

Development of low-loss minimal exposure technique for thallium foil fabrication

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Abstract. Despite its availability as a solid bead or ingot, non-isotopic thallium metal is no longer commercially produced as a foil because of its high toxicity. To conduct fundamental studies on the material, the Stable Isotope Materials and Chemistry Group (SIMC) at Oak Ridge National Laboratory (ORNL) was approached to develop a safe method to process thallium and produce 40 non-isotopic thallium foils. The commercially sourced metal was consolidated into an ingot by melting the material in a special tube furnace under a reducing atmosphere. The resulting ingot was cold rolled using a work-hardened, stainless-steel pack and oil lubricant before cutting the final foils to $2.5 \times 2.5 \text{ cm}^2$ area and thickness of $50\text{--}75 \text{ mg/cm}^2$. The appropriate safeguards used at each step are outlined to ensure the safe and consistent production of high-quality foils. The low-loss process enables future requests for isotopic thallium and other hazardous and rare materials.

1 Introduction

In June 2021, The Stable Isotope Materials and Chemistry (SIMC) group at Oak Ridge National Laboratory (ORNL) was requested to develop a method to fabricate 40 natural thallium metal foils, each sized at $2.5 \times 2.5 \text{ cm}^2$ area and thickness of $50\text{--}75 \text{ mg/cm}^2$, for applications in the production of radioisotopes at national laboratories across the United States. SIMC is well-established as one of the major stewards and producers of stable, isotopically enriched targets in the United States. Because of the highly limited supply and high cost of the materials used, many of the projects executed require extremely low-loss and high-efficiency processes. Herein, the specific difficulties associated with thallium metal are explored, especially as they relate to health, safety, and contamination concerns. The fabrication procedure used for the completion of this specialized task is also outlined.

2 Health and safety concerns

Thallium metal is known for its high acute toxicity and how easily it absorbs through the skin and contaminates other metals and materials [1]. Sigma Aldrich sets its workplace control parameters at a 0.1 mg/m^3 time-weighted average (TWA), half of the parameter for lead, and a dermal exposure of 0.02 mg/m^3 TWA [2]. Exposure to skin and mucous membranes results in an 80–100% absorption of the metal [3–4]. In adults, the lethal dose has been found to vary between 6 and 40 mg/kg; however, acute effects begin well below this range.

The excretion of thallium from the body has an estimated half-life of approximately 10–30 days, which increases the danger of continued exposure to the material. The high acute toxicity of this metal is why commercial suppliers have largely forgone processing thallium on a large scale. Thus, the process development of this project was partially dedicated to finding ways of working safely with thallium.

2.1 Work controls

According to the safety data sheet [2], the suggested engineering controls include a face shield and safety glasses, wearing nitrile gloves along with vigorous handwashing, a complete Tyvek or Tychem suit, and either a full-face air supplying respirator or a full-face particle respirator, as determined by risk assessment. In this procedure, individuals must dress out fully, donning double nitrile gloves (taped at the wrists), chemical resistant suits, and powered air purifying respirators (PAPRs), and they must work within a chemical hood as often as possible and limit access to the room. All work is conducted through a buddy system to account for human error.

2.2 Health and safety monitoring

Individuals working with thallium were placed on a thallium monitoring program through the Health and Safety Program at ORNL. When individuals are actively working with the material, biological sampling at the end of the work week is imperative to account for cumulative dosing during normal work conditions. Because cumulative dosing may also result in chronic intoxication, the individuals were

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monitored for at least 90 days after the conclusion of the project [5].

Airborne particulate was monitored by NIOSH 7303 sampling. NIOSH 7303 has a limit of detection of approximately $0.044 \mu\text{g/mL}$ in a 25 mL sample. The amount found in the four samples was found to be below the limit of detection, thus the PAPRs will not be necessary in future iterations of the process if all steps are followed as described herein.

Surfaces that could be contaminated during processing were sampled using the IOP 01-12.05 [6] method and analyzed using EPA Method 6010C [7] to determine if thallium had contaminated the lab space. IOP 01-12.05 is a method traditionally used for toxic metal contamination collection by surface wipe sampling. Because of the nature of the sampling method, it is used as a test for removable contamination. It was decided that individuals working in spaces with unconfirmed levels of fixed contaminant would continue to be monitored yearly.

3 Fabrication of thallium foils

3.1 Specialized equipment

Two pieces of equipment were developed: a tube furnace tube with a water-cooled copper mesh and coil vapor capture system to combat the high vapor pressure of molten thallium (Fig. 1) and an argon shower box to prevent oxidation of the reactive metal (Fig. 2). As a safety precaution, both items were assembled to fit inside the available chemical hood during processing and to be disposed of after processing.

