

# Determination of Th and U in High Purity Ni

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## 1 Introduction

We are investigating possible sources for high purity Ni to be used for neutral current detector bodies. Our strawman design<sup>1)</sup> called for tubes having 2 inch outer diameter with 10 mil wall thickness. There are 380 2-meter long tubes and 64 1-meter long tubes. This represents a Ni mass of 301 kG. Our purity goal is to limit the intrinsic radioactivity to a level which will result in less than 1 neutron/day produced in the heavy water volume ( $\sim 11$  ppt Th or  $\sim 134$  ppt U).

Two generic types of Ni have been analyzed. The first is "high purity" rolled Ni and the second is "CVD" Ni formed from the thermal decomposition of  $\text{Ni}(\text{CO})_4$ . Samples from these two processes were analyzed using two different techniques. The rolled Ni was done using glow discharge mass spectrometry and the CVD Ni by RNAA.

## 2 Rolled Nickel

Two rolled nickel samples were analyzed for gross U and Th content by glow discharge-mass spectrometry (GD-MS). In this technique the metal sample is inserted into a cell where an argon gas glow discharge is produced by applying a negative potential (approximately -1000Vdc) to the sample. The sample, thus, becomes the cathode in a small electrically grounded vessel filled ( $\sim 1$  Torr) with argon. The sputtering of the sample by energetic positive argon ions consumes the sample at a rate of  $\sim 1$ -100  $\mu\text{g}/\text{min}$ , producing ample amounts of neutral atoms which are subsequently ionized by penning ionization and electron impact processes in the discharge. The ionized metal species are sampled from the cell by a small opening leading to a mass spectrometer. In these experiments a low resolution quadrupole mass spectrometer is used. The sputtering and ionization processes are fairly uniform across a large number of matrices, making standard-less quantification possible. This was important due to the unavailability in our laboratory of trace U and Th certified standards of nickel. The accuracy of the

method can only be stated from prior work with other metals as being within a factor of three of the real U and Th content of the metal at ppb concentrations. This accuracy is acceptable for a quick survey method (~ 1-2 hrs total analysis time per sample).

The experiment is performed on a clean cut nickel sample sliver ~ 1.5" x 0.65". The sample surface is simply cleaned with alcohol and acetone and inserted into a liquid nitrogen cooled glow discharge cell. The lead signal was monitored for about 45 min. until it stabilized before starting the quantitation. One of the nickel isotopes is used as an internal reference and monitored on the low level sensitivity with the assumption that the sample is 100% nickel. The relative sensitivity factors for U, Th, Pb and Ni are set to 1.00. That is, it is assumed that the relative sputtering and ionization efficiencies for these elements are equal. A good assumption for this technique within a factor of three. The U, Th and Pb signals are monitored at masses 238, 232, and 208, respectively, on the high sensitivity ion counting multiplier of the mass spectrometer. The mass regions of interest are scanned 30 times on a continuous basis for ~ 15 min. Each scan is a composite of 256 signal averaged scans from which a concentration is calculated. The indicated uncertainty is one standard deviation of the mean concentration calculated for each scan. Thus, it is not a statement of the accuracy of the technique but of precision. The concentrations are calculated from the relative strengths of each of the signals assuming that the sample is essentially 100% nickel.

Further improvements in this analytical technique which may make it more attractive for routine analysis of SNO materials include the use of certified standards for quantitation, and the use of a high resolution mass spectrometer which is known to have sensitivities in the ppt range for these elements.

The results from the analysis were:

High Purity Rolled Nickel

Contaminant	Sample 1	Samples 2
Pb	220 ppb	293 ppb
Th	19 ± 4 ppb	13 ± 1 ppb
U	47 ± 3 ppb	12 ± 2 ppb

These results show the Th and U levels to be about 3 orders of magnitude greater than acceptable for SNO. This new technique makes glow discharge mass spectrometry a rapid method for surveying Ni, but currently its sensitivity is not adequate to address the ppt levels required for the neutral current detector bodies.

