SNO-STR-90-63

Acrylic Radioactivity Report Summary by Earle
Sudbury Meeting, April 18,1990

At a workshop on this subject verbal reports where presented by Clifford, Milton and Earle, CRNL, by Jagam and Simpson, Guelph and by Fowler and Wilhelmy, LANL. In some cases there is hard copy on file backing up these presentations.

1) Clifford: Evidence for a heterogeneous distribution of Th in acrylic by Clifford, Lee and Edwards. Hard copy tabled.

A 37 g sample of Polycast material was neutron irradiated at CRNL and gamma counted at CRNL. The result indicated that the sample contained 8.9 +- 1.6 ng of Th (237 ppt).

This sample was shipped to QueenUs where it was split into 4 packages and each package was gamma counted several times. The packages registered 50 to 650 ppt with statistical errors around 10% and repeated measurements indicated systematic errors of less than a factor of 2. The reliability of these measurements were questioned by Wilhelmy who worried about geometric efforts contributing to the large variations observed. Nevertheless inhomogenities in the sample would appear to be a contributing factor. The measured Th in the 4 packages was 7.9 +-0.2 and 6.0 +-0.2 ng or about 7 ng with a 0.5-1 ng systematic error. This value is similar to the CRNL result of 9 ng quoted above.

The packages were returned to CRNL for vaporization and mass spectroscopy. One package contained 0.48 ng but the following rinses contained 0.29 and 0.51 ng (c.f. 1.3 ng at QueenUs). The sum of the other three packages was 0.91 ng with following rinses below 0.1 ng (c.f. 7.1 ng at QueenUs). The total Th comes to 2 ng which is 4 times less than the neutron activation result and suggests loss of Th during the vaporization.

2) Milton: Alpha Spectrometric Report: Hard copy tabled.

Gwen has improved her radioisotope separation and collection procedures so that she now can get Ra sources with about 50% recovery efficiency. Two 15 kg acrylic samples have been analysed and compared with mass spect. There is consistency within a factor of 2 for both the Th and U. The Th chain is in equilibrium, the U238 and Ra226 are in equilibrium but the U234 was significantly higher. This indicates a different source of contamination for the Cryo and stores acrylic than for the Polycast and Rohm material examined earlier but as long as the Ra226 is measured the background contribution for SNO is determined. (The U234 is not a problem).

3) Earle: TIMS results since Jan T90

Ten Cyro samples have been vaporized and the rinses analysed by mass spec. The Th/U values in ppt for nine of the ten ranged from 6/4 to 17/9 while the tenth one was 64/10. Two Cyro samples were vaporized slowly at 325 deg C instead of 550 deg C. These had Th/U ratios of 5/5 and 39/2.

Six pieces of polycast material were treated similarly. Values ranged from 3.5/1.2 to 5.8/2.8 with one sample at 12/4.5 ppt.

In addition, 15.54 kg of stores acrylic had a Th/U ratio of 2.5/0.9 similar to the alpha counting result of 2.8/1. A slow vaporization of stores material was much higher i.e. 10/3 ppt.

It would appear that looking at 1 kg samples inhomogenities of the order of 2 to 3 are common in this Cyro and Polycast material. More information is required to determine if the differences between the slow and fast vaporizations are significant indicating that we are losing Th in the vaporization.

4) Fowler: Chemical separation of Pa and Np at LANL. Hard copy in the mail.

Mac reported on his chemical procedure of preparing irradiated acrylic samples for gamma counting. The 3.5 g samples are irradiated in a fluence of 2.4 x 10(17) n/cm2, tracers are added, the acrylic is volatilized under vacuum, fumed with HClO4/HNO3 and then with HCl. Additional chemistry is performed, and the solution is passed through an anion exchange column. The Pa and Np fractions are separated for gamma counting in a well Ge detector.

5) Wihelmy: RNAA results from LANL.

Jerry reported on results from LANL. Initially chemical separation was not performed on two samples of Reynolds acrylic. Values of 26 +-6 and 21+-2 ppt were obtained. After chemistry the first sample measured 15 +-4 ppt. The second sample was cleaned in ultra pure HCl/HF and then counted to give 4 +-2 which suggests surface contamination.

A sample of Polycast material from CRNL, after chemistry gave 0.9 +-1.4 ppt for Th and 0.09 +-0.15 ppt for U.

Samples of Swedlow acrylic came in at 19, 16, 93 and 11 +-3 ppt Th and 15 and 11 ppt U.

6) Jagam: Correlation of acrylic contaminations.

