



Ricerca di Sistema elettrico

1.

## Validazione sperimentale della procedura di analisi offline della purezza del litio e stima della cinetica di purificazione

P. Favuzza, A. Antonelli, R. Traversi, M. Severi

VALIDAZIONE SPERIMENTALE DELLA PROCEDURA DI ANALISI OFFLINE DELLA PUREZZA DEL LITIO E STIMA DELLA CINETICA DI PURIFICAZIONE

P. Favuzza, A. Antonelli (ENEA)

R. Traversi, M. Severi (Università di Firenze)

Settembre 2014

Report Ricerca di Sistema Elettrico

Accordo di Programma Ministero dello Sviluppo Economico – ENEA

Piano Annuale di Realizzazione 2013

Area: Produzione di Energia Elettrica e Protezione dell'Ambiente

Progetto: Attività di fisica della Fusione complementari a ITER

Obiettivo: Validazione del sistema di purificazione del litio e calibrazione del sistema di monitoring online per misura delle impurezze in litio per l'impianto LiFus 6

Responsabile del Progetto: Aldo Pizzuto, ENEA

Si ringrazia *l'Istituto per lo Studio degli Ecosistemi* del CNR di Sesto Fiorentino (Fi) per il supporto fornito nelle analisi MIP per la caratterizzazione dell'area superficiale del getter di Titanio

## Index

SUMMARY.....	4
1 INTRODUCTION.....	5
2 DESCRIPTION OF ACTIVITIES AND RESULTS .....	5
2.1 VALIDATION OF THE OFFLINE ANALYSIS FOR THE QUANTIFICATION OF NITROGEN IMPURITIES IN LITHIUM .....	5
2.1.1. OPTIMIZATION OF THE CHROMATOGRAPHIC ANALYSIS FOR THE AMMONIUM ION ( $\text{NH}_4^+$ ) DETERMINATION.....	5
2.1.2. LITHIUM-WATER REACTION EXPERIMENTS .....	10
2.2 ESTIMATION OF THE TIME FOR THE NITROGEN PURIFICATION .....	13
2.2.1. CHARACTERIZATION OF THE TITANIUM GETTER .....	13
2.2.2. THEORETICAL KINETIC CONSIDERATIONS.....	15
3 CONCLUSIONS.....	16
4 REFERENCES.....	17
5 ABBREVIATIONS AND ACRONYMS .....	17

## Summary

This report deals with the experimental aspects related to the purity of Lithium flowing inside *Lifus 6* plant and it's divided in two main parts.

The first parts describes the work performed during the last year for the final validation of the offline chemical quantitative analysis of Nitrogen contained inside Lithium. This work completes what already done during the previous year and detailed in RdS/2013/125 [1], through the further optimization of the chromatographic analysis of the Ammonium ion solutions, the study of the Lithium-water reaction, the check of the overall procedure precision and accuracy. The validity of the procedure and its suitability for Lithium samples taken from the plant have been proved, also by the good agreement with the results provided by another independent laboratory (JAEA).

The second part deals instead with the theoretical estimation of the time required by the Hot Trap to realize the purification of Lithium from Nitrogen. For this purpose, a characterization of the Titanium sponge employed as getter inside the Hot Trap has been executed, especially for what concerns its Specific Surface Area (SSA). Based on the achieved result and on the assumed starting degree of Lithium purity, it has been possible to calculate that even the longest purification step could be accomplished in less than 1 second, in other words could be immediate, provided a good contact is guaranteed between all the Lithium mass and the getter surface. Even if the calculation is surely approximated and relies on some assumptions, the order of magnitude of the result is such to guarantee an high efficiency of Hot Trap getter. Lifus 6 experimental activity, which is to start in the next month, will confirm, hopefully, the prevision.

## 1 Introduction

This report deals with the experimental aspects related to the purity of Lithium flowing inside *Lifus 6* plant. The quantification of Nitrogen impurities contained inside Lithium in fact is of fundamental importance, since these impurities strongly enhance the corrosive behavior of the liquid metal [2,3]. For this reason, a Nitrogen concentration value lower than 30 wppm has been set as a requirement for the *Lifus 6* corrosion-erosion experimental tests: the check of Nitrogen concentration is therefore mandatory, both before starting the tests and during the whole experimental campaign.

The adopted procedure is an offline procedure, since it doesn't provide a continuous real time result, but provides a result related to a specific Lithium sample, taken discontinuously (but at defined time spans) from the plant, after a batch analysis in a chemical lab. The procedure has been already introduced and described in Rds/2013/125 Report [1]; here is hence reported the outcome of the work made during last year, leading, through a strong experimentation, to the optimization of all the involved steps and to the final validation of the achieved results.

The quantification of Nitrogen concentration is hence the instrument to verify if and how the Hot Trap, in charge of Lithium purification from Nitrogen, will actually fulfill its duty. This answer will be obtained only during real plant operations and trap functioning; anyway, a prior theoretical estimation of the time required for the purification has been possible, based on the assumed starting degree of contamination and on the surface characterization executed on the Titanium sponge employed as a getter for the Hot Trap.

## 2 Description of activities and results

### 2.1 Validation of the offline analysis for the quantification of Nitrogen impurities in Lithium

#### 2.1.1. Optimization of the chromatographic analysis for the Ammonium ion ( $\text{NH}_4^+$ ) determination

As reported in [1], the offline analysis for the determination of Nitrogen concentration in Lithium entails to react the sampled Lithium with water, quantitatively converting all the Nitrogen into Ammonia ( $\text{NH}_3$ ), distill the Ammonia, collect it into an acidic water solution, so obtaining the formation of its conjugate acid ( $\text{NH}_4^+$ ), and finally quantify the concentration of  $\text{NH}_4^+$  in this solution through an ionic chromatography technique (IC-HPLC). This last step is performed by the University of Firenze, with whom a collaboration has been set, after delivery of the  $\text{NH}_4^+$  solution from ENEA chemical lab. The sense of the procedure is that the amount of Nitrogen found in the final  $\text{NH}_4^+$  solution has to exactly match the amount of Nitrogen in the starting Lithium.