### 3 RNAA on CVD Nickel

Three nickel samples from two different vendors (together with U and Th standards) were sent to the University of Missouri Research Reactor in Columbia, Missouri. Each company (referred to herein as vendors "M" and "B") supplied a CVD nickel tube and, in addition, vendor "M" supplied a sample of sheet CVD nickel which had been deposited onto Teflon<sup>TM</sup>. The samples were irradiated for 8 hrs. in a thermal neutron fluence of  $5 \times 10^{13} \text{ cm}^{-2}\text{sec}^{-1}$ . Each sample had a contact dose rate of  $\approx 100 - 200 \text{ mR/hr}$  7 days after bombardment; nearly all of which was due to 71 d  $^{58}\text{Co}$  produced via the n,p reaction on  $^{58}\text{Ni}$ .

From a chemical standpoint, the determination of pg quantities of Th and U in gram quantities of Ni was twofold; 1.) to clean and then protect the samples from contamination prior to irradiation, and 2.) to remove large amounts of bulk Ni and  $^{58}\text{Co}$  from the desired Np and Pa activities following irradiation. The analytes  $^{239}\text{Np}$  and  $^{233}\text{Pa}$ , resulting from neutron capture on  $^{238}\text{U}$  and  $^{232}\text{Th}$  respectively, were isolated according to the procedure given below.  $^{235}\text{Np}$  and  $^{231}\text{Pa}$  were used as chemical tracers.

#### Sample Preparation

Ni samples were cut to an appropriate size and washed with reagent grade acetone in order to remove most organics from the surface. The samples were then submerged in 9 M HCl/1M HF and heated for approximately 15 minutes. The length of acid treatment was somewhat arbitrary; carried out until the solution was noticeably green in colour, indicating that considerable etching of the Ni surface had occurred. The samples were subsequently rinsed with 18 M $\Omega$  water, transferred to a class 100 clean-room, and rinsed again. The samples were loaded into pre-cleaned Suprasil<sup>TM</sup> quartz tubes which were covered with parafilm<sup>TM</sup> before being removed from the clean-room and sealed with a torch.

#### Radiochemistry

Each Ni sample was dissolved in aqua regia and reduced in volume several times with conc. HCl in order to remove  $\text{HNO}_3$ . The final solution was adjusted to 9 M in HCl and passed through an anion exchange column wherein the Pa and Np were sorbed and the Ni passed through.

The Pa was eluted from the column with 9M HCl/0.025M HF and taken to soft dryness in a teflon beaker. It was then passed through a second anion exchange column with 9M HCl/0.025M HF and counted. Overall Pa yields were 70-80%.

After elution of the Pa, the Np (together with  $^{58}\text{Co}$ ) was eluted with 4M HCl. La and Co carriers were added to the sample and the Np reduced to the (IV)

state with hydrazine. The Np was precipitated with  $\text{LaF}_3$ , leaving the bulk of the Co in solution, and then again with  $\text{La}(\text{OH})_3$ . Following reduction to Np(IV) with freshly prepared ferrous sulfamate, final purification of the Np was achieved by sorbing it onto an anion exchange resin from 3.5M  $\text{HNO}_3$  and eluting it with dilute HCl. Overall Np yields were 40-60%.

Calibrated "well-type" germanium detectors were used for the quantitative determination of the  $^{235}\text{Np}$ ,  $^{239}\text{Np}$ , and  $^{233}\text{Pa}$  activities by gamma counting. The  $^{231}\text{Pa}$  was determined by alpha counting the Pa sample using a gas proportional counter.

## Results

CVD Nickel

Sample	U (ppt)	Th (ppt)	Np yield (%)	Pa yield (%)
B-Tube	$17 \pm 2$	$57 \pm 3$	65	77
M-Teflon	$14 \pm 1$	$32 \pm 2$	42	80
M-Tube	$\leq 0.8$	$7.4 \pm 0.4$	42	77

- All errors are  $1\sigma$  uncertainties. Each represents counting errors for the analyte and tracer combined in quadrature.
- The upper limit given for the U content of the M-Tube sample represents (signal-bkg)/bkg of  $\approx 0.8$ . This is the level at which it is assumed that a distinctive photopeak would be observed.

## 4 References:

J.B. Wilhelmy, "New Monte Carlo Calculation for Neutron Detection in SNO", SNO-STR-92-058 (1992).