Jagam reported on measurements of various metals in acrylic from NAA. There was no correlation from supplier to supplier, indicating that the sources of contamination are varied. It would appear that the Th or U concentrations can not be deduced from the concentration of some other more easily detected element.

7) Simpson: On acrylic measurements at Guelph.

Recently three samples have been measured at Guelph.

Supplier	Th in ppt	U in ppt	235U (equil nat U)
CYRO #1	23 +-7	58 +-18	1700
Cyro #2	29 +-6	240 +-40	4000
Poly.	15 +-6	1720 +-130	2400

Conclusions:
It would appear that inhomogenities require the perfecting of large volume techniques i.e. vaporization followed by mass spec. or neutron activation.

1) LANL - Get Swedlow to make acrylic with fewest ingredients.
2) CRNL - Distribute Rohm material to LANL and Guelph.
3) CRNL - Compare NAA and TIMS on the same samples.
4) CRNL & Guelph - Improve NAA handling techniques.
5) CRNL - Get and install Ge anti-Compton device.
6) CRNL & LANL - Examine monomer and certain ingredients.
7) ALL - Build up statistically significant data sets.
8) ALL - Check on Pa and Np peaks if no chemistry done on sample.

Acrylic Radioactivity Mass Spectroscopy results at CRNL since the LANL collaboration meeting.

CYRO:

Ten Cyro samples from the same sheet of acrylic were vaporized in three suprasil tubes and the residue analysed for Th and U at CRNL. The tubes containing the residue were washed out with a HCl/HNO3/HF mixture. The backgrounds were from HNO3/HF rinses done after the residue rinse. This procedure was found to be most effective in earlier runs in Dec-89.

The results listed below indicate that at least 90% of the Th and U is removed in the first rinse, that there is still a U contamination problem with the CRNL mass spect. procedure, that the Th content of this Cyro material is too high for SNO and that the concentrations of Th routinely vary by a factor of 3 (from 6 to 18 ppt) with one sample in the set of ten about 10 times higher.

In order to convert the ng numbers to ppt, we have added the 1st bdg number to the acrylic rinse in the case of Th since we are not convinced that the first rinse gets all of the Th but in the U case since we know that we have a U background problem at CRNL we have subtracted the 1st bgd number from the acrylic rinse. This procedure may be introducing a 10% systematic uncertainty into the Th number and possibly a factor of 2 into the U number. For production runs we will want to make the U procedure more reliable.

		Th (ng)	U (ng)	Th/U (ppt)
Jan 10	Tube 6 bdg	2.5	1.7	
	0.685 kg C1K	7.1	6.2	11/6
	Bdg	0.40	1.6	
Jan 15	Bdg	0.02	2.6	
	0.682 kg C1N	5.0	4.3	8/3
	Bdg	0.30	2.3	
Jan 19	Bdg	0.14	1.2	
	0.685 kg C1Q	6.8	3.1	11/4
	Bdg	0.72	0.72	
Jan 25	Bdg	1.3	0.48	
	0.641 kg C1T	9.0	3.2	15/4
	bdg	0.68	0.43	

Jan 10	Tube 7 bdg	0.08	0.84	
	0.682 kg C1L	9.7	2.6	15/2
	Bdg	0.46	1.2	
Jan 16	Bdg	0.23	3.2	
	0.666 kg C1P	4.0	4.2	6/3
	Bdg	0.13	2.2	
Jan 25	Bdg	0.15	0.24	
	0.666 kg C1S	10.5	3.1	16/4
	bdg	0.24	0.22	
Jan 12	Bdg Tube 8	0.07	0.62	
	0.679 kg C1M	43.4	6.6	66/8
	Bdg	1.1	1.0	
Jan 16	Bdg	0.39	2.3	
	0.675 kg C1O	4.3	4.2	8/3
	bdg	0.86	2.3	
Jan 24	bdg	0.14	0.18	
	0.645 kg C1R	10.9	2.5	18/3
	bdg	0.75	0.33	

Polycast Material:

Six samples of Polycast acrylic taken from material recently received from Polycast have been vaporized and checked by TIMS. Polycast shipped us seven pieces and two of these pieces (B1 & B2) were cut into three lots, or panels, each (SB is the central panel, SA & SC the outside panels) and measured. The Th in the 2nd rinse was **added** to the acrylic rinse to get the Th ppt concentration whereas 0.3 ng U bdg was **subtracted** from the U acrylic rinse numbers. The piece with 11.9 ppt Th can from the first panel vaporized and in this case, only, the ID markings on the edge of the panel was not complete washed off before the vaporization. Still I would be surprised if that explained the relatively high value. So as in the case of the 10 Cyro runs above there seems to be one high value out of this set.