The instrument employed for the chromatographic analysis is a *Dionex DX120* Chromatograph (shown in Figure 1). This instrument is equipped with a guard column and a separation column specific for cationic species (precolumn: *Dionex CG12A*; chromatographic column: *Dionex CS12A* – both having a 4 mm diameter) and with an electrochemical cation suppressor *CSRS 4mm*. The employed eluent is  $\text{H}_2\text{SO}_4$  22.5 mN; the chosen volume of the loop (liquid injected in the column) is 25  $\mu\text{L}$ . With the adopted operating conditions, it is possible to achieve the best separation of  $\text{NH}_4^+$  from other cationic species with similar retention time ( $\text{Na}^+$ ,  $\text{K}^+$ ), which have been individuated in the sample matrix.

As a first investigation of the potentiality of the IC-HPLC technique,  $\text{NH}_4\text{Cl}$  water solutions characterized by exactly known values of concentration ( $\text{NH}_4^+$  standard solutions) up to about 30 ppm (=mg/L) of  $\text{NH}_4^+$  ion have been prepared both in University and ENEA laboratory and analyzed through IC-HPLC (samples having concentration > 5 ppm have been diluted prior of the analysis). For this purpose a commercial concentrated  $\text{NH}_4\text{Cl}$  water solution has been employed (1000 mg/L *CERTIPURE Ammonium Chloride, Merck-Millipore, code 119812*), which has been each time diluted with the proper quantity of demineralized MilliQ water to the desired concentration. From the appearance of the fitting curve (conductivity vs concentration), a significant disagreement has been observed for  $\text{NH}_4^+$  concentration higher than about 3.5-4 ppm. In fact, for very low concentrations of  $\text{NH}_4^+$  there is an almost linear relationship between the concentration and

the conductivity of the solution; for intermediate concentrations the relation is best fitted with a parabolic equation (introducing a small second order corrective term), while, for higher concentrations even the parabolic equation is no more able to guarantee good agreement all over the investigated concentration range. For this reason, we then decided to limit our investigated concentration of  $\text{NH}_4^+$  ion to values lower than about 4 ppm.

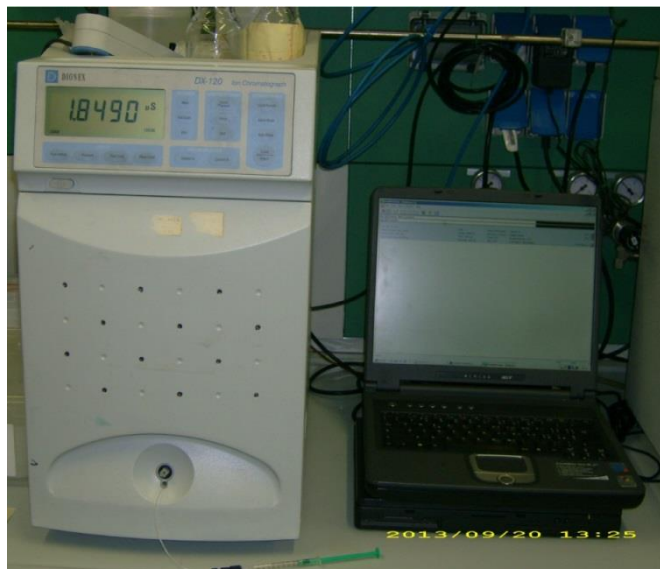


Figure 1: *Dionex DX-120* employed by the University of Firenze for the Ammonium Ion ( $\text{NH}_4^+$ ) analysis, together with the interfaced PC

Figure 2 shows an example of the conductivity [nS] vs concentration plot, for standard solutions up to 3.3 ppm prepared in the University laboratory: the experimental points (red), together with the best fitting curve, are reported.

