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Summary

A method of transformation of pure isotopically enriched salts into pure 0.1 M lithium hydroxide solutions using an anion exchanger in the hydroxyl form is described.

Alkali and alkali earth contaminations are $\leqslant$ 100 µg/g Li, and residual chloride and sulfate contents $\leqslant$ 0.01 eq %. The carbonate content of the solutions is $\sim$ 0.25 eq. %. No alterations of isotopic enrichments could be detected.

KEYWORDS

C O N T E N T S

THE PREPARATION OF PURE ISOTOPICALLY ENRICHED LITHIUM HYDROXIDE SOLUTIONS BY BATCH OPERATION WITH A STRONG ANION-EXCHANGER

1. INTRODUCTION (*)

The preparation of pure - with respect to both anions and cations - isotopically enriched lithium hydroxide solutions from purified lithium salts is important for the preparation of accurately defined lithium isotope mixtures using four methods of assaying described elsewhere [1].

Lithium, purified by an earlier described method [2], and containing ≤ 50 ppm alkali- and alkali earth traces, has to be transformed, without important cationic contamination, to the hydroxide containing as few as 0.01 - 0.02 eq. % interfering anions. Preparations of dilute standard base solutions from alkali salts using elution anion exchange chromatography were described by R.W. Grunbaum [3], Davies [4] and J. Steinbach [5], but in these publications no attention was paid to the cationic purity of the prepared NaOH or KOH solutions, and chloride concentrations up to 2 eq. % were tolerated.

It is nevertheless important to note that the above mentioned authors have obtained base solutions essentially free from carbonate ions, which is essential in the case of lithium determinations by acid-base titration [1].

2. PRINCIPLE OF THE METHOD

Based on the high selectivity of Dowex 1 for chloride ions, it can theoretically be calculated that lithium chloride (cfr. 2.1.) can be transformed into lithium hydroxide by successive batch operations with the above mentioned resin. In practice this was limited by the residual anionic impurities contained in the ion exchanger. The main impurity found was chloride. For the resin used - AG 1-X8 - the chloride level was of the order of 1 eq. %. Using analytical grade sodium hydroxide, this level can be reduced by elution to approximately 0.15 eq. % [6].

It was calculated (cfr. 2.2) that, using AG 1-X8 of this chloride level, it would be possible to prepare lithium hydroxides with only 0.006 eq. % residual chloride ions.

During experiments, however, it was seen that large sodium contaminations could arise due to the use of large amounts of AG 1 at high pH-values. To eliminate this the anion-exchanger was washed with analytical grade lithium hydroxide instead of sodium hydroxide, and secondly less anion-exchanger was used. For this it was calculated (cfr. 2.3 and 2.4.) that if lithium hydroxide is previously transformed into the sulfate, equal results can be obtained using 2.5 times less anion-exchanger.

2.1. <u>Theoretical calculation of the transformation of LiCl to LiOH</u>
Schematically, the problem can be represented by the following figure:

	Cl^-	OH^-
Solu.	Cl'_s	OH'_s
Resin	Cl'_r	OH'_r

batch operation $\longrightarrow$

	Cl^-	OH^-
Solu.	Cl''_s	OH''_s
Resin	Cl''_r	OH''_r
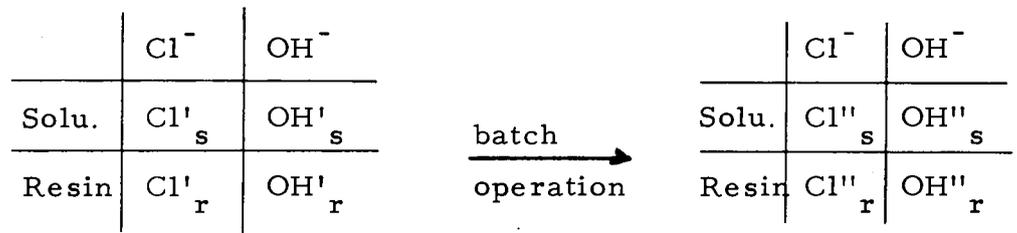
in which Cl'_s and OH'_s represent resp. the number of equivalents of chloride and hydroxyl ions in the solution, and Cl'_r and OH'_r the number of equivalents of AG 1 in the chloride and in the hydroxyl form before the batch operation. Cl''_s, OH''_s, Cl''_r and OH''_r are the corresponding equivalents after the batch operation. These corresponding equivalents can be calculated from the equation of the selectivity coefficient β :