		Th (ng)	U (ng)	Th/U (ppt)
Mar 7	Bdg (tube 10)	0.19	0.37	
	1.16 kg P9-B1-SA	13.3	5.6	11.9/4.5
	Bdg	0.56	0.40	
	Bdg	0.22	0.46	

Mar 8	Bdg (tube 11)	0.19	0.44	
	1.21 P9-B1-SB	3.7	2.2	3.5/1.7
	Bdg	0.55	0.23	
	Bdg	0.09	0.28	
Mar 9	Bdg (tube 10)	0.1	0.28	
	1.17 kg P9-B1-SC	5.7	3.6	5.3/2.8
	Bdg	0.45	0.18	
	Bdg	0.05	0.30	
Mar 12	Bdg (tube 11)	0.20	0.36	
	1.18 kg P9-B2-SA	6.2	3.4	5.8/2.6
	Bdg	0.59	0.33	
	Bdg	0.08	0.31	
Mar 13	Bdg (tube 10)	0.15	0.33	
	1.2 kg P9-B2-SB	5.6	1.7	4.9/1.2
	Bdg	0.31	0.35	
	Bdg	0.08	0.45	
Mar 14	Bdg (tube 11)	0.07	0.31	
	1.3 kg P9-B2-SC	4.7	2.5	3.8/1.7
	Bdg	0.20	0.22	
	Bdg	0.07	0.32	
Feb 28	new HF/HNO3	0.14	0.31	
Feb 22	Beaker BDG	0.02	0.06	
Mar 30	20 ml HF/HNO3	0.03	0.34	

DDD Water:

DDD water from the 115 still had not more than 0.1 ppt Th which is inconsistent with the neutron activation results on the same water (> 3 ppt). ????

A second DDD sample was irradiated but upon opening the container the water was absent. The container leaked. Two of three other containers with DDD water also leaked. These containers had been modified to prevent leaking.

		Th (ng)	U (ng)	Th/U (ppt)
Jan 16	16 ml Aqua	0.07	2.2	Th/U
Jan 15	Beaker (acid)	0.22	2.2	
Jan 30	Beaker bdg (acid)	0.21	2.1	
	500 ml DDD in beaker	0.05	2.0	0.1/4
	Beaker bdg (acid)	0.29	2.2	

Alpha Counting:

A quanity of stores acrylic was vaporized for alpha counting. This sample was also checked with TIMS. The two results were consistent. Th/U concentrations 2.5/0.86 ppt for the TIMS and 2.8/1 ppt for the alpha counting.

In addition, 1.27 kg was vaporized slowly at 325 C instead of 550 C these took 24 hours whereas at 550 C it would have taken only 3 hours.

		Th (ng)	U (ng)	Th/U (ppt)
Feb 23	6% of 15.54 kg	2.2	0.76	2.5/0.86
Tube 2	Bdg	3.7	1.2	
	Bdg	2.1	0.6	
Stores	94% of 15.54 kg alpha counting			2.8/1
Mar 23	Bdg (tube 7)	0.14	0.26	
Slow burn	1.27 kg Stores	10.3	2.9	8.4/2.0
	Bdg	0.39	0.43	
Late Mar	T-6 Tube bdg	0.21	0.17	
Late Mar	T-8 Tube bdg	0.07	0.14	

RNAA & TIMS comparison:

Irradiated samples gamma counted at CRNL and at Queen's were vaporized and measured by TIMS.

		Th (ng)	U (ng)	Th/U (ppt)
Feb 20	Bdg(acid)	0.07	5.7?	
T-7	Bdg	0.06	0.6	
	Acrylic irrad. #1	0.48	1.3	
	Bdg	0.29	0.37	
	Bdg	0.51	0.36	
Mar 9	Bdg	0.07	0.49	
	Acrylic irrad. #2	0.91	0.75	
	Bdg	0.07	0.24	
	Bdg	0.07	0.42	

Total Th in acrylic from TIMS 2.2 ng. cf Edwards claims from Pa 233 counting
8.9+-1.6 ng or 237 ppt.

Slow burn on Cyro material.

Since the difference between the RNAA and TIMS on the same material suggested that we might have lost some Th in the vaporization we did several slow vaporization on two cyro samples. These were from the same sheet as the earlier set of 10 runs where the results were 6-17 ppt Th except for one at 64 ppt. The slow burn takes 4 hours for 200 g at 325 C as compared to the fast burn of 0.5 hours for 200 gms at 550 C. The results are consistent with the 10 fast burn results. There was an additional slow burn of stores acrylic which came in at three times the fast burn work. The U does not seem to vary as much. More work is required to check this slow vs fast burn So it would seem the the jury is still out on whether or not we are losing Th during the burn phase.