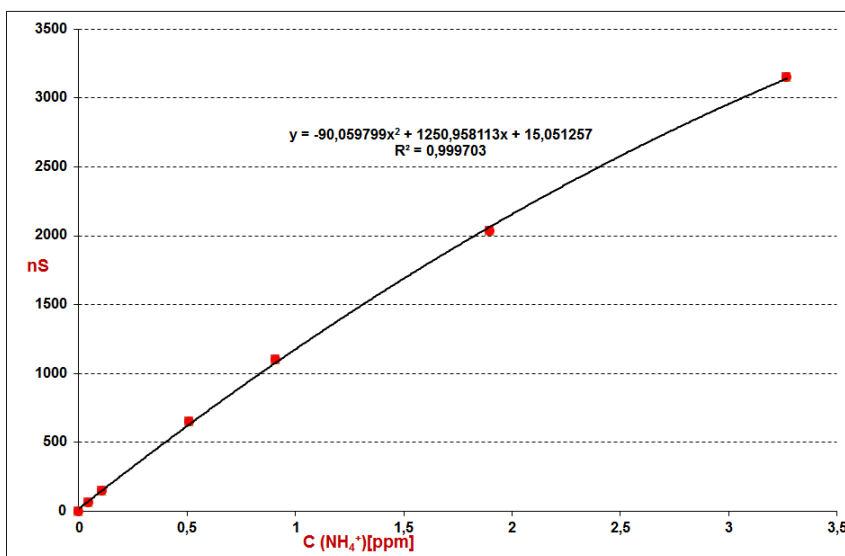


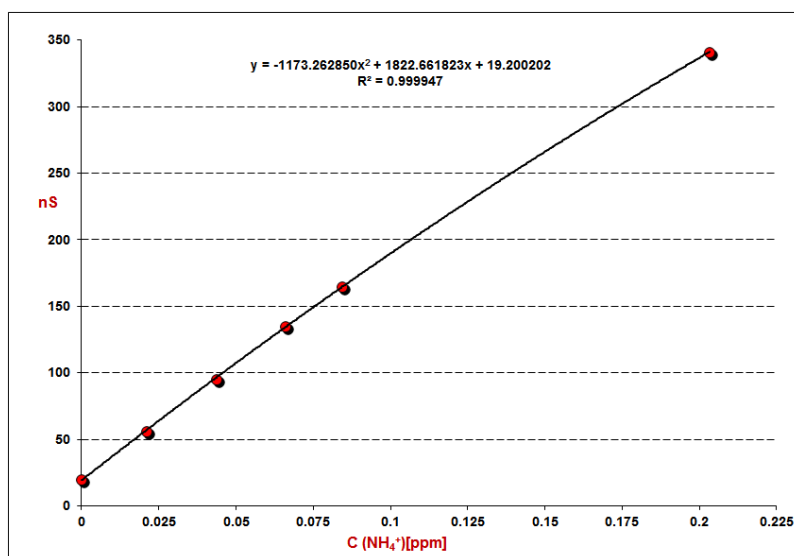
Figure 2: experimental points, relating known  $\text{NH}_4^+$  concentrations (STD) up to 3.3 ppm with their measured conductivity values, together with the best fitting curve

If we employ the best fitting equation to recalculate the concentrations associated to the corresponding measured conductivity values, the relative error (recalculated vs theoretical) is  $\leq 3.6\%$  in the 0.1 - 3.3 ppm range of  $\text{NH}_4^+$  concentration, as detailed in table 1. For the smallest concentration point (0.043 ppm), the relative error is instead higher (15.9%): in this case, just a few ppb difference (6) is able to significantly produce a large relative disagreement.

**Table 1: theoretical concentration values and recalculated ones, employing the best fitting equation, for  $\text{NH}_4^+$  concentration samples up to 3.3 ppm**

Std	Theoretical Conc [ppm]	Conductivity [nS]	Recalculated Conc [ppm]	Difference (%)
1	0.043	60.6	0.037	-15.87
2	0.109	150.7	0.109	0.48
3	0.510	650.8	0.528	3.59
4	0.906	1100.4	0.930	2.60
5	1.898	2033.0	1.863	-1.86
6	3.268	3149.7	3.281	0.39

We shall not worry about this, however. In fact, the standard solutions considered in this first case cover a range of concentration equal to almost two magnitude orders. A choice of standard with such a wide range of concentrations will be used very seldom, being useful only when the operator has no idea at all of the expected concentration. In practical cases, during the operations, it will be often possible to have a rough idea of the investigated sample concentration and construct a fitting curve more suitable for that sample, employing standard solutions closer to that sample. Figure 3 shows, as an example, the experimental conductivity/concentration points for  $\text{NH}_4^+$  standard solutions with concentration up to about 0.20 ppm (and defining a narrower range of concentrations), together with their best fitting curve.



**Figure 3: experimental points, relating known  $\text{NH}_4^+$  concentrations (STD) up to ~ 0.20 ppm with their measured conductivity values, together with the best fitting curve**

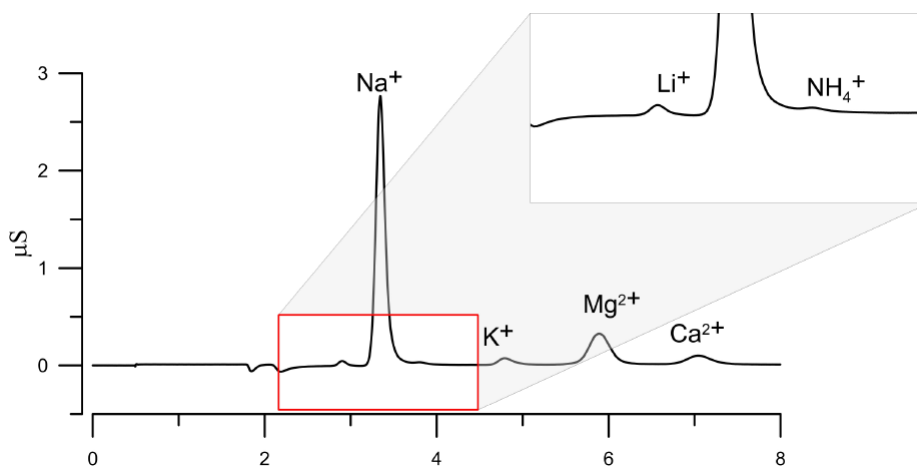
In this case, employing the best fitting equation to recalculate the concentration values associated to the corresponding conductivity values, the maximum relative error (recalculated vs theoretical) is  $\leq 2.4\%$  all over the range, and the mean error is about 1% (see table 2).

**Table 2: theoretical concentration values and recalculated ones, employing the best fitting equation, for  $\text{NH}_4^+$  concentration samples up to 0.20 ppm**

Std	Theoretical Conc [ppm]	Conductivity [nS]	Recalculated Conc [ppm]	Difference (%)
0	0	20.1	0.000	
1	0.021	55.9	0.020	-2.43
2	0.044	95.5	0.043	-1.39
3	0.066	135.2	0.066	0.65
4	0.084	165.0	0.085	0.31
5	0.203	341.1	0.203	-0.03

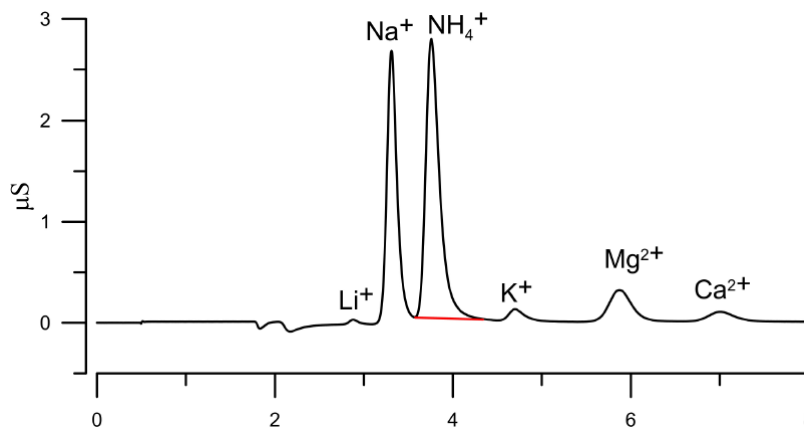
So, in order to achieve the best agreement between theoretical and calculated values, it would be better, when possible, to reduce  $\text{NH}_4^+$  concentration in the sample and employ a narrower range of standard concentrations. Especially for very diluted sample ( $< 0.1$  ppm), the fitting curve should be constructed around such low concentration values. When managing a completely unknown sample, the full range of concentration up to about 4 ppm can however be analyzed with a significant confidence on the achieved result.

