

# Lithium and Uranium Sampling and Preservation Methods at Y-12 National Security Complex

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Y-12 National Security Complex  
Managed and Operated by Consolidated Nuclear Security, LLC

## BACKGROUND OF Y-12

The Y-12 National Security Complex (Y-12) was constructed during World War II for the enrichment of the Uranium 235 isotope, used in the first atomic bomb which was dropped on Hiroshima, Japan. After World War II, Y-12 continued its isotope enrichment mission focusing on medical isotopes and morphed other facilities into a nuclear production mission. The Y-12 site consists of more than 811 acres of land stretching for more than 2 miles in length and about ½ mile wide along an east Tennessee valley (see Fig.1). The site contains hundreds of buildings comprised of over seven million square feet of chemical, metallurgical, machining, and assembly production processes. Y-12 houses a number of unique facilities and equipment found nowhere else in the world.

Today, Y-12 produces many specialty materials, but the main mission focuses upon two material streams; namely 1) enriched uranium 235 isotope material and 2) enriched lithium 6 isotope compounds. Because of the abundance of these resources the National Nuclear Security Administration (NNSA) has requested that Y-12 collect and preserve numerous physical samples of its uranium and lithium materials for various programs (e.g., NA-22, NA-83, etc.). These materials may be used for analytical reference, nuclear forensics analysis, evaluation, comparison, and other applications. This document will discuss future forensic activities planned to be conducted at Y-12.



**Fig. 1 Image of the Y-12 National Security Complex**

This document has been reviewed by a DC/RO and confirmed to be UNCLASSIFIED.

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## URANIUM CHALLENGES AND FORENSICS SAMPLING APPROACH

### URANIUM REACTIVITY

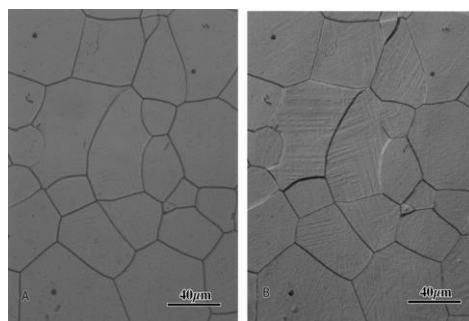
Elemental uranium is strongly electropositive, very reactive, and is comparable to magnesium or lithium in its reactive characteristics. The surface of bulk metal is rapidly oxidized by air and reacts vigorously with hydrochloric acid and nitric acid. In the form of turnings and powder, it is extremely pyrophoric, often igniting from mechanical friction, a small addition of acid or water, or even spontaneously. In addition to the usual dangers inherent in handling pyrophoric metal, uranium fires, even when the metal is unirradiated can lead to radioactive contamination. Due to many factors, finely divided uranium turnings or powders are not the ideal storage form. After the initial surface oxidation occurs, the oxidation rate of uranium drops significantly with lower surface area to mass ratio. All uranium metal readily reacts with oxygen and sampling cannot be practically conducted in inert atmospheres. Years of research across the DOE Complex have discovered repeatable preparation methods for dealing with the readily oxidizing uranium metal to provide consistent analytical results. These consistent results apply to highly analytical methods and also qualitative/quantitative metallography.

### URANIUM FORENSICS AND METALLOGRAPHY

Metallography is the study and examination of the microstructure of all types of metallic alloys. It can be more accurately defined as the science of observing the spatial distribution of the grains, phases, or inclusions in metallic alloys, including uranium and uranium alloys. Creating forensic samples utilizing metallography tools is an art form and is critical for analyzing more in-depth uranium forensic signatures.

Many important macroscopic properties of metallic materials are highly sensitive to the microstructure. Critical mechanical properties, like toughness, elongation, or tensile strength, as well as other electrical or thermal properties, are directly related to the microstructure.

Different metallographic techniques are used to reveal the microstructural features of metals. Most examinations are carried out with incident light microscopy in brightfield mode, but other less common contrasting techniques, like darkfield, polarized light, or differential interference contrast (DIC) are expanding the scope of light microscopy for metallographic applications. The use of scanning electron microscopes (SEM) are often utilized at Y-12 in the metallography analysis process. Use of chemical or electrochemical etchants are commonly used to preferentially reveal specific microstructural features including grain boundaries, inclusions, or other surface features not observable in brightfield in the as-polished state. The image of a uranium alloy in Fig. 2 to the left (A) was taken in brightfield mode, the right (B) is a DIC micrograph of a uranium alloy. The brightfield image (A) has well-defined grain boundaries and some evidence of twinned martensite. The DIC image (B) has much better definition of the twinned martensite and inclusions.