$$\beta = \frac{(Cl)_r \times (OH)_s}{(Cl)_s \times (OH)_r} = \frac{Cl''_r \times OH''_s}{Cl''_s \times OH''_r} \qquad (1)$$

in which $(Cl)_s$ and $(OH)_s$ represent the chloride and the hydroxyl concentrations in the solution (meq./ml) and $(Cl)_r$ and $(OH)_r$ their concentrations in the resin (meq./g), and from the equations that follow from the fact that the total number of chloride ions (2), the total number of hydroxyl ions (3), the number of free ions

bound to the resin (4) and the number of ions in solution (5) must remain constant.

$$Cl'_r + Cl'_s = Cl''_r + Cl''_s \qquad (2)$$

$$OH'_r + OH'_s = OH''_r + OH''_s \qquad (3)$$

$$Cl'_r + OH'_r = Cl''_r + OH''_r \qquad (4)$$

$$Cl'_s + OH'_s = Cl''_s + OH''_s \qquad (5)$$

From these equations one can resp. calculate:

$$OH''_s = Cl'_s + OH'_s - Cl''_s \qquad (6)$$

$$OH''_r = OH'_r - Cl'_s + Cl''_s \qquad (7)$$

$$Cl''_r = Cl'_r + Cl'_s - Cl''_s \qquad (8)$$

Substitution of (6), (7) and (8) in (1) leads to the following equation:

$$(\beta - 1) \cdot Cl''^2_s + [\beta(OH'_r - Cl'_s) + (2\, Cl'_s + Cl'_r + OH'_s)] \cdot Cl''_s$$
$$(Cl'_s + Cl'_r) \cdot (Cl'_s + OH'_s) = 0 \qquad (9)$$

The solution of equation (9) gives the residual chloride content of the solution after one batch operation:

$$Cl''_s = \frac{-[\beta(OH'_r - Cl'_s) + (2Cl'_s + Cl'_r + OH'_s)] + \sqrt{[\beta(OH'_r - Cl'_s) + (2Cl'_s + Cl'_r + OH'_s)]^2 + 4(\beta - 1)(Cl'_s + Cl'_r)(Cl'_s + OH'_s)}}{2\,(\beta - 1)} \qquad (10)$$

Influence of the chloride content of the ion-exchanger on the transformation of LiCl to LiOH .

Formula (10) allows to calculate how the chloride content of the lithium solution is influenced by residual chloride content of the ion-exchanger. For the case of batch operations on 100 meq. of lithium and resin, the results of such calculations are summarized in Table 1.

2.3. Theoretical calculation of the transformation of Li_2SO_4 to LiOH

A similar theory can be developed for the case of transformations of bivalent ions into hydroxyl. The development and the general equation for $SO_4''{}_s$ are nevertheless more complicated. Just as in 2.1. one can represent the problem by :