The optimization of the chromatographic analysis has also led to replace the Boric Acid ( $\text{H}_3\text{BO}_3$ ), employed as acidifying agent in the collecting solution in the first experiments [1], with Hydrochloric Acid (HCl). In fact, considering to use 1 g of Boric Acid per each expected mg of  $\text{NH}_3$  to be trapped by the solution, as suggested by [4], it could become necessary to put 2 g of Boric Acid or more in the solution, when managing a very concentrated Lithium sample. But, with such high Boric Acid amount, the chromatographic analysis has shown a high relative error, up to 10-15% in defect. This is probably due to the presence of significant  $\text{Na}^+$  impurities in  $\text{H}_3\text{BO}_3$ , as shown by the chromatograms in figure 4 and 5. The  $\text{NH}_4^+$  impurity in  $\text{H}_3\text{BO}_3$  is rather small indeed (figure 4), but, since the peak of  $\text{Na}^+$  is very close to the  $\text{NH}_4^+$  one, there is a tail of the  $\text{Na}^+$  peak extending over the  $\text{NH}_4^+$  peak position, which makes difficult the evaluation of its background line (red in figure 5), hence the precise evaluation of the peak area.



**Figure 4: chromatogram of a blank solution, containing only 1.8g ( $7.2\text{g/L} = 0.12\text{ M}$ ) of  $\text{H}_3\text{BO}_3$ , and its enlargement in the  $\text{Na}^+$  peak region**





**Figure 5: chromatogram of a real  $\text{NH}_4^+$  solution, containing also 1.8g (7.2g/L = 0.12 M) of  $\text{H}_3\text{BO}_3$ , with the background line marked in red**

For this reason, a different acidifying agent has been investigated, the Hydrochloric Acid (HCl). Taking into account that Hydrochloric Acid is a strong acid, completely dissociated in water solution, and that in this case condensed  $\text{NH}_3$  is trapped reacting directly with  $\text{H}^+$  ion, minor amount of acid was considered necessary respect to Boric Acid case. Firstly, a series of sample and standard  $\text{NH}_4\text{Cl}$  solutions containing 625  $\mu\text{L}$  of concentrated HCl (37% by weight, *Fluka*, product code: 84415; 12M) were prepared and analyzed (resulting  $\text{H}^+$  concentration in the 250 mL solutions = 0.03M); later, many series of sample and standard  $\text{NH}_4\text{Cl}$  solutions containing the reduced amount of 250  $\mu\text{L}$  of concentrated HCl were investigated (resulting  $\text{H}^+$  concentration in the 250 mL solutions = 0.012M). In all these hydrochloric solutions, the  $\text{Na}^+$  impurity content was significantly minor respect to Boric Acid solutions and no systematic error was evident, with difference between theoretical and recalculated concentrations both in defect and in excess (maximum relative error found all over these experiments: ~8%). Considering the more concentrated HCl solutions (0.03M) are characterized by a pH (1.52) which could be slightly high for the chromatographic column and produce the risk to damage it or modify its answer with time, we decided to work, as a standard procedure, with the less concentrated HCl solutions (0.012M, pH = 1.92). These solutions contain however a large  $\text{H}^+$  excess respect to the incoming  $\text{NH}_3$ : 250  $\mu\text{L}$  of concentrated HCl correspond in fact, stoichiometrically, to about 50 mg of  $\text{NH}_3$ , which is surely at least ten times the amount of  $\text{NH}_3$  expected from the reaction of Lithium with water.

Finally, also the general reproducibility of the chromatographic analysis has been checked. For this purpose, a sample solution has been analyzed 5 times consecutively, and the conductivity outputs have been translated into concentration results through the same fitting curve. For a solution characterized by a large value of  $\text{NH}_4^+$  concentration, around 4.1 ppm, the obtained results are below reported (table 3): it appears that the relative standard deviation is about 0.3% of the average value.

**Table 3: reproducibility results for a high concentration  $\text{NH}_4^+$  solution**

Analysis n°	$\text{NH}_4^+$ concentration [ppm]
1	4.11
2	4.11
3	4.09
4	4.12
5	4.12
Average	4.110
Standard dev.	0.01225
<b>Stand. dev. %</b>	<b>0.298</b>

Similarly, a very diluted sample solution has been checked for the reproducibility of the chromatographic analysis. The solution, having a  $\text{NH}_4^+$  concentration around 0.030 ppm, has given the results reported in table 4. In this case, the standard deviation is clearly higher in relative terms (respect to the average value), but it's anyway rather small (1.76%).

**Table 4: reproducibility results for a low concentration  $\text{NH}_4^+$  solution**

Analysis n°	$\text{NH}_4^+$ concentration [ppm]
1	0.0296
2	0.0305
3	0.0308
4	0.0297
5	0.0306
Average	0.03022
Standard dev.	0.00053
<b>Stand. dev. %</b>	<b>1.76</b>

The random uncertainty linked to each single chromatographic analysis has been hence shown to add, in any case, a very small contribution to the other errors introduced in the preparation/analysis of the sample solution. For this reason, in real applications, a single chromatographic analysis will be considered sufficient to correctly quantify the amount of Nitrogen in the solution.

### 2.1.2. Lithium-water reaction experiments

In the month of October 2013, a new glovebox from *Iteco Srl* has been procured in ENEA lab (**SGS 40** model), featuring also an internal Oxygen and a moisture sensor. This glovebox (figure 6, left) has been located close the glassware apparatus for the Lithium-water chemical reaction (figure 6, right), being exclusively dedicated to the handle of Lithium samples for this application. The glovebox is emptied from air employing *Air Liquide Argon Alphagaz II* (Ar purity > 99.9995%).



