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PREPARATION OF HIGH-PURITY, ANHYDROUS LITHIUM IODIDE

Ray H. Sampley

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by

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1.0 ABSTRACT

Preparations are described for high-purity anhydrous lithium iodide and the necessary starting materials. The lithium iodide prepared as described has been satisfactory for the preparation of single crystals of lithium iodide for evaluation as neutron-absorbing phosphors in scintillation counters.

2.0 FOREWORD

The ORNL Physics Division is evaluating neutron-detecting phosphors for use in scintillation counters. Single crystals of high-purity, anhydrous lithium iodide have shown promise for this use. The ORNL Analytical Chemistry Division has prepared this material for the Physics Division for a period of about two years. The procedures used for purifying the starting materials and preparing the high-purity, anhydrous lithium iodide have proven entirely satisfactory and are described herein as a matter of record.

3.0 SUMMARY

The preparation of high-purity, anhydrous lithium iodide necessitated the purification of the reagents used. Reagent-grade lithium chloride was used as a basis of the preparation.

The LiCl was dissolved in distilled water that had been passed through an ion-exchange column. Elements of the following groups were then removed from the LiCl solution: ammonium hydroxide, hydrogen sulfide, ammonium sulfide, ammonium oxalate, and the carbonate groups; and elements removed by electrolysis in alkaline solutions at 2 volts for two hours, using platinum electrodes.

Ammonium carbonate was purified by distillation in a quartz still.

Lithium carbonate was precipitated from the purified lithium chloride solution by use of the distilled ammonium carbonate solution. Ammonium compounds were removed from the lithium carbonate precipitate by washing the precipitate thoroughly with boiling-hot, demineralized distilled water and drying it overnight at 110°C. The lithium carbonate was then ignited in a muffle at 450°C for six hours or until all ammonium compounds had been expelled.

Pure hydriodic acid was prepared by reacting reagent-grade, resublimed iodine with hydrogen sulfide in demineralized distilled water. The prepared hydriodic acid solution was filtered through Whatman No. 5 filter paper to remove free sulfur. The filtrate was then boiled under vacuum to remove the excess hydrogen sulfide. The hydriodic acid was distilled from a quartz still, the fraction distilling between 115° and 130°C being retained.

The high-purity lithium carbonate was reacted with the freshly distilled hydriodic acid. The lithium iodide trihydrate was crystallized twice from the solution. The trihydrate was then dehydrated.

4.0 PREPARATION OF $LiI \cdot 3H_2O$ AND STARTING MATERIALS

4.1 Starting Materials

4.1.1 LiCl Solution

Dissolve 2 lbs of reagent-grade LiCl in 1500 ml of demineralized distilled water that contains 10 ml of concentrated ammonium hydroxide solution. Filter the solution through Whatman No. 5 filter paper. Cool the filtrate to room temperature and electrolyze it for 2 hours at a potential of 2 volts; use platinum electrodes. After the electrolysis, adjust the pH of the solution to approximately 3 with HCl and warm it. Pass in H_2S gas for one-half hour. Let the solution stand for 1 hour or longer and then filter it through Whatman No. 5 filter paper. Now add 25 ml of freshly prepared saturated solution of ammonium sulfide and let the solution stand overnight. Filter the solution, using suction, through Whatman No. 5 filter paper. Make the filtrate acidic with HCl and boil off the H_2S. Neutralize the filtrate with NH_4OH. Make the filtrate just acidic with a saturated solution of oxalic acid. Precipitate the oxalate group by adding 25 ml of a saturated solution of ammonium oxalate. Stir vigorously. Let the solution stand until the precipitate settles. Filter the solution through Whatman No. 5 filter paper. Discard the precipitate, heat the filtrate to 70° to 80°C, and add 10 ml of distilled ammonium carbonate solution with vigorous stirring. Keep the solution hot and filter it through Whatman No. 5 filter paper. Store the filtrate in a pyrex bottle.