**Fig. 2 Images of Uranium Alloy in Brightfield vs. DIC**

Analysis of a material's microstructure aids in determining if the material has been processed correctly. In addition to this, it can help determine what part of a manufacturing process a material has been cycled through, thus aiding forensic study.

## URANIUM FORENSIC SAMPLE CREATION

The basic steps for proper metallographic forensic sample creation include: sampling, specimen preparation (sectioning and cutting, mounting, planar grinding, rough and final polishing, etching), microscopic observation, digital imaging and documentation, and quantitative data extraction through image analysis methods.

These are the overall steps to metallography forensic specimen analysis at Y-12:

- Sample Preparation
- Cutting the Sample
- Mounting the Specimen
- Curing
- Grinding and Polishing
- Etching
- Analyzing the specimen

The first step of metallographic analysis – sampling – is critical to the success of any subsequent study: the forensic specimen to be analyzed has to be representative of the material being evaluated. Secondly, the material needs to be cut using rough methods such as a bandsaw or lathe and then transferred to a precision saw that utilizes thin abrasive blades that use materials composed of Alumina or Diamond. The saw shown in Fig. 3 below is used at Y-12 to complete precision sectioning of samples.



**Fig. 3 Precision Cut-off Machine**

The third step is to correctly prepare a metallographic forensic specimen. At Y-12 metallographic forensic specimens are planned to be “mounted” using a hot compression thermosetting resin or epoxy that reduce shrinkage during curing, resulting in a better mount with superior edge retention. A typical mounting cycle will compress the forensic specimen and mounting media to 4,000 psi (28 MPa) and heat to a temperature of 350 °F (177 °C). Shown below in Fig. 4 are photos similar to the machines utilized at Y-12 for “hot mounting”. When specimens are delicate, thin, or very sensitive to temperature or pressure, “cold mounts” may be made with a two-part epoxy resin. Mounting a forensic specimen provides a safe, standardized, and ergonomic way by which to hold a sample during the grinding and polishing operations.



**Fig. 4 Examples of Hot Mounting Press Machines**

After mounting, the forensic specimen is wet ground to reveal the surface of the metal. The specimen is successively ground with finer and finer abrasive media. Silicon carbide abrasive paper was the first method of grinding and is

still used today. Recently, Y-12 has moved toward using grinding disks, embedded with diamond media which last much longer than silicon carbide (SiC) sandpaper, while still providing consistent results. After grinding to a fine grit of 800-1200 the use of diamond suspensions are utilized starting at particle sizes of 9  $\mu\text{m}$  and finishing at 1  $\mu\text{m}$  (or less than one). The process of using diamond suspension and pads is now referred to as polishing. Generally, polishing with diamond suspension gives finer results than using SiC papers, especially when revealing porosity, which silicon carbide paper sometimes “smear” over. The forensic specimen is then polished with a slurry of diamond or alumina on a napless cloth to produce a scratch-free mirror finish, free from smear, drag, or pull-outs and with minimal deformation remaining from the preparation process. Depicted in Fig. 5 are images of grinders and polishers similar to those utilized at Y-12 for grinding and polishing.

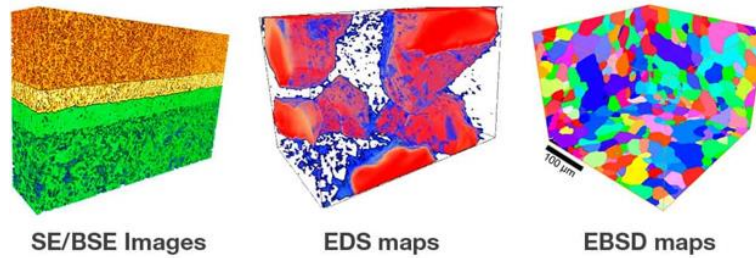


**Fig. 5 Automatic Grinders and Polishers**

After polishing, certain microstructural constituents can be seen with the microscope, e.g., inclusions and nitrides. If the crystal structure is non-cubic (e.g., a metal with an orthorhombic room temperature crystal structure, such as pure uranium) the microstructure can be revealed without etching using crossed polarized light (light microscopy). For nearly all uranium alloys, the microstructural constituents of the specimen are revealed by using a suitable chemical or electrolytic etchant. A great many etchants have been developed to reveal the structure of metals and alloys, ceramics, carbides, nitrides, and so forth. While a number of etchants may work for a given metal or alloy, they generally produce different results, in that some etchants may reveal the general structure, while others may be selective to certain phases or constituents. Metallographic preparation of uranium tends to require the use of a chemical etchant, such as oxalic acid, combined with electricity, referred to electrolytic etching. Electrolytic etching is a technique in which the surface of a metal object is etched by submerging it in an electrically conductive solution and applying electricity as direct current.

