 0.40$  percent. The extent of the purification of the lithium product is indicated in Table 10.

### Discussion

A preliminary survey of the available procedures for determining lithium in lithium aluminate included flame photometry as a useful interim method. Samples of lithium aluminate were prepared for direct flame analysis by fusing the insoluble lithium aluminate with a potassium carbonate-boric acid flux, dissolving the cooled melt in dilute hydrochloric acid, and diluting the solution to exactly 500 milliliters. Aliquots from these sample solutions were then directly compared against standards with a similar lithium content by a flame photometric determination (Tables 1 and 2). An analysis of the data in Tables 1 and 2 will disclose that there was a close control of the samples by frequent measurement of the standards. This unusual programming was resorted to in order to evaluate any subtle instrumental variations.

To assure an achievement of minimum error, an equation was developed and a definite order of determining samples recommended. The equation is as follows:

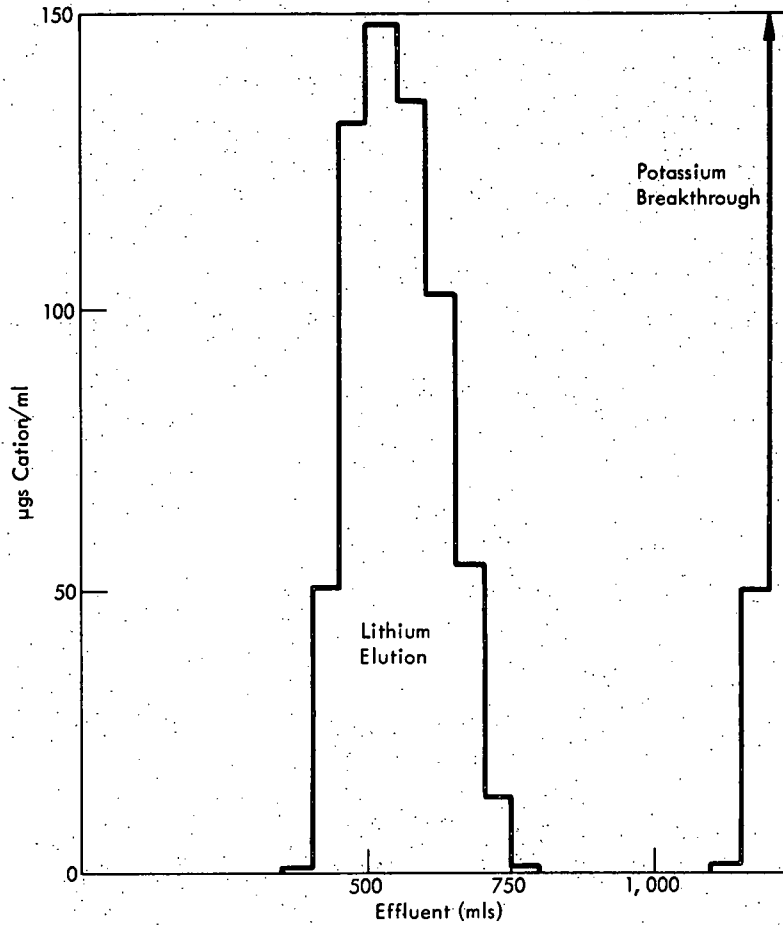


Figure 4. ELUTION CURVE FOR LITHIUM AND POTASSIUM. (Employing the 25-mm-D  $\times$  1,842-mm-L Dowex 50-16X Resin Bed and 0.5 Molar HCl)

$$\text{Lithium (ppm)} = bCR - a,$$

where:

$$b = \frac{\bar{H} - \bar{L}}{R(\bar{H}) - R(\bar{L})}, \text{ and}$$

$$a = bR(\bar{L}) - \bar{L}.$$

CR represents the chart reading for the samples,

$\bar{H}$  the average of the high lithium standards in ppm,

$\bar{L}$  the average of the low lithium standards in ppm,

$R(\bar{H})$  the average chart reading for the high lithium standards, and

$R(\bar{L})$  the average chart reading for the low lithium standards.

Table 6  
 ION EXCHANGE AND GRAVIMETRIC DETERMINATION  
 OF LITHIUM AS THE SULFATE  
 (Dowex 50-16X Resin - 0.5 M HCl System)

Sample	LiAlO <sub>2</sub> (gm)	Effluent Aliquot as Li <sub>2</sub> SO <sub>4</sub> (gm)		Recovery (%)
		Theoretical	Found	
A-1	0.5000	0.1668	0.1627	97.54
A-2	0.5009	0.1671	0.1634	97.79
A-3	0.5000	0.1668	0.1623	97.28
A-4	0.5005	0.1670	0.1634	97.84
A-5	0.5000	0.1668	0.1629	97.66
A-6	0.5000	0.1668	0.1633	97.90
B-1	0.5008	0.1671	0.1625	97.25
B-2	0.5009	0.1671	0.1624	97.19
B-3	0.5005	0.1670	0.1629	97.54
B-4	0.5000	0.1688	0.1624	97.36
B-5	0.5000	0.1688	0.1624	97.36
B-6	0.5000	0.1688	0.1627	97.54