	SO_4^{--}	OH^-			SO_4^{--}	OH^-
Solu.	$SO_4'{}_s$	$OH'{}_s$	batch operation $\longrightarrow$	Solu.	$SO_4''{}_s$	$OH''{}_s$
Resin	$SO_4''{}_r$	$OH''{}_r$		resin	$SO_4''{}_r$	$OH''{}_r$

and can write analogous equations (11) to (18):

$$\beta = \frac{(SO_4)_r \cdot (OH)_s^2}{(SO_4)_s \cdot (OH)_r^2} = \frac{SO_4''{}_r \cdot OH''{}_s^2}{SO_4''{}_s \cdot OH''{}_r^2} \times \frac{g_r}{ml_s} \qquad (11)$$

$$SO_4'{}_r + SO_4'{}_s = SO_4''{}_r + SO_4''{}_s \qquad (12)$$

$$OH'{}_r + OH'{}_s = OH''{}_r + OH''{}_s \qquad (13)$$

$$SO_4'{}_r + OH'{}_r = SO_4''{}_r + OH''{}_r \qquad (14)$$

$$SO_4'{}_s + OH'{}_s = SO_4''{}_s + OH''{}_s \qquad (15)$$

$$OH''{}_s = SO_4'{}_s + OH'{}_s - SO_4''{}_s \qquad (16)$$

$$OH''{}_r = OH'{}_r - SO_4'{}_s + SO_4''{}_s \qquad (17)$$

$$SO_4''{}_r = SO_4'{}_r + SO_4'{}_s - SO_4''{}_s \qquad (18)$$

In this case, however, the equilibrium changes when the weight

of the resin (g_r) or the volume of the solution (ml_s) is changed, and it is suitable to introduce an "apparent" selectivity coefficient

$$\beta' = \frac{SO_4''_r \cdot OH''_s{}^2}{SO_4''_s \cdot OH''_r{}^2} \qquad (11 \ bis)$$

which is only constant for constant quantities of resin and solution.

Substitution of (16), (17) and (18) in (11 bis) leads to the following equation:

$$(1 + \beta') \ SO_4''_s{}^3 + [2\beta' \ (OH'_r - SO_4'_s) - 3(SO_4'_s + SO_4'_r)] - 2(OH'_s - SO_4'_r)]$$

$$\cdot \ SO_4''_s{}^2 + [\beta'(OH'_r - SO_4'_s)^2 + 2(SO_4'_s + SO_4'_r)(SO_4'_s + OH'_s) + (SO_4'_s + OH'_s)^2]$$

$$\cdot \ SO_4''_s - (SO_4'_s + OH'_s)^2 \cdot (SO_4'_s + SO_4'_r) = 0 \qquad (19)$$

This is an equation of the type $ax^3 + bx^2 + cx + d = 0$. Its solution gives the residual sulfate equivalents in the solution after the batch operation.

If one considers that the sulfate content of the ion-exchanger is negligible $(SO_4'_r = 0)$, one can calculate the values given in Table II for the transformation 1 1 0.1 N Li_2SO_4 (100 meq.). For 0.1 N sulfate solutions and equivalent quantities of solution and resin β' was experimentally determined to be 400.

2. 4. Influence of the chloride content of the ion-exchanger on the transformation of Li_2SO_4 to LiOH

The second solution of table II seems to be the most interesting. We have calculated for this case the expected chloride content in the LiOH due to an anion-exchanger containing 0.15 eq. % of chloride (cfr. 3.2.).

If we assume that during the first batch operation the resin is practically converted to the sulfate form and that all chloride ions are going into solution, and that during the 2 following batch operations we dispose over resp. 38 and 50 meq. of resin in the OH⁻form, we can calculate from formula (9) that Cl_s'' will be resp. 0.017 and 0.007 eq. % after the 2nd and the 3rd batch operations.

3.   EXPERIMENTAL DETAILS OF THE METHOD

3.1.   Determination of the elements of interest

3.1.1.   Traces of chloride on AG-1

Chloride ions were determined with a radiochemical method, using ^{110m}Ag, described elsewhere [6].

3.1.2.   Traces of chloride in lithium hydroxide solution

Following the first batch operations chloride was determined by potentiometric titration of 5 ml aliquots with 0.1 M silver nitrate.

For Cl^-/OH^- ratios below 0.1/100 this method is no more sensitive enough. In this case 8 ml aliquots of 0.1 M LiOH and 0.1 M LiCl standard were successively activated for one hour in a thermal neutron flux of 10^{11} n. sec^{-1} cm^{-2}.