**Figure 6: Equipment in Brasimone ENEA lab. Left: the new glovebox, employed for Lithium handling; right: apparatus for the Lithium-water reaction and the distillation of the produced Ammonia**

A commercial Lithium product (*granular Lithium 99%, Aldrich*, product code: 499811) has been employed for the study of the reaction with water. Unfortunately, a precise characterization of the impurity degree of this product is not available: the supplier only declares that the maximum Nitrogen content is 300 wppm. The Lithium employed was fresh, never used before, but, since its original packaging had been already opened for other applications (the same kind of Lithium was used also for Lifus 3 experiments), a small contamination, slightly increasing the Nitrogen content above the previous value, cannot be excluded. The adopted procedure is the following:

- 1) The Lithium container, together with an empty and clean 500 mL two necks pyrex flask, is inserted inside the glovebox. At the same time, 200 mL of demineralized water are put in the dropping funnel of the glassware apparatus (refer to figure 6, right) and 90 mL of demineralized water + 250  $\mu$ L HCl are put in the collecting flask (tip of the condenser must be dipped inside the solution).
- 2) When the residual content of Oxygen inside the glovebox has decreased below 10.0 ppm (as indicated by the sensor), the Lithium container is opened and the proper amount of the alkaline metal is transferred into the flask: the exact value of the transferred mass is known by weighting by difference, employing an analytical balance permanently located inside the glovebox. The flask is then closed with two fitting teflon caps, extracted from the glovebox, brought to the adjacent chemical hood and joined in 1 second to the rest of the glassware apparatus, already evacuated from air: the central neck to the dropping funnel, the lateral neck to the splash-guard adapter, beyond which the rest of the distilling/condensing apparatus goes on. Figure 7 shows the shining Lithium inside the main flask (in Argon atmosphere), at the end of this step.



**Figure 7: shining Lithium inside the main flask (in Argon atmosphere)**

- 3) After a couple of minutes of Argon flowing through the flask at 500 mL/min, 200 mL of demineralized water are slowly added to Lithium from the above dropping funnel, still keeping the same Argon flow rate. The addition is executed very slowly especially at the beginning, when just one/few water drops per time are addressed to Lithium and many tens of seconds may occur between two additions. After the first water comes in contact with the metal, in fact, the granules fizzling is evident, as well as the formation of a gaseous product (Hydrogen). Moreover, the heat released by the reaction (very localized) is able to lead to the vaporization of water itself, leaving only a solid residue, no more shining but dark; some water condensation appears on the top surfaces of the flask.

With time, the addition of water can proceed quickly, especially when the liquid phase in contact with Lithium inside the flask has become significant. Generally, after the addition of the first 100 mL of water, the Lithium has been completely solved and no residual particle is more evident: the

last 100 mL can hence be added without hesitating too much. On the whole, the addition of the entire water volume requires about 15-20 minutes.

- 4) The Ammonia (NH<sub>3</sub>) formed in the previous step is distilled setting the inner temperature of the heating mantle to 275°C and reducing the Argon flow rate to 60 mL/min. The end point of the distillation is reached when about 80 mL of solution have been transferred into the collecting flask (final volume is hence about 170 mL): this condition is reached after about 45 minutes.
- 5) The solution obtained in the collecting flask at the end of the distillation process is diluted to 250 mL with additional water and analyzed for NH<sub>4</sub><sup>+</sup> through IC-HPLC.

It must be noted that, since NH<sub>3</sub> is a gas at room temperature, solved in water but rather volatile, it's likely that during step 3, in which local temperature may grows significantly (and water itself partly vaporizes), the few formed NH<sub>3</sub> may already get out of the main flask and be driven by the Argon carrier to the collecting flask, to be adsorbed by the acidic solution. Step 4 could perhaps be not necessary, anyway it is performed to be 100% sure of the quantitative transfer of all the Nitrogen to the final solution: as reported in [1] and confirmed by similar additional experiments, the distillation was proved to be 100% quantitative in this condition.

Generally ~ 0.6-1 g of Lithium were reacted with water in this kind of experiments. In one experiment we increased anyway Lithium mass to 2.0393 g: during this experiment, the heat released by the metal in the water addition phase was extremely high and a Lithium fire took place inside the flask (maybe also for some unexpected air contamination); the glass flask was deformed by such a local temperature increase, cracking and even originating some small holes. Safety conditions were restored suddenly increasing the Argon flow rate through the flask, anyway the procedure was stopped and led to no analytical result: the only lesson was that, for safety reasons, it's better not to react with water more than ~ 1g of Lithium. Table 5 reports the results of these experiments, in terms of Nitrogen amount/concentration found in the analyzed Lithium. It must be observed that each of the values in the third column (Nitrogen mass) has been calculated after subtracting a reference blank value, i.e. the Nitrogen mass found in a blank experiment, where water has been added to an empty flask not containing Lithium. This 'blank' Nitrogen (due for instance to NH<sub>3</sub> gas wandering in the lab atmosphere, to NH<sub>4</sub><sup>+</sup> compounds in not perfectly cleaned glassware....) has been generally quantified around 10-20 ppb, depending on the external experimental conditions.

**Table 5: results of Nitrogen amount found in commercial Lithium samples**

Experiment n°	Lithium mass reacted [g]	Found Nitrogen Mass [mg] <sup>1</sup>	Nitrogen conc. in Lithium [wppm]
1	0.6521	0.0115	17.6
2	0.9885	0.0178	18.0
3	0.8415	0.0175	20.8
4	0.8784	0.0221	25.2
Average 1-4			20.4
Standard dev.			3.50
5	0.8545	0.0377-0.0194= 0.0183	21.4

The analysis on the commercial Lithium appear reproducible, taking into account the rather small concentrations of Nitrogen found inside the metal (during Lifus 6 operation we could find concentrations

<sup>1</sup> Nitrogen Mass is calculated by multiply NH<sub>4</sub><sup>+</sup> concentration value (in ppm unit) from HPLC analysis by 0.7765 (mass conversion from NH<sub>4</sub><sup>+</sup> to N) and then multiplying by 0.250 (volume of the analyzed solutions, in Liters).

more than 500 times higher), and that the each value in the last column of table 5 follows from the entire chemical process, including weighing the sample, preparing the solution, diluting, transferring, calibrating, analyzing...; moreover, the possible external contamination, which is small in absolute terms, can become important in relative terms for so small Nitrogen amounts (the blank subtraction can affect results up to 10-15%).