The challenge with these uranium alloys is to offset their natural tendency to self-passivate rapidly in the presence of oxygen. To effectively process uranium, etching must be done immediately after final polishing. Rinsing, drying and etching should be performed without delay. When etching these highly reactive alloys, the etchant should be prepared in advance of the polishing process. This advance planning will minimize the length of time between polishing and etching, thus permitting a more effective microstructural evaluation. Forensic samples should be polished and etched individually rather than processed in batches.

After light microscopy, if a specimen must be observed at higher magnification, it can be examined with an SEM. When equipped with an energy dispersive spectrometer (EDS), the chemical composition of the microstructural features can be determined. Due to the rapid oxidation of uranium surfaces, some highly desirable techniques such as Electron Backscatter Diffraction (EBSD) is next to impossible. In EBSD, the electron beam is scanned across the surface of a tilted crystalline sample and the diffracted electrons form a pattern that can be detected and then analyzed using dedicated hardware and software. At each point the indexing process provides information about the phase and the crystallographic orientation from which the microstructure can be effectively reconstructed. This enables a full characterization of the microstructural properties of the sample. Recently, Y-12 acquired an SEM with EBSD capabilities and a plasma focused ion beam (PFIB) feature that can mill off any oxides inside the inert vacuum chamber. This will allow the creation of large volume multi-modal 3D maps, by milling successful layers from the sample below any oxide. Shown below in Fig. 6 are some representative EBSD maps possible with this new tool.



**Fig. 6 PFIB SEM Material Analysis**

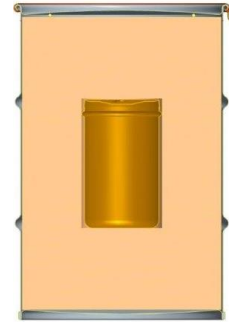
## URANIUM FORENSIC SPECIMEN LONG-TERM STORAGE PLAN

Forensic specimens of uranium in various forms (e.g., metal, powder, oxides) are packaged in glass sample bottles at several different Y-12 processing facilities as they are collected in support of nuclear forensics programs. In order to be placed in long-term storage for certain programs these bottles are inerted with argon gas and over packed in one-gallon stainless-steel crimped-sealed cans. Secondly, the cans need to be placed in an additional on-site outer storage container. At this point, the cans are suitable for long-term storage at Y-12.

In an effort to consolidate the forensic specimens, up to 10 glass sample bottles may be over packed in the stainless-steel can (see Fig. 7). Less than 10 glass sample bottles may be placed inside the stainless-steel can to segregate material of forensic interest. At the long-term storage facility, the stainless-steel cans may remain in their on-site shipping package (see Fig 8 and 9) or be repackaged and stored in a high-capacity, facility-specific, long-term storage unit (see Fig. 10). This long-term storage unit may store up to six stainless-steel cans inside.



**Fig. 7 Sample Bottles and One-Gallon Can**



**Fig. 8 Cut view of On-site Shipping Package**



**Fig. 9 Outside View On-site Shipping Package**



**Fig. 10 High-Capacity Long-term Storage Unit**

Forensic specimens slated for immediate analysis are packaged in small 50 ml glass sample jars, inserted in foam inserts, and transported offsite in Department of Transportation-compliant shipping containers. The nominal load for these analytical forensic specimens are two grams. The nominal material load of the forensic specimens, located inside the larger 120 ml glass bottle to be placed in long-term storage is 50 g of bulk material (metal, oxide, or alloy).

## LITHIUM CHALLENGES AND FORENSICS SAMPLING APPROACH

### LITHIUM REACTIVITY

The natural reactivity of lithium compounds represents a challenge when sampling these materials for analysis and also for long-term storage. As a general rule, samples of any lithium compound except for lithium metal must be taken under an inert dry nitrogen environment. Samples of lithium metal must be taken under an inert dry argon environment since lithium metal reactions with nitrogen can produce a shock sensitive compound.