4.1.2 $(NH_4)_2CO_3$ Solution

Prepare a solution of 300 g of $(NH_4)_2CO_3$, 200 ml of conc. NH_4OH solution and 700 ml of demineralized distilled water. Filter the solution if necessary. Steam distill the solution and catch the distillate in a pyrex container that is immersed in an ice bath. Store the distillate in suitable pyrex bottles until it is needed.

4.1.3 Li_2CO_3

Heat two liters of the purified LiCl solution to 70° to 80°C and add the heated $(NH_4)_2CO_3$ solution until all the lithium is precipitated as Li_2CO_3. Bring the solution to a boil. Allow the precipitated Li_2CO_3 to settle. Decant the supernatant liquid. Wash the Li_2CO_3 four or five times with boiling-hot demineralized distilled water; decant the supernatant liquid after each wash. Filter the Li_2CO_3 suspension through Whatman No. 5 filter paper and wash the Li_2CO_3 several times with boiling-hot, demineralized distilled water. Dry the Li_2CO_3 on the paper as much as possible by means of suction. Place the funnel that contains the Li_2CO_3 in a drying oven at 110°C overnight. Transfer the dried Li_2CO_3 to a platinum dish and ignite it at 450°C in a muffle furnace for about 6 hours or until all ammonium compounds have been expelled. Store the pure, dry Li_2CO_3 in moisture-proof bottles until it is needed.

4.1.4 HI

React 2 lbs of reagent-grade, resublimed iodine with H_2S in 1600 ml of demineralized distilled water that has been saturated with H_2S. Add the iodine in small portions while at the same time passing H_2S into the solution. Filter the solution through Whatman No. 5 filter paper to remove the free sulfur. Boil off the excess H_2S under suction and filter the solution again to remove any free sulfur. Distill the solution from a quartz still, collect and retain the distillate that comes over between 115° and 130°C. React the hydriodic acid thus obtained with Li_2CO_3 by adding the Li_2CO_3 in small portions, while stirring, until an excess of Li_2CO_3 is present.

4.2 $LiI \cdot 3H_2O$

React 350 g of Li_2CO_3 with the hydriodic acid (see Section 4.1.4). Filter the solution through Whatman No. 5 filter paper to remove the excess Li_2CO_3. Make the solution acidic with about 3 ml of hydriodic acid. Transfer the solution to a platinum dish and evaporate it over a water bath until the $LiI \cdot 3H_2O$ starts to crystallize out. Stir until crystallization is complete. Cool the solution to room temperature. Centrifuge out the crystals and discard the mother liquor. Dissolve the crystals in pure water and crystallize out the $LiI \cdot 3H_2O$ as before. Centrifuge out the crystals and discard the mother liquor. Wash the crystals with demineralized distilled water and again centrifuge, discarding the wash solution. Store the $LiI \cdot 3H_2O$ crystals in a suitable pyrex container inside a vacuum desiccator over P_2O_5 at a pressure of 25 microns until they are to be dehydrated.

5.0 DEHYDRATION OF $LiI \cdot 3H_2O$

Use a 500-ml quartz or Vicor, round-bottom flask that is fitted with a ground-glass joint adaptable to the vacuum system to be used for dehydration purposes. Fill the flask about 80% full of $LiI \cdot 3H_2O$ taken from the stored material (see Section 4.2). Connect the flask to the vacuum system and surround it with Glas-col heaters. Connect the heaters to a power-driven Variac that will increase the voltage to the heaters at the rate of 0.5 volts per hour. Allow the power-driven Variac to operate until a temperature of 325°C is reached. Maintain the 325°C temperature for at least 8 hours or until the pressure in the vacuum system remains constant. The pressure should stabilize at about 0.05 microns. Seal the flask by means of the stopcock provided and remove it from the vacuum system. Preserve the LiI in the evacuated flask until it is to be used for growing a large, single crystal of the material.