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A Summary of Analytical  
Developments of Li(DT) to Date

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Techniques currently employed in LiDT analyses are being evaluated and new methods are being investigated to develop a more accurate and more comprehensive analysis of both the metal and the salt. This study was initiated to improve the analyses of salt associated with the weapons surveillance program, nuclear device production, and to demonstrate to the design agencies both an interest and a technical competence in the analytical chemistry of LiDT. This report is a brief review of the progress and plans to date for the investigation of LiDT.

Oxygen

The determination of the oxygen content of the metal and the salt is being investigated by neutron activation analysis. The installation of the double axis rotator and the new five-inch counting crystals have lowered the detection limit for oxygen to 20 micrograms. The duplicate analyses of a 1.4 grams LiD sample, contained in a stainless steel capsule, gave values of 5.52 milligrams and 5.21 milligrams oxygen. The oxygen content of the 304 stainless steel container used was approximately 0.3 milligram. The limiting factor of the oxygen determination is the availability of suitable interference-free sample containers. Other low oxygen content containers are being sought.

Additional studies are planned to determine the accuracy of the analysis. Various known quantities of oxygen bearing material will be added to a given quantity of LiD. The background of the container and the salt will be subtracted from the total oxygen content of the prepared samples to determine the accuracy and validity of the method.

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The pneumatic transfer system of the neutron activation analysis facility has been completely enclosed and connected to the radioactive exhaust stack. This precaution was taken to minimize the possible exposure of personnel to tritium in the event a container should rupture during transfer.

### Nitrogen

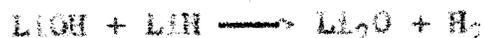
Neutron activation analysis for the nitrogen content of the metal and salt is being investigated. The detection limit for nitrogen by this method is 250 micrograms.

The principle problem encountered with this analysis is the availability of interference-free sample containers. Irradiation of 304 stainless steel containers indicated a significant interference due to trace amounts of copper. Copper-free stainless steel cannot be obtained. Teflon containers were found to have large amounts of nitrogen. Tantalum containers, although virtually free of copper and nitrogen, were found to have a relatively high background at 0.51 Mev (nitrogen detection peak) due to the metal itself. This background was much greater than the energy emission resulting from the nitrogen content expected to be present in the salt. Other metals and organic polymers are being investigated.

After a satisfactory sample container has been obtained, a study, similar to the one planned for oxygen, will be conducted to determine the accuracy of the nitrogen analysis.

### Hydroxide

The hydroxide content of the salt is determined by heating the salt and measuring the amount of gas liberated. The hydroxide is calculated using the formula:



The completeness of this reaction will be ascertained by adding various known amounts of hydroxide to a given quantity of salt and accurately measuring the gas evolved.





Attenuated total reflectance (infrared spectroscopy) is being investigated as a non-destructive technique for the analysis of the hydroxide in the salt. The relative peak heights given by the hydroxide and oxide of the salt, in conjunction with the total oxygen content obtained by neutron activation analysis, will be used to determine the amount of oxygen present as the hydroxide.

#### Deuterium and Tritium

The gas analysis of the LIDF is presently performed by amalgamating the salt with mercury. The volume of the evolved gas is measured and samples are submitted for a mass spectrometer analysis of the gas constituents. A calorimetric analysis for the tritium remaining in the mercury amalgam has been performed to determine the completeness of reaction. After the gas evolution, the amalgam was divided into two fractions, the surface residue and the remaining bulk of the mercury. A trace of tritium (0.1 milligram) was detected (estimated accuracy  $\pm 0.1$  milligram, detection limit 0.1 milligram) in one of the surface residues. No detectable amount of tritium was found in the remaining seven samples.

Although the mercury amalgamation is generally accepted as a satisfactory analytical method, other gas evolution techniques will be investigated. Other lithium-alloying metals, in conjunction with the use of an induction furnace, may give comparable results in less time than the six hours required by the mercury amalgamation method.

The tritium content of the salt is routinely determined by a calorimetric analysis. However, an alternate, non-destructive method will be investigated. The bremsstrahlung (low energy x-ray) resulting from the collision of tritium emitted  $\beta^-$  particles with the salt and container can possibly be counted and correlated with the calorimetry data and the gas analysis of the salt. The salt sample may be analyzed in one-half hour with an estimated accuracy of five per cent.