### OVERVIEW OF LITHIUM FORENSIC SAMPLE CREATION

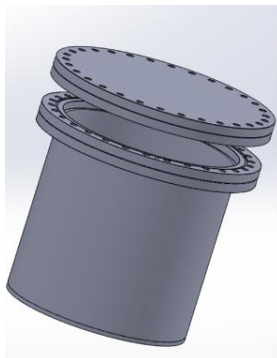
Profiles of protected shapes must be removed by placing small pieces of components through a jaw crusher for obliteration. Aqueous solutions of LiOH and LiCl must be dried by evaporation to produce a solid material. New chemical and physical property analysis must be taken on each sample taken. The enrichment level of the material will be quantified utilizing Thermal Ionization Mass Spectrometry or TIMS. Trace contaminants will be quantified by high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS) and inductively coupled plasma optical emission spectroscopy (ICP-OES). The density of solid forms will be measured by pycnometry.

New chemical and physical property analysis result will be kept for the duration of the forensics program as well as any historical analysis result that was taken at the time the materials was produced provided that information is still available.

All samples will be placed into a mylar bag while contained in the inert environment. Mylar is a polyethylene film made from stretched polyethylene terephthalate, otherwise known as biaxially-oriented polyethylene terephthalate. The mylar bag will be heat sealed and placed into a specially designed long term storage container (see Fig. 12). The lid to the long term storage container will be attached and bolted down while still under the inert environment. Multiple mylar bags may be placed in each long term storage container as long as the material contained in the mylar bags represents the same material type.

The long term storage container utilizes a 13.25 inch upper and lower conflat flange to seal the vessel for atmospheric intrusion and the designed vessel is approximately 12 inch tall. The bored 13.25 inch conflat flange has a diameter of about 10.75 inches which will accept a 10-inch pipe. Schedule 20 file will be utilized to minimize the weight of the vessel. The free volume of the container is about 963 cu-in. The density of broken lithium hydride is about 0.3 g/cc or about 5 g/cu-in. Assuming no gas is present in the mylar bag, a single container will hold about 5,000 g of material.

Once removed from the inert environment, the long term storage container will be placed into the vacuum chamber for leak checking (see Fig. 13). A mass spectrometer will be utilized to detect mass 28 (diatomic nitrogen) and mass 40 (argon).



**Fig. 12 Image of Long Term Storage Container**



**Fig. 13 Vacuum Chamber**

The long term storage container is suitable of maintaining the high quality inert environment for 100 years. The long term storage container has an inner diameter of 10.25 inches and a height of 10 inches for empty volume of 825 cu-in. Accounting for the volume between the upper and lower flanges, the actual free volume of the container is 963 cu-in (15,781 cc). At a leak rate of  $1 \times 10^{-6}$  cc/sec (the standard to be used), at total of 2.19 cc of gas can be exchanged while the container is at a pressure differential of approximately one atmosphere over the 100-year duration. That volume represents about 0.23% of the total container volume.

It should be noted that the long term storage container will be maintained in desiccator boxes (see Fig. 14) which will be continuously purged with small amount of either nitrogen or argon such that there will only be a very minor pressure difference.



**Fig. 14 Desiccator Box**

## **LITHIUM HYDRIDE FORENSIC SAMPLE CREATION**

Retired legacy components of lithium hydride have issues with surface contamination that must be removed prior to sampling. Once the surface cleaning has been accomplished, the components are placed in a mylar bag for transportation. Selected components will be introduced into the nitrogen purged glovebox shown in Fig. 15 and the mylar bag will be removed. A dead blow hammer will be utilized to break away piece(s) of the selected component. Only one component will be processed in the glovebox at a time. The pieces of the component will be fed to the jaw crusher shown in Fig. 16 to remove the profile of a protected shape. Once the desired mass of material has been obtained, the forensic sample material will be weighed and placed into a mylar bag and heat sealed. The heat sealed mylar bag will be labeled and placed inside the long term storage container. A separate chemical and physical characterization sample will be weighed and containerized with its identification and removed from the glovebox. The remnants of the component will be weighed and placed in a new mylar bag labeled with its identity. The remnant and all debris will be removed from the glovebox. This process will be repeated until all the component identified for inclusion in the long term storage container has been processed. Once all identified material has been placed in the long term storage container, a copper gasket will be placed on the conflate flange and the lid will be bolted down. The container will be removed from the glovebox, leak checked, and placed in the nitrogen desiccator box.