In order to verify the accuracy of the results, since, as said, a standard Lithium with a known Nitrogen concentration is not available, an additional experiment was performed (n°5 in table 5), in which, instead of adding 200 mL of pure demineralized water to Lithium (step 3), 200 mL of a proper Ammonium Chloride solution have been added, containing exactly 25  $\mu\text{g}$  of  $\text{NH}_4^+$  ion (which correspond to 19.4  $\mu\text{g}$  of Nitrogen). The result obtained after subtracting the known added amount (21.4 wppm) appears very close to the average of the previous ones, indicating that no significant loss or contamination happens during the overall procedure and assessing the soundness of all the results.

A further confirmation of the validity of the procedure is given by the comparison of the analysis results of another different Lithium sample, shipped to ENEA by JAEA<sup>2</sup>, with the results of the analysis of the same Lithium performed by JAEA itself, in its own Japanese laboratory, in the frame of a Round Robin Test. ENEA results are summarized in table 6.

**Table 6: results of Nitrogen amount found by ENEA in Japanese Lithium**

Experiment n°	Lithium mass reacted [g]	Found Nitrogen Mass [mg]	Nitrogen conc. in Lithium [wppm]
1	0.3579	0.0817	228.3
2	0.5030	0.1068	212.3
3	0.4385	0.1004	229.0
4	0.3557	0.0801	225.2
<b>Average</b>			<b>223.7</b>
Standard dev.			7.8

The values of concentrations are higher than for the previous Lithium, with a smaller (in relative terms) standard deviation; the average value is:  $223.7 \pm 3.9$  wppm. The result obtained from JAEA, which adopted a very similar chemical process, on the same Lithium is:  $231 \pm 7$  wppm. The agreement of the two independent results is good, and there exists an overlapping region of the two uncertainties windows of the average values. The Round Robin results will be more deeply detailed in a next dedicated publication in an International paper.

## 2.2 Estimation of the time for the Nitrogen purification

### 2.2.1. Characterization of the Titanium getter

Purification of Nitrogen from Lithium must be performed at the beginning of Lifu 6 operation, after the first charging of the plant, and during the entire experimental activity, at defined time spans or whenever suggested by the online output of the Resistivity Meter, in order to guarantee Lithium complies with IFMIF requirements (Nitrogen  $\leq 30$  wppm). As reported in [5,6], this operation is assigned to the Hot Trap, which contains a commercial Titanium sponge (figure 8) acting as a getter for the Nitrogen. In order to roughly estimate the time required for the purification, a characterization of the getter has been executed, particularly for what concerns the value of its Specific Surface Area (SSA), since the adsorption of Nitrogen process necessarily takes place at the interface between Lithium and Titanium.

The supplier of the sponge (*Sigma-Aldrich*) only declares that the product is in the form of chunks having a size in the range of 2-12 mm and that the purity is 99.5%. In ENEA lab, the apparent density of the sponge

<sup>2</sup> JAEA: Japanese Atomic Energy Agency

has been measured as  $\sim 0.54 \text{ Kg L}^{-1}$ , translating into a void factor, due to both channels and pores inside each pellet (intragranular void) and to the packing of the many pellets in the space (intergranular void), equal to  $\sim 88\%$  (in other words, the sponge fills only  $\sim 12\%$  of the available space).



**Figure 8: random array of Sigma Aldrich sponge chunks**

In order to gain more info about the getter, a BET (Brunauer–Emmet–Teller) surface analysis has been performed in collaboration with the *Center for Colloid and Surface Science* of the University of Florence (I), employing Nitrogen as the adsorptive gas. Unfortunately, the value of the Specific Surface Area has been not achieved, since, despite the presence of evident macroscopic channels on each Titanium pellet, the sponge resulted not microporous and the surface area result was very small and affected by a large measurement error.

The Titanium sponge has been then subjected to the *Mercury Intrusion Porosimetry* (in cooperation with the *Institute of Ecosystem Study* of the *National Research Council* of Sesto Fiorentino, employing a *Porosimeter 2000* from *ThermoQuest*), which is a technique able to characterize materials with rather low values of SSA, that are not microporous but own anyway pores up to 100 micron. The sponge has been shown to own a very irregular structure (not homogeneous), resulting from the aggregation of smaller particles (submicron scale) and featuring both macro and meso pores. For this reason, the MIP analysis has been repeated several times, averaging the results and getting a sample as much representative as possible. The cumulative inner volume per unit mass vs the pore size of the sponge (starting from larger pores and going to smaller ones, down to 37 Armstrong) is shown in figure 9 for each of the three analysis. Similarly, figure 10 shows the cumulative surface area per unit mass vs the pore size of the sponge (starting from larger pores and going to smaller ones, down to 37 Armstrong) for each of the three analysis. It is evident that the differences, between the analysis, in the measured surface area per unit mass are more pronounced than the differences in the measured inner volume per unit mass, but this makes sense, considering that small radius pores contribute poorly to the cumulative inner volume, while contribute very significantly to the cumulative surface area.

The most reliable result of the Surface Area of the getter is obtained making the weighted average of the Surface Area results:  $4.68 \text{ m}^2/\text{g}$ . This value is surely not exact, because many approximation are introduced in the calculation (for instance, the MPI technique assumes that all the pores have a cylindrical shape), but it can anyway give an idea of the order of magnitude of the overall surface available for the interaction with Nitrogen solved in Lithium.

