

# THERMAL IONIZATION MASS SPECTROMETRIC ANALYSIS FOR THE SNO PROJECT

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## Introduction

The heart of the neutrino detection system of the proposed Sudbury Neutrino Observatory will be 1,000 tonnes of heavy water contained in an acrylic tank. In order to minimize background interferences, the acrylic used in the fabrication of the tank must be very pure with respect to uranium and thorium. Specifically, a concentration of 0.74 ng/kg of thorium or 6.6 ng/kg of uranium in the acrylic would result in one background photon per day. This report describes the analysis procedures used for the determination of the uranium and thorium impurity levels in various acrylics.

## Experimental

### (a) Reagents and Materials

Nitric and hydrofluoric acid solutions are prepared from double sub-boiling distilled acids (Seastar Chemicals Inc., Sidney, B.C.) and distilled, deionized water. Polyethylene microvials, doll bottles, and Eppendorf pipette tips are washed in 4 M HNO<sub>3</sub>, then soaked overnight in distilled, deionized water before use. Acropor (Gelman Instrument Co.) anion-exchange paper is cut into 1 mm diameter discs and equilibrated with 2 M HNO<sub>3</sub> prior to use. The centre filament of Cathodeon type 553 triple filament assemblies is replaced with zone-refined rhenium ribbon (Rhenium Alloys, Inc., Elyria, OH) and outgassed at 1850°C for 3 hours in order to remove any surface uranium or thorium contamination. All containers, filaments, etc. are used once and discarded, with the exception of the Teflon dishes used for spiked sample evaporation. These are cleaned by wiping with a Kimwipe, then they are treated with hot 8 M HNO<sub>3</sub> for 1 hour, then soaked overnight in distilled, deionized water.

### (b) Apparatus

The laminar flow hood is a Canadian Cabinets (Nepean, Ont.) dual mode vertical laminar flow work station equipped with 2 HEPA filters rated 99.99% efficient on all particulates 0.3 microns and larger. The mass spectrometer is a Nuclide (Nuclide Corp., State College, PA) 90° magnetic sector instrument with a Vacumetrics (Vacumetrics, Ventura, CA) ETP AEM 1000 electron multiplier and an IBM PC-based automation system [1].

### (c) Primary Standards and Spikes

National Bureau of Standards SRM 960 was used to prepare an isotopically natural uranium primary standard by precise dilution of the original solution. The thorium primary standard was prepared from natural thorium

metal. The metal was first cleaned in 13 M HNO<sub>3</sub>/0.05 M HF to remove the oxide layer, then rinsed thoroughly with water. After drying in a dessicator, 0.2 g metal was weighed to the fifth decimal place. The metal was dissolved in 15 mL of 13 M HNO<sub>3</sub>/0.05 M HF, then the solution was repeatedly evaporated to near-dryness to remove the HF. The solution was then diluted, by weight, with 1 M HNO<sub>3</sub> to give a <sup>232</sup>Th concentration of 4.8348 x 10<sup>-2</sup> mole/kg.

The uranium spike solution was prepared from U-235 enriched UO<sub>2</sub> powder received from Nuclear Materials Branch. Stoichiometric U<sub>3</sub>O<sub>8</sub> was prepared by first oxidizing 0.6 g UO<sub>2</sub> at 490°C for 4 hours, then firing at 910°C for approximately 16 hours until a constant weight was obtained. The U<sub>3</sub>O<sub>8</sub> was quantitatively dissolved in concentrated HNO<sub>3</sub>. For the <sup>230</sup>Th spike solution, ThO<sub>2</sub> powder enriched in Th-230 (Oak Ridge National Laboratory, Oak Ridge, TN) was dissolved in 13 M HNO<sub>3</sub>/0.05 M HF, then diluted in 1 M HNO<sub>3</sub>. The uranium and thorium spike solutions were combined to give a double spike solution which was calibrated against the combined primary standards by isotope dilution mass spectrometry. The average of three determinations showed the <sup>230</sup>Th concentration was (6.80 ± 0.01) x 10<sup>-7</sup> mole/kg, and the <sup>235</sup>U concentration was (6.01 ± 0.04) x 10<sup>-7</sup> mole/kg. The atomic ratio of <sup>230</sup>Th/<sup>232</sup>Th in the double spike solution was 3.853 ± 0.027, and the atomic ratio of <sup>235</sup>U/<sup>238</sup>U was 3.214 ± 0.067 (Table 1). The spike and standard solutions were stored in sealed 2 mL glass ampoules.