**Fig. 15 Typical Nitrogen Glovebox Arrangement**



**Fig. 16 Jaw Crusher**

### LITHIUM METAL FORENSIC SAMPLE CREATION

Lithium metal buttons are normally stored under mineral oil to prevent reactions with atmospheric moisture. Lithium metal buttons selected for forensic sampling will be taken to a hood where they will be washed with Solvent 142. Solvent 142 is a high-purity mixture of hydrotreated isoparaffins and naphthenics with very low levels of polynuclear aromatics. This solvent is used for its high flashpoint and low viscous nature. A hammer and chisel will be used to part a section of the button which will pass through the air lock of the smaller argon glovebox shown in Fig. 17. The cleaned section will then be placed in the smaller argon glovebox and weighed. A hammer will be used to drive the tool through the section to produce a clean sample. Once the desired mass of material has been obtained, the forensic sample material will be weighed and placed into a mylar bag and heat sealed. The heat sealed mylar bag will be labeled and placed inside the long term storage container. A separate chemical and physical characterization sample will be weighed and containerized with its identification and removed from the glovebox. The remnants of the section will be weighed and placed in a new mylar bag labeled with its identity. The remnant and all debris will be removed from the glovebox. This process will be repeated until all the metal buttons identified for inclusion in the long term storage container has been processed. Once all identified material has been placed in the long term storage container, a copper gasket will be placed on the conflate flange and the lid will be bolted shut. The container will be removed from the glovebox, leak checked, and placed in the argon desiccator box. The remnants of the sections utilized will be taken back to a hood where they will be coated with mineral oil and returned to their original container.



**Fig. 17 Smaller Argon Glovebox**



## LITHIUM HYDROXIDE AND LITHIUM CHLORIDE FORENSIC SAMPLE CREATION

Aqueous solutions of either lithium hydroxide or lithium chloride will be placed near a hood. Those solutions will be added to a beaker containing a magnetic stirring rod and placed upon a hot plate. The water will be evaporated via boiling. Once cooled, the now powdered/crystallized lithium hydroxide or lithium chloride will be weighed and placed in a zip-locked mylar bag and sealed.

All forensic samples of powdered/crystallized lithium hydroxide and lithium chloride will be containerized in a zip-locked mylar bag and placed in nitrogen. The powdered/crystallized lithium hydroxide or lithium chloride will be spread out in a containment pan and allow to dry for a minimum of 24 hours. Once the desired mass of material has been obtained, the forensic sample material will be weighed and placed into a new mylar bag and heat sealed. The heat sealed mylar bag will be labeled and placed inside the long term storage container. A separate chemical and physical characterization sample will be weighed and containerized with its identification and removed from the glovebox. The remnants of the powder/crystalline material will be weighed and placed in a new mylar bag labeled with its identity. The remnant and all debris will be removed from the glovebox. This process will be repeated until all the material identified for inclusion in the long term storage container has been processed. Once all identified material has been placed in the long term storage container, a copper gasket will be placed on the conflate flange and the lid will be bolted down. The container will be removed from the glovebox, leak checked, and placed in the nitrogen desiccator box.

## SOLID LITHIUM HYDRIDE MATERIALS CHARACTERIZATION

To determine hydride of LiH classical chemical methods are currently used to thermally decompose the lithium hydride. The released hydrogen is then oxidized to form water. Atom percent and weight percent are performed to accomplish this.

For atom percent, LiH is heated in presence of tin metal at >700 °C to release the H isotopes which are oxidized to their corresponding oxides over copper oxide at ~800 °C. The density is measured with a density meter and the atom % is calculated (numerically the atom % D is the same as the atom %).

For weight percent, LiH and mixtures of LiH samples are heated to ~800 °C to thermally dissociate the gaseous hydrogen isotopes. The gases are converted to their respective oxides by flowing through hot cupric oxide. The resulting “water” ( ${}^1\text{H}_2\text{O}$  and  ${}^2\text{H}_2\text{O}$ ) is absorbed in a trap and weighed. The oxygen is at its natural abundance isotopic ratio. The weight percent hydrogen isotopes are calculated with the determination of the gravimetric factor which is calculated with the use of the isotopes atomic weight values which requires the atom % D.