A non-destructive ( $\nu$ ,  $\alpha$ ) analysis for the deuterium content of the salt can probably be developed if required.

#### Trace Impurities

A sample of lithium metal has been dissolved, heated to dryness with sulfuric acid, and submitted for emission spectrographic analysis. The extension of this method to Li(DT) will necessitate the complete removal of tritium before the sample can be analyzed by the emission spectrographic laboratory. The Research Department is investigating the thermal evolution of gas (without addition of lithium-alloying metals) to remove and recover the major portion of the deuterium and tritium without introducing metallic impurities into the sample.

The following methods are currently employed at Union Carbide's Oak Ridge Y-12 Plant for the analysis of LiH and LiD:

#### Nitrogen

The nitrogen content of the salt is determined by a Kjeldahl analysis (decomposition and steam distillation of ammonia through a silver tube). The gas is collected in a boric acid solution and the ammonium borate is titrated with a standard acid. Addition of Nessler reagent and subsequent colorimetric analysis is performed if the nitrogen content is too small to be determined by titration.

#### Total Hydrogen and Deuterium

The total hydrogen and deuterium content of the salt is determined by placing the salt in a stainless steel boat with a ten to twentyfold excess of tin shot. The sample is heated with a high frequency induction furnace (Burrell Combustion Model 330F-1), and the evolved gas swept with helium through a copper (II) oxide column where it is oxidized to water and subsequently collected in a cooled container of magnesium (II) perchlorate. An analysis can be performed in approximately 20 minutes.

The isotopic ratio of the gas in the salt can be determined by a falling drop density determination of the aforementioned water or by a mass spectrometer analysis of the evolved gas.



  
Carbon

A low level carbon analysis on the salt is currently being developed. A Leco conductometric carbon analyzer has been modified by the addition of a copper (II) oxide column and a cold trap. The thermally evolved hydrogen gas is oxidized to water and frozen out in the cold trap while the carbon forms carbon dioxide and is swept by the oxygen into the barium hydroxide solution. The change in conductance due to the formation of barium carbonate is measured.

Carbonate

The carbonate content is determined by heating the dissolved salt with sulfuric acid. The evolved carbon dioxide is swept with helium through a series of drying and purification towers, absorbed in a tared bulb containing ascarite and magnesium perchlorate, and weighed.

Hydroxide

The hydroxide content of the salt is quantitatively analyzed by the Karl Fischer titration method. The hydroxide (oxide and carbonate also) reacts with a methanol-benzoic acid solution and the water formed is titrated with Karl Fischer reagent.

Oxygen

The oxygen content of the salt is calculated from the data obtained from the hydroxide and the carbonate analyses.

Sodium, Potassium, Calcium

The calcium, potassium and sodium content of the salt is determined with a Beckman Instrument Company DU flame photometer and the chloride content with an American Instrument Company chloride titrator (catalog number 4-4420A).



  
Isotopic Lithium

The lithium isotopic ratio of the salt is determined by the addition of a few drops of hydroiodic acid to the sample and the subsequent mass spectrometer analysis of the solid.

Free Lithium

A method to analyze the free lithium content in the salt was developed by W. C. Dietrich of Y-12 approximately twelve years ago. The salt is refluxed with anhydrous ethyl bromide and the excess ethyl bromide distilled. Cool methanol is slowly added to the residue to decompose the hydride. Water is added to the solution and the bromide content of the LiBr formed by the reaction of metallic lithium with ethyl bromide is titrated with standard silver nitrate solution.

Total Lithium

The total lithium content of the salt is determined by reacting the sample with methanol and then water. The excess of standard hydrochloric acid added is back titrated with standard sodium hydroxide solution.

Apparently the comprehensive analysis of LiH and LiD performed at the Y-12 Plant is both rapid and accurate. It must be pointed out, however, that the application of these wet analytical techniques to tritiated lithium salts may necessitate slight alterations in these methods and will produce problems associated with the handling, storage, disposal and/or recovery of tritiated water and organic solvents.

T. Ben Shinehammer

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