## Procedure

### (a) Sample Preparation

Initial sample preparation and vaporization is performed by N&SS Physics Branch personnel as follows. Approximately 1 kg of acrylic is vaporized in high purity Supracil tubing at 550°C under a nitrogen atmosphere. The residue is leached from the Supracil tube by repeated washings with 10 mL hot 13 M HNO<sub>3</sub>/0.05 M HF. The wash is collected in Teflon bottles and its volume is reduced to approximately 0.5 mL by heating under IR lamps. These samples are sent to the mass spectrometry laboratory for determination of uranium and thorium.

The sample solution is drawn into a pre-weighed doll bottle, then the Teflon bottle is rinsed twice with 0.5 mL 2 M HNO<sub>3</sub>, and each rinse is drawn into the doll bottle. The doll bottle is then reweighed to give the total solution weight, and after shaking to mix the solution, approximately half of the solution (accurately weighed) is aliquotted onto a Teflon dish in the laminar flow clean hood. This aliquot is spiked with 30 μL of double spike solution using an Eppendorf pipette. The spiked sample is evaporated to dryness under an infrared lamp to ensure isotopic equilibration, then redissolved in 5 μL 8 M HNO<sub>3</sub>. The solution is transferred to a 1 mL micro-vial, and equilibrated with a 1 mm diameter Acropor anion-exchange disc, which adsorbs approximately 0.3 ng of <sup>235</sup>U and 3 ng of <sup>230</sup>Th [2]. After 1 hour of equilibration, the disc is removed from solution using a fine-tipped glass rod and mounted on the centre rhenium filament of a triple-filament assembly with resistive heating at 2A current.

(b) Mass Spectrometry

The filament assembly is inserted into the source, and after a brief outgassing period at low temperature, the centre filament is heated to 1700°C for uranium isotopic analysis. With a constant accelerating potential of 10.4 KV, the magnetic field is stepped between <sup>235</sup>U and <sup>238</sup>U in an ABBA fashion, and the average of 8 readings at the top of each peak is used to calculate the atomic ratio. After 18-24 consistent ratios are obtained, the filament temperature is raised to 1900°C for analysis of thorium in the same manner.

Results and Discussion

(a) Isotope Ratios

The isotopic composition of the double spike solution was determined by 5 repeat analyses of 30 μL of the spike solution. The spike isotopic ratio is also periodically checked to verify lack of procedural or spike contamination. Table I shows the data accumulated over the past year. The overall uranium results show poorer precision than the thorium values. This is probably due to the smaller load on the filament (- 0.4 ng total uranium) coupled with the greater likelihood of ambient uranium contamination. For individual sample analysis (Table II), either element may show optimal precision, depending on the time devoted to each element. Combined analysis of uranium and thorium on a single disc is known to degrade the ionization efficiency of both, resulting in a relatively weak signal and limited analysis time before signal decay. If increased sensitivity is required, it could be attained by single element analysis. The disadvantage would be an effective doubling of the time required for an analysis.

(b) Quantitation

The amount of natural uranium and thorium in the samples is calculated using isotope dilution equations.

For uranium:

$$[^{238}\text{U}] = \frac{m_{sp}}{m_s} \cdot [^{235}\text{U}]_{sp} \cdot \left[ \frac{R_{8/5,n} - R_{8/5,sp}}{1 - \frac{R_{8/5,n}}{R_{8/5,s}}} \right]$$

and for thorium:

$$[^{232}\text{Th}] = \frac{m_{sp}}{m_s} \cdot [^{230}\text{Th}]_{sp} \cdot (R_{2/0,n} - R_{2/0,sp})$$

where  $m_{sp}$  and  $m_s$  are mass (g) of the spike and sample aliquots, respectively.  $R_{8/5,n}$ ,  $R_{8/5,sp}$ ,  $R_{8/5,s}$  are the atomic ratios of 238/235 in the sample-spike mixture, the spike, and the sample,

respectively. The definitions for thorium are similar, and the calculation is simplified since natural thorium is monoisotopic. The volume of spike solution in 4 M HNO<sub>3</sub> is converted to weight with consideration for the specific gravity of the acid.