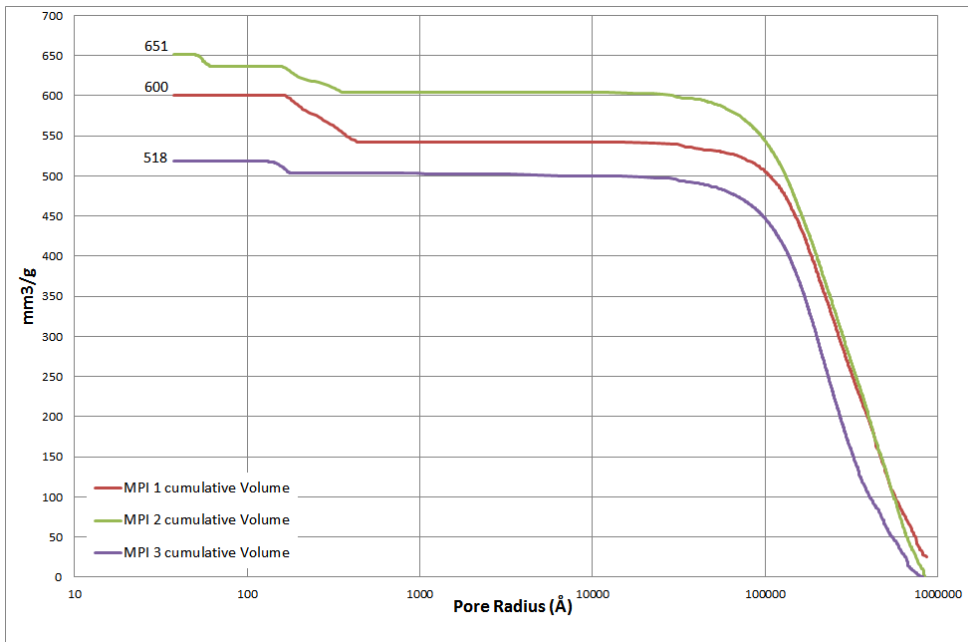


Figure 9: cumulative Volume per unit mass of the sponge vs pore radius from 3 different analysis results

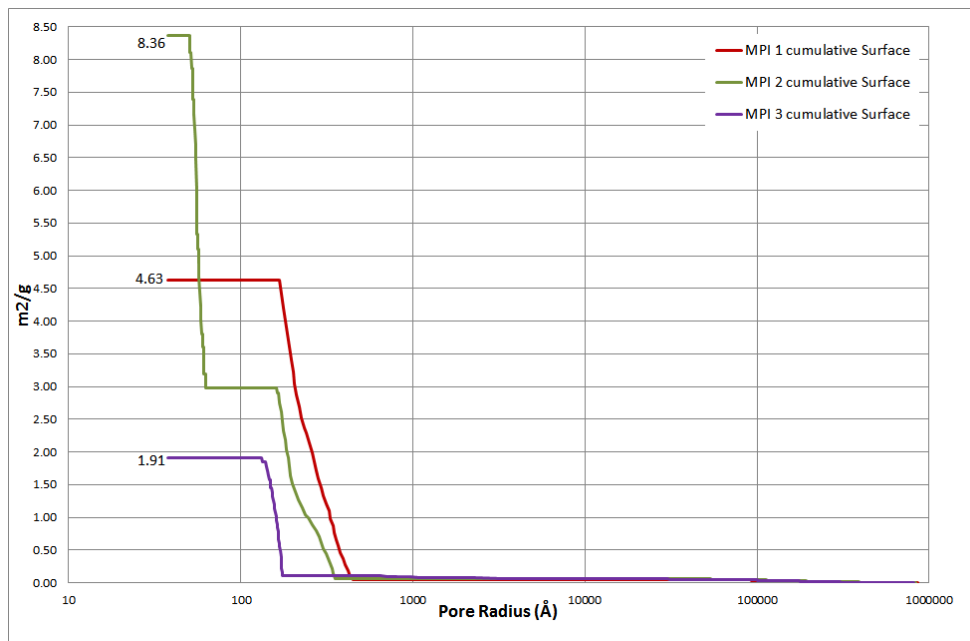


Figure 10: cumulative Surface Area per unit mass of the sponge vs pore radius from 3 different analysis results

### 2.2.2. Theoretical kinetic considerations

The most time consuming step of Lithium purification will be surely the one performed at the start of the operation, since Lithium loaded inside Lifus 6 is not fresh, but it's the same already circulated inside the old Lifus 3 plant. Once initially purified, we are confident that contamination of Lithium during the erosion-corrosion tests will be not dramatic and that each of the following purification steps will be surely faster.

The amount of Titanium getter in contact with Lithium inside the Hot Trap, during the purification, is about 7.48 Kg. According to the found value for the SSA of the getter (4.68 m<sup>2</sup>/g), this translates into an overall

getter surface, available for the adsorption of Nitrogen from Lithium, equal to about 35000 m<sup>2</sup>. Lithium in contact with Titanium inside the Hot Trap is about 8.36 kg. If the Nitrogen concentration in Lithium was so high to match its solubility at the Cold Trap temperature (1461 wppm), we should remove from Lithium about 12.2 g of Nitrogen. With a Titanium:Nitrogen stoichiometry = 1:1 and a TiN density equal to 5.22 g/mL [7], we'd need to form a TiN layer having the following overall volume:

$$V = 12.2 \text{ g} * [(14.01 + 47.90) / 14.01] / (5.22 \text{ g/cm}^3) = 10.3 \text{ cm}^3$$

Therefore, considering this volume is homogeneously distributed over the whole getter surface, the thickness [d] of the resulting TiN layer would be:

$$d [\text{cm}] = 10.3 \text{ cm}^3 / (35000 * 10^4 \text{ cm}^2) = 2.94 * 10^{-8} \text{ cm} = 2.94 \text{ Angstrom}$$

Considering as value for the Diffusion coefficient of Nitrogen in Titanium Nitride  $D = 2.63 * 10^{-15} \text{ cm}^2/\text{s}$  [7], we calculate the time for the complete gettering of Nitrogen as [7,8]:

$$t = d^2 / (6.25 * D) = (2.94 * 10^{-8} \text{ cm})^2 / (6.25 * 2.63 * 10^{-15} \text{ cm}^2/\text{s}) = 0.0526 \text{ s}$$

The value calculated for the TiN thickness is surely trivial (it would correspond to the order of magnitude of an atomic layer): the risk of saturation is surely non-existent. Moreover the corresponding time (0.0526) tells the process would be immediate. Even if we admit that the overall getter surface was actually on order of magnitude smaller, we'll get a thickness 1 order of magnitude higher, which is anyway still a very low value (2.94 nm), far from saturation condition [9], and a time 2 orders of magnitude higher (~ 5 s), which is minimal too. Similarly, even if the Diffusion coefficient was actually a bit lower, the time would increase inversely, but it would remain very small as well.