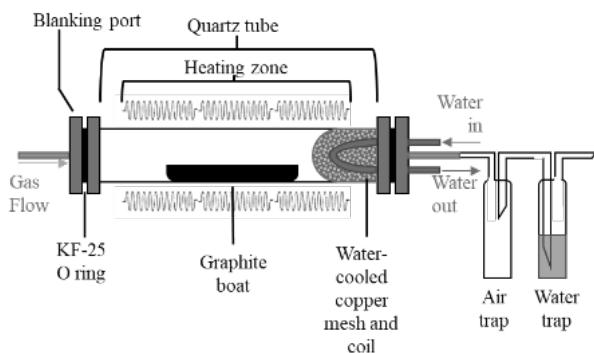


Fig. 1. Schematic of disposable tube furnace.



Fig. 2. Argon shower box with glove inserts.

In addition to being sized to fit the chemical hood, the tube furnace included a water-cooled copper mesh to act as a thallium vapor collector. In line with the collector, a water trap was used at the outlet of the tube. These traps prevent backflow of any oxidizing species in air.

3.2 Melting

The natural material was received from the supplier as 100 g of 6 mm diameter shot. The beads arrived under an aqueous salt solution. After rinsing them with ethanol and wiping clean, they were transferred to pre-dried graphite boats (Fig. 3A) and introduced to the tube furnace. After being sealed and leak checked, the volume of the quartz tube was purged with argon for $4\times$ the volume of the tube to ensure a fully inert atmosphere. To reduce any oxide that may have formed on the thallium shot during transfer, hydrogen was introduced to the tube during the melt.

Using the tube furnace, the material was rapidly heated to 320°C and consolidated to an ingot (Fig. 3B) of ~ 5 cm length. Minimal amounts of thallium were lost to vaporization caused by the rapidity of the melting, and the resulting ingot appeared shiny and oxide-free. Three large ingots $\sim 10\text{--}12$ cm long were made using the same process to improve final storage of the material and use in rolling the material to a foil.



Fig. 3. Thallium in the tube furnace [A] as shot, before melting, and [B] as an ingot.

3.3 Cold rolling

The resulting ingots oxidized quickly when removed from the inert atmosphere of the tube. One ingot quickly turned dull and black. The material was always kept in the argon box unless it was actively in process. In accordance with the “As Low As Reasonably Achievable” principles, it was decided that the reactive metal would be rolled in open air in the largest available rolling mill. This allowed for the maximum amount of material to be rolled per pass, decreasing prolonged exposure to the metal by orders of magnitude and made cleanup and post-fabrication sampling more accessible. The metal was rolled inside a work hardened stainless steel rolling pack. Because this process could not be done under inert atmosphere or vacuum due to the size and accessibility of the chosen rolling mill, the thallium metal was covered in an oil to act as a lubricant in the pack, to slow oxidation of the surface, and to capture any of the flaky, black oxide that could escape as a toxic particulate.

The metal was rolled out to 90 mm in width before being turned 90° and rolled on the perpendicular axis until the piece approached the customer’s desired thickness (Fig. 4). Thallium proved to be gummy and soft, with a tendency to adhere to the pack. The

lubricating oil was key to keeping the metal mobile, and periodic shifting of the foil and reapplication of the oil within the pack were essential. A lower force per unit area supplied by the rolls also assisted in preventing adherence to the pack. Like many other soft metals, thallium was expected to stick to the pack more readily when passing through smaller diameter rolls.



Fig. 4. Thallium foil, rolled in a stainless-steel rolling pack.

Despite these precautions, the metal was still fragile and tore easily during handling and processing. During rolling, if the rolling pack was passed through the mill seam first, then the curved pack could spring open when it was released from the rolling mill rolls and tear the foil. Instead, the pack was rolled so the seam would be last to pass through the active area of the mill, minimizing the chance of snapping the foil. Although this is not an option for many metals, the malleability of thallium allowed it to be easily rolled without deforming the pack.

3.4 Cutting and sealing

Once the correct areal density was assured, the material was meticulously cut to shape (Fig. 5) using a $2.50 \times 2.50 \text{ cm}^2$ template, cleaned of oil using a Kimwipe and ethanol, and had its dimensions recorded while within the argon shower box.

To seal the foils, a piece of 2 in. wide Kapton tape was placed adhesive side up. The foil was placed with one edge in contact with the tape, and allowed to fall toward the center, where it was carefully pressed into the tape. A second piece of tape was bent in a U shape, brought into contact with the thallium foil, and gently pressed into the bottom piece of tape. Air bubbles were removed using gentle pressure and a straight edge. The tape was then cut to a $2.50 \times 2.50 \text{ cm}^2$ square and wiped clean with an ethanol-wetted Kimwipe.