For LiH, the following equation is used:

$$H_H = \frac{B_G - B_T - B_B}{S_G - S_T} \times F \times 100$$

$H_H$  = percent hydrogen (natural abundance) in the LiH sample

$B_G$  = gross weight of Nesbitt bulb

$B_T$  = tare weight of Nesbitt bulb

$B_B$  = net weight of blank for Nesbitt bulb

$S_G$  = gross weight of test sample

$S_T$  = tare weight of test sample

F = natural abundance hydrogen gravimetric factor ( $2\text{H}/\text{H}_2\text{O} = 0.1119$ )

### Density by Gas Pycnometer

The density of lithium material will be determined by gas pycnometer analysis. Lithium powder will be loaded into a specialized chamber with known total volume. This chamber is exposed to an inert gas with known pressure – typically helium – which will flood the space around the sample – including any penetrable pores. After the pressure stabilizes, a valve opens between the sample chamber and a reference chamber (with known volume). The pycnometer will measure the drop in pressure that occurs as the gas expands into the second chamber, and this pressure difference is used to calculate the true density of the sample.

## LITHIUM METAL CHARACTERIZATION

### Isotopic ratio by TIMS

The isotopic ratio of lithium-6 and lithium-7 material will be determined by thermal ionization mass spectrometry (TIMS). A TIMS is a magnetic sector mass spectrometer that is capable of making very precise measurements of isotope ratios of elements that can be ionized thermally, usually by passing a current through a thin metal ribbon or ribbons under vacuum. The ions created on the ribbon(s) are accelerated across an electrical potential gradient (up to 10 KV) and focused into a beam via a series of slits and electrostatically charged plates. This ion beam then passes through a magnetic field and the original ion beam is dispersed into separate beams on the basis of their mass to charge ratio. These mass-resolved beams are then directed into collectors where the ion beam is converted into voltage. Comparison of voltages corresponding to individual ion beams yield precise isotope ratios.

TIMS are composed of three primary components: 1) ion source, the region in which ions are produced, accelerated, and focused; 2) analyzer, the region in which the beam is separated based on mass/charge ratios; and 3) collector, a region in which the ion beams are measured either sequentially (single collector) or simultaneously (multi-collector). The electronics of these instruments must operate to very close tolerances in order to produce isotope ratios that are precise to 0.01-0.001%.

## LiH, LiOH, and LiCl POWDERED MATERIALS CHARACTERIZATION

### Impurities analysis by HR-ICP-MS

A high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) will be used to determine the impurities in the lithium material. This type of ICP-MS is able to reduce interferences for the highest level of confidence. It provides ultra-sensitive and reliable multi-element analyses at trace-level concentrations, so sample preparation is easier as well as method development.

In mass spectrometry, spectral interferences occur when the mass-to-charge ratio ( $m/z$ ) of interfering ions overlap with analyte ions. These interferences are the primary limitation of ICP-MS. The high mass resolution potential of a sector-field mass spectrometer can physically distinguish and separate an analyte from interferences by exploiting small differences in mass-to-charge ratios. Therefore, high resolution (HR) ICP-MS can quantify concentrations and determine precise isotope ratios for elements across nearly the entire periodic table, regardless of the sample matrix.

### Al and Si by ICP-OES

Inductively coupled plasma – optical emission spectrometry (ICP-OES) measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by an inductively coupled plasma (ICP). The spectra are dispersed and the intensities of the lines are monitored. Interferences will be assessed and valid corrections applied.

### Cl by Titration and g per g Li in LiH

Cl can be determined in LiH by dissolving the powder with  $H_2O$  and methanol. The samples can be acidified with nitric acid and then with the use of NaCl and  $AgNO_3$  as titrants the  $Cl^-$  will be determined by electrochemical titration. Another aliquot of this sample prep can then have the g/g LiH determined through the electrochemical titration discussed below.

Lithium in g/g analysis will be done with HCl titration. The LiH dissolved in  $H_2O \rightarrow LiOH$ . LiH contains varying amounts of  $CO_3^{2-}$  (carbonate) and after  $H_2O$ , the alkaline solution absorbs more  $CO_3^{2-}$  from the air. In electrochemical titrations the  $CO_3^{2-}$  interferes with the  $OH^-$  titration and the end point detection cannot determine the exact endpoint peak. This is corrected by pipetting dissolved LiH over crushed dry ice to convert all the  $OH^-$  to  $CO_3^{2-}$  for one clean endpoint. Also, there is an interference when using  $CO_3^{2-}$  when samples are exposed to air. This will prevent it from absorbing the  $CO_3^{2-}$  in the air as well.