Set A - Average = 97.67%  
 LE<sub>x</sub> = ± 0.59%

Set B - Average = 97.37%  
 LE<sub>x</sub> = ± 0.37%

Table 7  
 SPECTROGRAPHIC ANALYSIS OF LITHIUM SULFATE RESIDUES  
 (Dowex 50-16X - 0.5 M HCl)

Element	µgs Element/gm Li
Iron	< 20
Aluminum	650
Potassium	50
Boron	20

This equation is based on the slope of a linear curve that exists between the values of two standard points which closely bracket the anticipated sample concentration. The recommended sequence for determining the standards and samples is: determine a low standard, a high standard, four measurements of the sample, a low standard, then a high standard.

Table 8  
ION EXCHANGE-GRAVIMETRIC SULFATE DETERMINATION OF  
LITHIUM IN SYNTHETIC LITHIUM ALUMINATE SAMPLES

Sample	LiCl Solution (gms)	Li <sub>2</sub> SO <sub>4</sub> Aliquot (gm)		Recovery (%)
		Expected	Found	
1	9.7579	0.1579	0.1572	99.56
2	9.7336	0.1565	0.1560	99.68
3	9.7676	0.1571	0.1563	99.49
4	10.4658	0.1683	0.1683	100.00
5	10.2781	0.1653	0.1655	100.12
6	10.2102	0.1642	0.1636	99.63
Average = 99.89				
LE <sub>x</sub> (0.95) = ± 0.65				

Table 9  
DETERMINATION OF LITHIUM IN A  
GENERALLY CONTAMINATED SAMPLE

Sample	LiCl Solution (gms)	2/5 Li <sub>2</sub> SO <sub>4</sub> (gm)		Recovery (%)
		Expected	Found	
1	10.1732	0.1636	0.1630	99.63
2	10.9245	0.1757	0.1750	99.60
3	10.1807	0.1637	0.1625	99.26
4	10.3904	0.1671	0.1662	99.46
5	10.2469	0.1648	0.1645	99.82
6	10.5035	0.1689	0.1682	99.59
Average = 99.56%				
LE <sub>x</sub> (0.95) = ± 0.49%				

Table 10  
SPECTROGRAPHIC ANALYSIS OF THE IMPURITIES IN  
GENERALLY CONTAMINATED LITHIUM

Element	Contamination (mgs element)	
	Initial Sample	Purified One-Gram Lithium Sample
Al	40,450	< 20
Co	9,220	< 20
Cu	8,160	30
Fe	8,940	< 50
K	157,344	< 20
Mn	13,000	10
N	9,392	30
Na	106,244	1,000

The flame-analysis method permitted a direct determination of lithium with an LE (0.95) of  $\pm 4.4$  percent for a single determination. Although better precision than this would eventually be required, the flame analysis was accepted as a valuable interim procedure.

Effort was then directed toward the separation of lithium by ion-exchange chromatography employing Dowex 50-8X resin and 0.25 molar hydrochloric acid as the elutrient. Sample solubilization required that 0.5000-gram portions of the ceramic material ( $\text{LiAlO}_2$ ) be fused with a flux (1.5 gms  $\text{K}_2\text{CO}_3$ -1 gm  $\text{H}_3\text{BO}_3$ ), then dissolving the cooled melt in a minimum quantity of dilute hydrochloric acid. Experience revealed that the large quantity of potassium added to the sample was very difficult to completely separate from lithium without resorting to oversized resin beds. Increased column resolution was anticipated by employing a methanol-hydrochloric acid elutrient<sup>(1)</sup>.

Preliminary studies with an 80 percent methanol-2 molar hydrochloric acid elutrient and Dowex 50-8X resin bed (50 - 100 mesh) showed that significant potassium contamination was eliminated from the lithium product. Analysis of the purified lithium product separated from the original solubilized lithium aluminate sample revealed significant contamination by aluminum, to the extent of 30,000 micrograms of aluminum per gram of lithium. Since aluminum adsorption follows a third power of the acid concentration, reductions of the acid content should reduce the aluminum contamination. The hydrochloric acid elutrient concentration was reduced from 2 to 1 molar. This change resulted in a reduction of aluminum in the residue to 2,000 micrograms of aluminum per gram of lithium. Potassium contamination was not significant.

Lithium in a series of solubilized lithium aluminate samples was purified by the Dowex 50-8X resin-80 percent methanol-1 molar hydrochloric acid system and determined gravimetrically as the sulfate (Table 4). The LE's (0.95) for a single determination shown in Table 4 were obtained after treating these sulfate residues with hydrofluoric acid to volatilize the residual boron present as lithium tetraborate. Prior to this treatment with hydrofluoric acid, the LE's were of the order of  $\pm 12$  percent.