^{6}Li, present in the same concentrations and conditions in sample and reference, was thereby used as an internal standard.

After irradiation, 1 ml 0.5 M HCl and 0.5 ml 10 M HNO_3 were added to the samples and to 1/250 of the reference. Chloride ions were precipitated with 10 ml 0.1 M $AgNO_3$, filtered and washed with 0.01 M nitric acid.

Filtrates and wash solutions were collected in 50 ml flasks and measured for ^{18}F, induced by the reactions ^{6}Li(n,α)T

and ^{16}O $(T, n)^{18}F$; the precipitates for ^{38}Cl, induced by(n, γ) reaction on ^{37}Cl. Measurements were performed with a NaI(Tl) scintillation counter and a multi-channel analyser.

3.1.3. Cationic impurities

Alkali- and alkali earth metals were determined in anion - exchanger ashes and in lithium chloride, sulfate and hydroxide by the emission spectrographic service of the C.B.N.M. Sodium was also determined by neutron activation analysis, using γ-spectrometry.

3.1.4. Traces of sulfate ions in lithium hydroxide.

Traces of sulfate were determined photometrically with cupric ion in acetate medium of pH 4.6 to 6.0, after reduction of sulfate ions to H_2S. [7]

3.2. The elimination of anionic impurities from AG 1 (OH⁻)

1 gram aliquots of AG 1 - X 8 (OH⁻)(Bio Rad Laboratories) were eluted with different quantities of 2 M NaOH (Analytical grade - U.C.B. - Belgium).

After eliminating Na^+-ions with carbonate free bidistilled water, the ion-exchanger was analysed as mentioned in point 3 1.1., and it was found that the chloride content of the sodium hydroxyde solutions used limits the obtainable hydroxyl content to 99.8 - 99.9 eq. %. As explained in the theoretical considerations given in point 2, this is sufficient to prepare lithium hydroxide solutions with less than 0.01 eq. % of chloride ions.

3.3. The elimination of cationic impurities from AG 1 (OH⁻).

From impurity studies it appeared that metallic traces present in the anion-exchanger before use, are nearly quantitatively transferred into the prepared solutions. This means that the ion-exchanger must be quite free of metallic impurities (less

than 0.25 μg/gram dry resin!).

Long washings with many liters of water did not give success-
ful results because traces of sodium ions absorbed during the
hydroxylation of the anion-exchanger could not be completely
eliminated. During a transformation of 50 meq. of lithium
chloride into lithium hydroxide by 5 batch operations with
50 meq. of AG 1, contaminations of the hydroxide up to
300 μg sodium per gram lithium were found. Nevertheless
it seemed probable that these traces of sodium could be eli-
minated by washing the ion-exchanger with lithium hydroxide
instead of sodium hydroxide. Trials resulted in a substantial
lowering of the sodium content of the anion-exchanger while
the residual chloride content was of the same order than with
sodium hydroxide.

The small natural lithium contamination that could arise from
uneliminated lithium adsorbed by AG 1 is of no importance,
because a contamination of 1 gram isotopically enriched ^{7}Li
or ^{6}Li with 300 μg of natural lithium only results in a
0.0023% change of the isotopic composition of 99.999% ^{7}Li,
and in a 0.027% change of the isotopic composition of 99.0%
^{6}Li.

4. ## RESULTS AND DISCUSSION

Different batches of AG 1-X8 were eluted with 12.5 l LiOH
2 M - prepared from 99.98% pure metallic lithium (Koch &
Light Laboratories (England)) - and with 40 l carbonatefree
bidistilled water per 100 meq. of resin. 1.194 g of purified
^{6}Li and 1.375 g of purified ^{7}Li were both transformed to
lithium sulfate with "suprapur" sulfuric acid (Merck A.G. -
Germany), diluted in 1.7 to 1.8 l bidistilled water, and treated
in 3 batch operations with resp. 200, 100 and 100 meq. puri-
fied resin. The whole treatment was done in a glove box,
filled with argon. Bidistilled water was directly distilled
into the box.

