Copper Electroforming Service at Laboratorio Subterráneo de Canfranc

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Abstract. Electroforming of copper can be very effective to obtain high radio-purity copper parts for low-background experiments. To support the construction of experiments at the Laboratorio Subterráneo de Canfranc in Spain, a Copper Electroforming Service (CES) set-up is in operation. In this work the electroforming system is described and results on the radio-purity of parts made are presented.

Keywords: Copper electroforming, gamma spectrometry measurement, ICP-MS assay.

INTRODUCTION

The Canfranc Underground Laboratory (LSC) is located at Canfranc Estación in the Spanish Pyrenees at about 1100 m above sea level [1]. Scientific activities at Canfranc started in 1985 inside the railway tunnel to measure the flux of muons underground. In 1994 a hall of 118 m^2 was built during the excavation of a roadway tunnel about 8.7 km long. This hall was used for early research activities at the Canfranc location. In 2006 two new and larger additional halls were made between the railway and road tunnels. The new underground infrastructure had a surface of about 1600 m^2. Finally, in 2010 the underground area at Canfranc became available for experimental activities. The main experimental area, named LAB2400, is divided in Hall A 40×15×12(height) m^3, Hall B and C 15×10×8(height) m^3. LSC has about 850 meters rock overburden, which corresponds to 2450 meters of water equivalent (m.w.e.) depth. This depth reduces significantly the flux of cosmic rays and allows carrying out rare event searches. At the underground facility the muon flux is ~ 4×10^{-3} m^{-2} s^{-1} [2]. At present, LSC is equipped with a number of ancillary infrastructures to support experimental activities. The Ultra-Low Background Service and the Copper Electroforming Service, discussed in this paper, are two examples. The underground infrastructure at LSC also includes an ISO 7 cleanroom (ISO 6 in a sector) [3], a machine shop, and a radon abatement system, which can deliver 220 m^3 h^{-1} of radon-free air at the level of mBq m^{-3} of radon. On surface the LSC has two buildings to support the work of researchers with a large machine shop, office space, and meeting rooms.

An international Scientific Committee meets at the LSC twice per year to review the status of existing projects and make recommendations on new proposals. The main scientific program at the LSC is focused on direct search for dark matter with ANAIS, ArDM and TREX, and for neutrinoless double beta decay with BiPo, NEXT and CROSS. In addition, at the LSC activities on nuclear astrophysics, neutron detection, geophysics, and research concerning life in extreme environments are carried out with the experiments CUNA, CROSS-N, GEODYN, ETSEC, and GOLLUM, respectively. The Ultra Low Background Service (ULBS) at the LSC is used to select low radioactivity Gadolinium salt to be used in Super-Kamiokande. This latter project is named SuperKGd.

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COPPER ELECTROFORMING

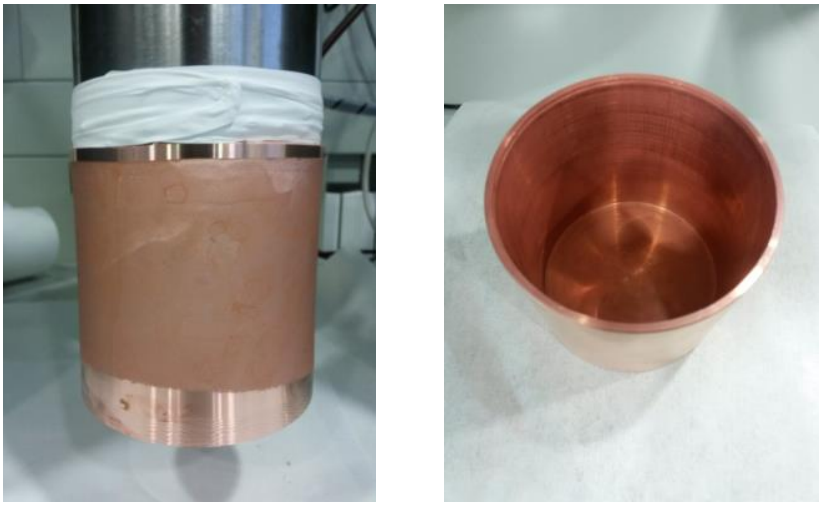
Copper electroforming is known to be an effective way to obtain high radio-purity copper. In addition, if the copper to make the final part has been kept in underground, the free cosmogenic contamination will be negligible [4]. Electroforming is a metal forming process producing parts through electrodeposition of a metal onto a mold (called mandrel), which is subsequently removed.

The Copper Electroforming Service (CES) at the LSC started in 2014 and it is located in the Chemistry Laboratory (Office Building above ground). The copper electroforming set-up is composed of a power supply unit, a process parameter control system, a tank, an engine, and a filter with a pump. A rigorous cleaning procedure of all materials and components of the set-up was done before the mounting. Two electroforming set-ups are operative at the LSC.