Results from a spectrographic analysis of the impurities in these residues are reported in Table 5. A study of Table 5 will disclose that there is a very high iron contamination. This iron contamination occurred during sample preparation, when the lithium aluminate sample material was briefly ground in a steel Wiggle Bug-type mortar. Since iron is a potentially common contaminant, greater column resolution was desired. A reduction in the acid content of the 80 percent methanol elutrient (from 1 to 0.5 molar hydrochloric acid) doubled the effluent volume without a significant removal of iron. A system of greater resolution was needed.

Previous work<sup>(2)</sup> with Dowex 50-16X resin intimated that some improvement might be realized over the Dowex 50-8X resin. Aliquots from synthetic lithium aluminate standards were added to a Dowex 50-16X resin column (17 mm D x 2,790 mm L) and

eluted with 0.5 molar hydrochloric acid. An elution curve for lithium and potassium showed that they were separated but with little margin for error (Figure 2). Improvement in the resolution was anticipated with a bed of larger diameter. Another aliquot of the synthetic sample solution was eluted through a bed that was 25 millimeters in diameter and 2,790 millimeters in length. Results from this elution are reported in Figure 3. In this case, considerable improvement in the separation of lithium from potassium was realized. However, it was indicated that a bed of shorter length would facilitate the lithium breakthrough with an attendant reduction in time for sample analysis and as a speedup of the resin bed regeneration between subsequent separations. A third column with a bed that measured 25 millimeters in diameter by 1,840 millimeters in length was prepared and another aliquot eluted. Figure 4 discloses that an adequate separation of lithium from potassium was achieved for the needs of the present problem. Several of these columns having the 1,840-millimeter length were prepared for intensive recovery and precision studies.

This optimized Dowex 50-16X resin-0.5 molar hydrochloric acid system was evaluated by gravimetric measurement of the purified lithium as the sulfate salt. Samples of lithium aluminate were fused and later dissolved in dilute hydrochloric acid. These samples were then eluted through the resin bed with 0.5 molar hydrochloric acid and the lithium as the chloride was collected in 500 milliliters of effluent. A 200-milliliter aliquot was taken from the effluent composite, evaporated to dryness, treated with a hydrofluoric acid-sulfuric acid mixture, and the lithium converted to the sulfate for its gravimetric evaluation. Results from these analyses are summarized in Table 6. Statistical analysis of the data in Table 6 revealed an average recovery of 97.67 percent for Set A and 97.37 percent for the Set B lithium aluminate samples. The limit of error for a single determination was  $\pm 0.59$  percent for Set A and  $\pm 0.37$  percent for Set B.

Spectrographic analysis of the sulfate residues revealed that there was significant contamination, as shown in Table 7. A comparison of the data of Tables 5 and 7 will disclose that there was a considerable improvement by using the Dowex 50-16X resin.

Attention should be directed to the importance of resin-bed purity prior to sample addition. A potassium contamination of 0.5 microgram/milliliter of effluent will be equivalent to 100 micrograms of potassium in a lithium sulfate residue (nominally 0.1668 gram) which, in turn, is equivalent to 4,762 micrograms of potassium/gram of lithium. Therefore, careful monitoring of the effluent purity during regeneration of the resin bed is essential for an accurate gravimetric evaluation of the lithium sulfate residue.

An accurate evaluation of the lithium recovery from lithium aluminate samples was handicapped by the absence of a lithium aluminate standard. An estimate of the extent of the recovery was attempted by preparing a synthetic sample equivalent to the prepared lithium aluminate, from solutions of lithium, potassium, and aluminum chlorides and boric acid. The lithium solution was standardized by converting



weighed aliquots of lithium sulfate for gravimetric evaluation. This standardization of the lithium occurred prior to compositing the potassium, aluminum, and boric acid solutions. Synthetic samples equivalent to 0.5 gram of lithium aluminate and the accompanying fusion mixture of potassium and boric acid were added to the Dowex 50-16X resin bed and the lithium separated and determined gravimetrically following the proposed procedure. Statistical analysis of the results (Table 8) reveals an average recovery of 99.89 percent with a limit of error for a single determination of  $\pm 0.69$  percent.

Performance of the Dowex 50-16X resin-0.5 molar hydrochloric acid-gravimetric sulfate system in the analysis of lithium in a generally contaminated sample was evaluated. Samples were prepared by spiking aliquots from the standardized lithium chloride solution with various contaminants. Lithium chloride was eluted through the bed, collected in a 500-milliliter effluent volume, evaporated to dryness from a 200-milliliter aliquot, and converted to the sulfate for gravimetric evaluation (Table 9). Reference to Table 9 will disclose an average recovery of 99.56 percent with an LE (0.95) for a single determination of  $\pm 0.49$  percent. Reference to Table 10 will show the extent of purification from the initial sample to the final product. In cases of heavy sodium contamination in the original sample, an extension of the resin bed length would be beneficial (Figure 3).

The proposed ion exchange-gravimetric sulfate determination of lithium in lithium aluminate or generally contaminated samples offers a method of analysis that is accurate and precise within the limits defined.

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