### 3 Conclusions

Summarizing the results of the wide experimental work performed during the last two years on the route to the setup and validation of the offline analysis for the Nitrogen quantification in Lithium, it is possible to conclude:

- it's better, for safety reason, not to exceed the amount of 1g of analyzed Lithium;
- the reaction of Lithium with water is quantitative in 15-20 minutes, so it's not much time consuming;
- the distillation of produced Ammonia (NH<sub>3</sub>) is quantitative;
- the Hydrochloric Acid (HCl) is preferable to Boric Acid (H<sub>3</sub>BO<sub>3</sub>) as a trapping agent for the Ammonia; the selected amount is 250 μL of concentrated HCl (12 M) in the 250 mL collecting flask;
- with the selected instrumental settings, the IC-HPLC allows to analyze concentration up to 4 ppm of Ammonium ion (NH<sub>4</sub><sup>+</sup>), corresponding to about 3 ppm of Nitrogen;
- the intrinsic precision of the chromatographic analysis translates into a relative error ≤ 3-4%, when employing a proper set of standard solutions for constructing the calibration curve;
- is necessary to perform some blank experiments in order to subtract from the analysis results the possible Nitrogen contamination from external sources. This blank subtraction (few wppm) is important for low concentration samples and becomes negligible the more the concentration increases;



- the overall analysis procedure has been proved to be reproducible (std. dev.  $\sim 3.5\%$  for 230 wppm concentration values);
- the validity of the results and the absence of significant systematic error in the procedure has been confirmed by the comparison with the analysis results provided by another independent laboratory (JAEA) on the same Lithium sample.

For what concerns the kinetics of Lithium purification from Nitrogen executed by the Hot Trap, an estimation of the time required in the worst condition (corresponding to the starting condition, with the Lithium just transferred in *Lifus 6* from the old *Lifus 3* plant) and based on the rough measured value of the specific surface area of the getter, has indicated that the process could be accomplished in less than 1 second, in other words could be immediate, provided a good contact is guaranteed between all the Lithium mass and the getter surface. For this reason, even if the result of this calculation is surely approximated and relies on some assumptions, we are quite optimistic about the expected high efficiency of the getter inside the Hot Trap. Only the real experimentation, during the validation phase of the purification system, will anyway be able to confirm our prevision and provide real results.

## 4 References

1. P. Favuzza, A. Antonelli, "Rapporto sulla procedura offline di analisi chimica della concentrazione di azoto in litio", Report RdS/2013/125, settembre 2013
2. K. Natesan, "Influence of nonmetallic elements on the compatibility of structural materials with liquid alkali metals", Journal of Nuclear Materials, 115 (1983), pp 251-262
3. O.K. Chopra and D.L. Smith, "Influence of Temperature and Lithium purity on corrosion of ferrous alloys in a flowing lithium environment", Journal of Nuclear Materials, 141-143 (1986), pp 584-591
4. APAT, IRSA-CNR, "4030. Azoto Ammoniacale", Manuali e linee guide 29/2003, pp 509-524, APAT
5. P. Favuzza, "Rapporto sulla validazione del sistema di purificazione del litio all'interno di Lifus 6 e del sistema di monitoring online di tali impurezze", Report RdS/2013/126, settembre 2013
6. A. Aiello, A. Tincani, P. Favuzza, F.S. Nitti, L. Sansone, G. Miccichè, M. Muzzarelli, G. Fasano, P. Agostini, "Lifus (lithium for fusion) 6 loop design and construction", Fusion Engineering and Design, 88 (2013), pp 769– 773
7. R. Kolowitz, J. Berg, W.C. Miller "Experimental lithium system Final Report", 173-181 (1985), Hanford Engineering Development Laboratory
8. R. J. Wasilewski, "Diffusion of Hydrogen, Nitrogen and Oxygen in Titanium," Doctor of Philosophy Thesis, Faculty of Pure Science, Columbia University, University Microfilm, Ann Arbor, MI, BNWL-QD,181.T6.2, October 1956
9. T.Sakurai, T. Yoneoka, S. Tanaka, A. Suzuki and T. Muroga, "Control of the nitrogen concentration in liquid lithium by the hot trap method", Journal of Nuclear Materials, 307-311 (2002), pp 1380-1385

## 5 Abbreviations and acronims

Ar	Argon
conc	concentration
H <sup>+</sup>	Hydrogen Ion
H <sub>2</sub>	Hydrogen Molecule
H <sub>3</sub> BO <sub>3</sub>	Boric Acid
HCl	Hydrochloric Acid

HPLC	High Performance Liquid Chromatography
H <sub>2</sub> SO <sub>4</sub>	Sulfuric Acid
IC	Ionic Chromatography
IFMIF	International Fusion Materials Irradiation Facility
JAEA	Japanese Atomic Energy Agency
K <sup>+</sup>	Potassium ion
M	Molar Concentration in solution (mol/L)
MIP	Mercury Intrusion Porosimetry
Na <sup>+</sup>	Sodium Ion
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium ion
NH <sub>4</sub> Cl	Ammonium Chloride
nS	NanoSiemens
ppb	Part Per Billion (in solution = µg/L)
ppm	Part Per Million (in solution = mg/L)
SSA	Specific Surface Area
std	standard
std dev	standard deviation
wppm	Weight Part Per Million (= mg/Kg)