Aliquots of the ion-exchanger used were analysed for Cl⁻ (cfr. 3.1.1.) and cationic impurities (cfr. 3.1.3.). Lithium chloride and hydroxide were analysed by emission spectrography, and lithium hydroxide furthermore tested for chlorine (cfr. 3.1.2.), sulfate (cfr. 3.1.4.) and carbonate[1].

The results are summarised in Table III.

Titrations with benzoic acid and lithium analyses as sulfate revealed that the Li-yield of the transformation was 85 to 90%. From table III it can also be concluded that if the anion exchanger is washed with LiOH instead of NaOH the final sodium contamination is only 30 to 50 μg/g Li instead of 300 μg/g Li. The total alkali- and alkali earth contamination is reduced to approximately 100 μg/g Li. Residual sulfate and chloride contents are below 0.01%.

Finally, mass spectrometric measurements of the prepared lithium hydroxides show that no alteration of the isotopic enrichments could be detected.

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Table I

Calculation of the influence of residual chloride of the ion-exchanger on the transformation of 100 meq. LiCl to LiOH with equivalent quantities of AG1-X8 ($\beta Cl^-/OH^- = 25$)

Residual Cl⁻ content of the resin	5 %	1 %	0.2 %	0.1 %	0 %
Number of batch operations	Residual chloride in the treated			solution	
1	19.32 %	17.17 %	16.77 %	16.72 %	16.67%
2	1.19 %	0.83 %	0.77 %	0.76 %	0.75%
3	0.25 %	0.07 %	0.038%	0.03 %	0.029%
4	0.21 %	0.04 %	0.009%	0.005%	0.0015%
∞	0.20 %	0.04 %	0.008%	0.004%	0%

Table II

Calculation of the transformation of 100 meq. Li_2SO_4 solution (0.1 N) to LiOH by batch operations with AG 1-X8.

3 batch operations with 50 meq. of resin ($\beta' = 800$)		1 batch operation with 100 ($\beta' = 400$) and 2 with 50 meq. of resin ($\beta' = 800$)		2 batch operations with 100 meq. of resin ($\beta' = 400$)	
Batch operations	meq. SO_4^{--} in solution	Batch operations	meq. SO_4^{--} in solution	Batch operations	meq. SO_4^{--} in solution
0	100	0	100	0	100
1	52.4	1	12.0	1	12.0
2	9.8	2	0.10	2	0.04
3	0.08	3	0.0005		

Table III

Results of the transformations of purified ^6LiCl and ^7LiCl to ^6LiOH and ^7LiOH by the method described.

Impurity	LiCl		AG - 1	LiOH	
	$\mu g/g$ ^6Li	$\mu g/g$ ^7Li	(oven dried)	$\mu g/g$ ^6Li	$\mu g/g$ ^7Li
Li	-	-	0.06 ppm	-	-
Na	10	25	<0.06 ppm	50	75
K	5	25	0.04 ppm	50	50
Mg	15	15	0.6 ppm	30	15
Ca	<5	< 5	< 0.06 ppm	35	35
Cl^-			0.10 - 0.17 eq. %	0.003 eq %	0.004 eq %
SO_4^{--}			Not determined	< 0.01 eq %	<0.01 eq %
CO_3^{--}			Not determined	0.26 eq %	0.23 eq %
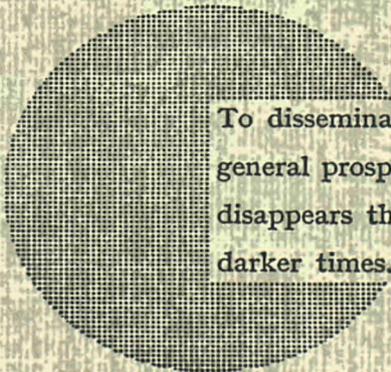
To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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