At the CES the used technique is direct fixed-current-density electroplating. Some process parameters, such as current density, rotation speed and rotation direction of the mandrel, were tunned to manufacture electroformed copper parts with smooth surface [5]. The employed materials are high-purity commercial chemicals, ultrapure water (18.2 MΩ cm at 25 °C), oxygen free high conductivity (OFHC) copper bars (Goodfellow, Ref. CV007970), and stainless steel 316L mandrel.

RADIOPURITY OF ELECTROFORMED COPPER

In order to measure the levels of radio-purity in the electroformed copper, an electroformed copper endcap with 81.35 mm internal diameter, 80 mm height and an estimated thickness of 2.5 mm was prepared. During the electroforming process the current density was set to 3 A dm^{-2} and the mandrel turned at 1.68 rev s^{-1} rotation speed, changing its rotation direction (forward or reverse direction) every 10 min. Although the electroformed copper was produced with a smooth external surface, it required a machining treatment on the edges to remove the "dog-bone" effect, as is shown in Fig. 1, a. At the end of the electroforming process (90 h 30 min), a final machining treatment was done over the whole external surface and the piece was removed manually from the mandrel. The final electroformed copper endcap is illustrated in Fig. 1, b. Every machining step was performed at the Mechanical Workshop (Office Building above ground) using a lathe, at manual mode, without lubricant.



(a) (b)

FIGURE 1. Electroformed copper over the mandrel after the machining treatment on the edges (a) and the final electroformed copper endcap (b).

The finished electroformed copper endcap (627.2 g) was carefully cleaned by the routine cleaning protocol (nitric acid etching and citric acid passivation) and was stored underground at LAB2400.

Gamma Spectrometry Measurement

The ULBS at the LSC started its activity in 2010 and is located in Hall C in the underground laboratory. Inside the laboratory seven HPGe p-type counters are already mounted and taking data. The shielding of each detector is made of 20 cm of lead with ^{210}Pb activity less than 29 Bq kg^{-1}. An internal shield of 10 cm of OFHC copper for 6 detectors and 5 cm for the remaining one is added to reduce the bremsstrahlung produced by the remaining ^{210}Pb activity. Before mounting, the materials were acid etched to remove surface contamination. At the exterior the detector is encased in a methacrylate box and gaseous nitrogen from boil-off evaporation is flushed through the sample cavity to purge the radon gas. All HPGe detectors are coaxial p-type (~100 % relative efficiency) made by Canberra.

A gamma spectrometry measurement of the electroformed copper part was performed using a HPGe detector (GeOroel, 2 Kg Ge coaxial p-type, ~100 % relative efficiency) at ULBS. Due to the limited free space inside the sample cavity, the height of the electroformed copper part had to be reduced cutting the piece with a saw (75.4 mm height and 577.8 g). This piece was located over a Marinelli container in vertical position with the bottom part close to the Ge detector. The measuring time was 50.4 days. Results of the gamma spectrometry measurement are reported in Table 1.

TABLE 1. Isotopes measured in electroformed copper with HPGe detector (GeOroel) at the LSC.

All the limits are 95 % C.L.

Isotope	^{234}Th	^{234m}Pa	^{235}U	^{228}Ra	^{228}Th	^{226}Ra	^{137}Cs	^{60}Co	^{58}Co	^{57}Co	^{56}Co	^{54}Mn	^{40}K
Units (mBq kg^{-1})	< 11.2	< 72	< 5.6	< 2.23	< 1.36	< 9.8	< 0.86	< 0.71	< 0.4	< 0.8	< 0.43	< 0.31	< 6.93

Inductively Coupled Plasma Mass Spectrometry Assays

According to the detection limits and results obtained from the gamma spectrometry measurement, several Inductively Coupled Plasma Mass Spectrometry (ICP-MS) assays were done.

Firstly, some ICP-MS assays were performed by the Chemistry Service at Gran Sasso National Laboratory (LNGS) to analyze the Th and U contamination at the surface and bulk in copper samples. Results of these ICP-MS assays are reported in Table 2.

Samples of the OFHC copper bar (named sample #1), the anode in the electroforming technique, and the electroformed copper endcap (named sample #2) were collected. These small samples were cut using a manual metallic saw and cleaned by a cleaning protocol at LSC.

As for the surface analysis, at LNGS the samples were partially etched with 7 mL of ultrapure nitric acid (obtained by sub-boiling system DUOPur, Milestone-Bergamo, Italy) and 9 mL of ultrapure water (18.2 MΩ cm at 25 °C) using preconditioned and measured vials. This step dissolved about 2 grams of copper each sample. Then 13 mL of each sample were treated with chromatographic extraction resins (TRU resin, Triskem-France) to have Th and U pre-concentration. Th and U were then eluted from the columns by ammonium oxalate 0.1 M. These solutions were directly measured by HR-ICP-MS for Th and U determination.