Table II shows the isotope ratios obtained for a typical spiked sample. Analysis of the unspiked samples is not necessary since the isotopic abundances of natural uranium and thorium are known.

In earlier work, the sample was spiked and analyzed in duplicate (Table III). Since the agreement was acceptable for trace analysis, it was decided to analyze the samples singly due to the lengthy nature of the procedure. A portion of the sample is retained for repeat analysis if necessary.

### (c) Detection Limits

The method blank is not consistent, and depends on many factors such as the quality and cleanliness of the Supracil tube, the purity of the acid used for leaching the tube, the number of times the tube has been used, and the amount of uranium or thorium contained in previous acrylic vaporizations. Table IV illustrates that background values of less than 0.1 ng for both uranium and thorium can be obtained on completion of the entire procedure. Table V illustrates more typical background levels. It has been noted that for a given Supracil tube, the background level tends to increase with time (i.e., increased use). The uranium values show a higher degree of random contamination (\*), whereas high thorium values are normally due to a very large amount of thorium present in the preceding acrylic analysis. For example, in the cases shown (\*\*), the preceding acrylic sample contained 69 and 23 ng of thorium, respectively.

The limit of detection (at the 95% confidence level) is defined by Currie [3] as  $L_D = 3.29\sigma_b$  for a "well-known" blank. In this instance, the detection limit is governed by the minimum level which is discernible from the uncertainty of the spike isotopic ratios. Solving the previously given isotope dilution equation using  $R_m = R_{sp} + 3.3\sigma_{sp}$  ( $\sigma$ 's from Table I), gives a detection limit of approximately 100 pg for uranium and 40 pg for thorium.

### Conclusions

An accurate method has been developed for the determination of trace uranium and thorium in acrylics by TIMS. Extension of the procedure to analysis of other materials such as monomer, teflon, and Kevlar fibre is also possible although these have been found to require purification by ion exchange chromatography before analysis.

The procedure requires 1½ to 2 days for the preparation and mass spectrometric analysis of one acrylic sample and two accompanying tube background leachates (prior- and post-vaporization). However, due to the dedicated nature of the laboratory to the SNO project, the results for a given sample can be obtained within 2 days of receipt of a sample, and over 170 analyses have been completed to date in 1991.

As in any trace analysis procedure, the possibility of error due to sample contamination exists. The use of ultra-pure reagents, scrupulously cleaned labware and Teflon sample containers minimize this possibility. Also, the above-mentioned background samples provide frequent checks for contamination problems. Assuming that no uranium or thorium is lost during the vaporization step, a falsely low result could not be obtained in this procedure. As well, due to the large sample size (1 kg), errors due to sample inhomogeneity are minimal.

#### References

- [1] L.W. Green, J.S. Barszczewski and N.L. Elliot. A Versatile Low-Cost Automation System for Thermal Ionization Mass Spectrometers. Int. J. Mass Spec. and Ion Processes, 67:253-265 (1985).
- [2] L.W. Green, N.L. Elliot and T.H. Longhurst. Separation and Mass Spectrometry of Nanogram Quantities of Uranium and Thorium from Thorium-Uranium Dioxide Fuels. Anal. Chem., 55:2394 (1983).
- [3] Lloyd A. Currie. Limits for Qualitative Detection and Quantitative Determination. Anal. Chem., 40:586 (1968).