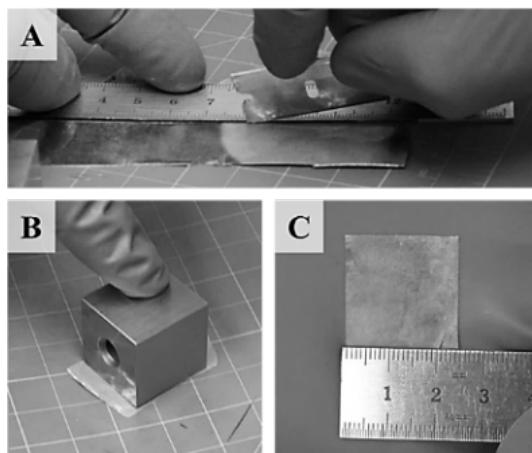


Fig. 5. Cutting thallium foil. [A] Trim to 2.5 cm. [B] Cut to $2.50 \times 2.50 \text{ cm}^2$ using template. [C] Final thallium foil.

After sealing between Kapton tape, each sealed foil was transferred to a vacuum chamber to remove any remaining air sealed within the Kapton tape before mounting. The target was placed carefully on the frame—with the foil at the center—and the corners of the tape were secured by 0.25 in. sized Kapton dots. Fig. 6 shows the final products.



Fig. 6. Forty-two thallium foils mounted to frames and packaged to be sent to customers.

3.5 Mitigation of surface contamination

To reduce the amount of thallium remaining on laboratory surfaces and to return equipment to a usable state, all surfaces were sampled using surface wipes per IOP 01-12.05. The surface wipes were analyzed via the EPA Method 6010C, which has an estimated limit of detection at approximately $27 \mu\text{g/L}$, within $\pm 20\%$ of the true value. Several surfaces within the possible contamination area were tested using this method (Table 1). According to the OSHA Technical Manual, *Surface Contaminants, Skin Exposure*,

Table 1. IOP 01-12.05 and EPA 6010C removable surface contamination results.

Sample location	Contamination ($\mu\text{g}/\text{cm}^2$)
Hood sash	<10
Working surface in hood	27
Right side wall in hood	<10
Small glove box in hood (outside)	14
Small glove box in hood (inside)	<10
Lab floor (by hood)	<10
Rolling mill (top roll)	180
Rolling mill (bottom roll)	400
Chair used during fabrication	<10
Field blank	<10

Monitoring and Other Analyses, the rule of thumb is to use the maximum allowable dose from skin contact ($20 \mu\text{g}/\text{cm}^2$) over 100 cm^2 (for a total of $200 \mu\text{g}/100 \text{ cm}^2$) as a pass/fail for the contamination of the tested surface. Table 1 reveals that the rolling mill rolls and the chemical hood exceeded this value and thus prompted additional decontamination efforts.

Additional cleaning measures were implemented to ensure the rollers of the Stanat 2-HI mill and the chemical hood were decontaminated to an appropriate level for continued work. The rollers were wiped repeatedly with a shop towel soaked in Formula 409 solution. The surface of the rollers was then wiped with Scrubs Stainless Steel Cleaning Wipes until the rollers returned to their pre-work condition. The conditioner in the wipes was allowed to soak into the rolls overnight. Afterward, ethanol and a shop towel were used to repeatedly wipe the rollers until the towel came away clean.

The amount of thallium contamination on the rollers was decreased significantly after conducting the rigorous cleaning protocol (Table 2). None of these limits reached the set limit of $200 \mu\text{g}/100 \text{ cm}^2$. Because of the presence of thallium remaining on the rollers, the Stanat 2-HI mill was designated as potentially contaminated until a definitive test could verify no fixed contamination was present, or the rollers are replaced.

Table 2. IOP 01-12.05 and EPA 6010C removable contamination results after cleanup.

Sample location	Contamination ($\mu\text{g}/\text{cm}^2$)
Working surface in hood	<10
Rolling mill (top roller)	19
Rolling mill (bottom roller)	19
Field blank	<10

4 Summary

SIMC at ORNL was able to develop a process for ensuring the fabrication of high quality, high demand natural thallium metal foils from commercially available material for use in national labs across the United States as well as ensuring the safety of the personnel working with this toxic element. All 42 foils produced were within customer-supplied specifications, affixed to customer supplied frames for use in their experiments, and successfully shipped to the customer. No individuals monitored during or after the completion of this campaign showed biological thallium concentrations above background and all surfaces showed near-background concentrations of removable thallium contamination.

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