In order to investigate the hypothesis concerning the surface contamination, the remaining copper samples were etched three times more to carry out a bulk analysis. The first two solutions of each sample were wasted while a portion of the third one was measured. For each sample, about 14 mL (1 g of Cu) of the final solution were treated with chromatographic extraction resins mentioned above to have Th and U pre-concentration. Th and U were eluted from the columns by ammonium oxalate 0.1 M and later these solutions were directly measured by HR-ICP-MS.

TABLE 2. Th and U concentration measured at surface and bulk in the copper samples. The error is estimated to be about 10%.

Sample	Description	Surface assay		Bulk assay	
		Th [ppt]	**U** [ppt]	**Th** [ppt]	**U** [ppt]
#1	OFHC copper, raw material	280	48	4.6	~ 1
#2	Electroformed copper obtained at CES	49	22	< 1	< 1

Secondly, some ICP-MS assays were performed at Pacific Northwest National Laboratory (PNNL) to analyze the Th and U contamination at bulk in copper samples. Results of these ICP-MS assays are reported in Table 3.

After the ICP-MS assay done at LNGS, the remaining copper sample #1 (OFHC copper, anode in the electroforming process) was sent from LNGS to PNNL. The copper sample #2 (electroformed copper) had been completely digested at LNGS, and therefore a new sample of the electroformed copper endcap had to be collected at LSC. This sample was cut with a manual metallic saw, cleaned by a cleaning protocol and sent directly from LSC to PNNL.

This assay was conducted in a Class 10,000 cleanroom and utilized a Class 10 laminar flowhood when applicable. Optima Grade acids were used in all preparations. Vials, implements, and columns/resins were validated previous to use. Isotope dilution methods were used for quantitation by spiking a known amount of ^{229}Th and ^{233}U in each sample and process blank. The remaining copper sample #1was fully digested in 8M HNO_3 to near saturated levels of digested copper. The electroformed copper sample #2 received at PNNL was cut into three samples. These three copper samples were digested in 8M HNO_3, etching away about a third of the mass. The remaining mass was then used as the sample which completely dissolved except for leaving a small dark ring in the vessel. Previous to analysis via ICP-MS, a pre-concentration step was conducted to maximize analyte (U and Th) while minimizing matrix via anion exchange separation.

TABLE 3. Th and U concentration measured in the copper samples. The instrumental precision (triplicate measurements of the same sample on the ICP-MS) is shown for each sample measurement as "Inst. +/- 1s".

Sample	Description	**Th** [ppt]	**+/- sd**	**U** [ppt]	**+/- sd**
#1	Remaining OFHC copper	0.967	0.059	0.196	0.011
#2_LSC_01	Electroformed copper obtained at CES, three pieces	0.0426	0.0019	< 0.0497	-
#2_LSC_02		0.0345	0.0037	< 0.0502	-
#2_LSC_03		0.0363	0.0050	< 0.0498	-

Comparison of Gamma Measurements and ICP-MS Assay Results

A comparison of the gamma measurements and the ICP-MS assays between the surface and bulk radio-purity in copper samples can be done considering secular equilibrium of the decay chain. Results are reported in Table 4. In bold, Th and U concentration values obtained directly from each analytical technique.

TABLE 4. Gamma spectrometry measurement and ICP-MS assay comparison for OFHC copper (upper) and electroformed copper (bottom) samples.

OFHC Copper	ICP-MS assay					
	LNGS surface [mBq kg^{-1}]	LNGS surface [ppt]	LNGS bulk [mBq kg^{-1}]	LNGS bulk [ppt]	PNNL [mBq kg^{-1}]	PNNL [ppt]
U	0.6049	**49**	0.01234	**~ 1**	0.00242	**0.196**
Th	1.1382	**280**	0.01869	**4.6**	0.00393	**0.967**

EF Copper	Gamma spectrometry		ICP-MS assay					
	LSC [mBq kg^{-1}]	LSC [ppt]	LNGS surface [mBq kg^{-1}]	LNGS surface [ppt]	LNGS bulk [mBq kg^{-1}]	LNGS bulk [ppt]	PNNL [mBq kg^{-1}]	PNNL [ppt]
U	**< 11.2 (^{234}Th)**	< 907.2	0.2716	**22**	< 0.012	**< 1**	< 0.000614	**< 0.0498**
Th	**< 2.23 (^{228}Ra)**	< 548.5	0.1992	**49**	< 0.0406	**< 1**	0.000147	**0.0363**

CONCLUSIONS

The CES facility at the LSC allows to carry out R&D activities and gives support to experiments at the LSC and in other laboratories. The CES can produce very high radio-purity copper. However, the handling and surface cleaning protocol is not yet sufficient to remove surface contamination. Further work is needed to understand the origin of this contamination. The comparison ICP-MS - gamma spectrometric measurements demonstrates that the two techniques are in agreement and complementary.

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