**TABLE I**  
**REPLICATE ANALYSIS OF U/Th SPIKE SOLUTION**

Analysis Number	Atomic Ratio	
	$^{230}\text{Th}/^{232}\text{Th}$	$^{235}\text{U}/^{238}\text{U}$
1	3.869	3.224
2	3.827	3.149
3	3.864	3.165
4	3.847	3.337
5	3.886	3.184
6	3.830	3.333
7	3.872	3.135
8	3.877	3.254
9	3.830	3.288
10	3.822	3.243
11	3.807	3.168
12	3.862	3.155
13	3.850	3.184
14	3.904	3.183
$\bar{R}$	3.853	3.214
s	0.027(0.7%)	0.067(2%)

TABLE II

SAMPLE ANALYSIS - POLYCAST P10-CR8-SA, SECOND RINSE

(a) Uranium Data

Run No.	Atomic Ratio
	235/238
1	2.675
2	2.649
3	2.729
4	2.696
5	2.669
6	2.708
7	2.675
8	2.682
9	2.673
10	2.666
11	2.689
12	2.679
13	2.695
14	2.669
15	2.671
16	2.714
17	2.681
18	2.681
19	2.693
20	2.691
21	2.688
22	2.688
23	2.674
24	2.698
$\bar{R}$	2.685
s	0.017 (0.6%)
$^{238}\text{U}(\text{ng})$	0.52

TABLE II  
(Continued)

SAMPLE ANALYSIS - POLYCAST P10-CR8-SA, SECOND RINSE

(b) Thorium Data

Run No.	Atomic Ratio
	230/232
1	3.478
2	3.495
3	3.413
4	3.366
5	3.412
6	3.458
7	3.510
8	3.411
9	3.473
10	3.478
11	3.433
12	3.446
13	3.498
14	3.391
15	3.546
16	3.469
17	3.516
18	3.465
19	3.508
20	3.433
21	3.464
22	3.377
23	3.451
24	3.448
$\bar{R}$	3.456
s	0.046 (1.3%)
$^{232}\text{Th}(\text{ng})$	0.27



**TABLE III**  
**DUPLICATE SAMPLE ANALYSES**

Sample No.	<sup>232</sup> Th(ng)	<sup>238</sup> U(ng)
1	0.37	0.38
	0.33	0.52
2	0.07	0.44
	0.05	0.43
3	0.10	0.36
	0.08	0.37
4	0.75	0.38
	0.76	0.40
5	1.16	2.18
	1.10	2.13
6	0.28	0.54
	0.28	0.51
7	0.04	0.15
	0.07	0.20
8	1.97	2.38
	2.05	2.37
9	0.47	0.31
	0.50	0.28
10	0.08	0.27
	0.08	0.27
11	5.5	7.8
	5.6	7.7
12	0.41	1.59
	0.48	1.56
13	0.37	0.26
	0.29	0.28
14	66.5	70.1
	67.6	70.9
15	20.6	9.3
	20.6	9.2
16	3.2	1.13
	3.2	1.18
17	0.35	5.5
	0.41	6.4
18	11.1	12.7
	11.4	12.8
19	1.82	1.84
	1.82	2.46
20	1.04	0.34
	1.06	0.33

**TABLE IV**  
**PROCEDURAL BLANK**

Sample I.D.	U(ng)	Th(ng)
90/05/02 Tube 8 pre-vap. bkgd.	.06	.07
90/05/04 Tube 10 pre-vap. bkgd.	.05	.03
90/05/09 Tube 10 pre-vap. bkgd.	.07	.03
90/05/09 Tube 10 post-vap. bkgd.	.08	.05
90/05/10 Tube 10 pre-vap. bkgd.	.05	.02
90/05/14 Tube 10 pre-vap. bkgd.	.08	.04
90/11/22 Tube 6 pre-vap. bkgd.	.07	.10
90/11/23 Tube 6 pre-vap. bkgd.	.11	.07

**TABLE V**  
**PRE-VAPORIZATION BACKGROUNDS, TUBE #6**

Date	U(ng)	Th(ng)
90/09/21	.13	.10
90/09/28	.95*	.23
90/10/11	.34	.28
90/11/22	.07	.10
90/11/23	.11	.07
90/11/27	.84*	.12
91/01/01	.18	.28
91/01/17	.16	.38
91/01/20	.38	.51
91/02/21	.19	.42
91/02/08	.33	.86**
91/02/22	.25	.51
91/05/31	.45	1.6**
91/06/14	.47	.29