			Th (ng)	U (ng)	Th/U (ppt)
Apr 6	C1U	Bdg	0.07	0.22	
T-6	0.863 kg	Cyro	4.1	4.7	5.1/5.4
		Bdg	0.34	0.19	
		Bdg	0.08	0.21	
Apr 11	C1V	Bdg	0.57	0.22	
T-6	0.875 kg	Cyro	32.3	2.1	38.5/2.4
		Bdg	1.4	0.14	
		Bdg	0.24	0.27	

Work in Progress:

Several liters of Polycast monomer with inhibitor from various collection points along their production line have been shipped to CRNL for mass spec. It addition, several samples of just monomer have arrived and one of them has been irradiated but there is no result yet. Bottles have been sent to Swedlow for monomer.

A sheet of Rohm material has arrived at CRNL. Ten kgs or 1/3 has been cut up for mass spect. and neutron activation. We will do 6 or so samples with fast and slow burns.

Cyro & Polycast acrylic sent to Jagam and several pieces of Polycast sent to LANL.

A quanity of Cyro acrylic has been laser cut at NRC for RNAA.

A piece of Swedlow whitened is on hand for RNAA. This has Pb in it and is 0.05% of acrylic.

Evidence for a Heterogeneous Distribution of Thorium in Acrylic

E.T.H. Clifford, H.W. Lee, and W.J. Edwards

April 16, 1990

1 Introduction

This report describes a measurement of the thorium concentration in acrylic by the method of neutron activation. Heterogeneity of the thorium distribution was studied by subdividing the sample *after* irradiation.

2 Method

A 36.7 g sample of "P2" acrylic (Polycast) was placed in a polyethylene bottle which was sealed by passing hot nitrogen gas around the lid of the container. A thorium and uranium standard was prepared by placing standard solutions in a supricil quartz apoule, evaporating them to dryness, and then flame sealing the ampoule. The ampoule was then placed in a hole in the polyethylene bottle and sealed there. The standard contained 1.4668μg of uranium and 1.5584μg of thorium.

The bottle was irradiated for 6 hours in the NRU reactor at Chalk River. The polyethylene bottle was cut open and the acrylic removed for counting. After irradiation the acrylic has swelled in volume, and has broken up into a coarse powder. The standard was removed from the bottle and dissolved in aqueous solution to provide a gamma ray counting standard.

The sample was counted at Queen's University using a Compton-suppressed germanium detector. The whole sample was counted several times and then it was divided into subsamples which were counted individually to search for evidence of a non-uniform distribution of the γ-ray activity. The masses of the subsamples are given in Table 1.

Finally, the sample was returned to Chalk River for analysis by mass spectrometry. Each of two sub-samples, of known radioactivity, was pyrolysed in a nitrogen atmosphere in a supricil quartz tube that subsequently was washed with aqueous solutions of HNO_3, HCl and HF. These solutions were then analysed for thorium (and uranium) content.

Table 1: Thorium Content of Acrylic Samples

Run	Sample	Counts	Time min.	Mass g	Rate s^{-1}	Std. rate s^{-1}	Thorium mass (ng)	Th Concentration $\times 10^{-12}$
4	ALL	2374 ±75	818.	36.7	2.90 ±0.09	572.	7.91 ±0.25	215.±7.
7	ALL	1188 ±41	733.	36.7	1.62 ±0.06	422.	5.99 ±0.21	163.±6.
8	A	1392 ±42	720.	20.02	1.93 ±0.06	422.	7.14 ±0.21	357.±11.
9	B	244 ±23	720.	16.44	0.34 ±0.03	422.	1.25 ±0.12	76.±7.
13	A1	521 ±31	708.	9.69	0.74 ±0.04	422.	2.72 ±0.16	280.±17.
14	A2	68 ±19	471.	10.33	0.14 ±0.04	422.	0.533 ±0.15	52.±15.
16	B	159 ±26	798.	16.44	0.20 ±0.03	422.	0.736 ±0.12	45.±7.
19	A1	261 ±26	638.	9.69	0.41 ±0.04	329.	1.94 ±0.19	200.±20.
21	A1a	345 ±26	543.	5.15	0.64 ±0.05	329.	3.01 ±0.23	585.±44.
24	A1b	281 ±26	541.	5.02	0.52 ±0.05	290.	2.79 ±0.26	557.±51.
26	B	140 ±25	564.	16.44	0.25 ±0.04	290.	1.33 ±0.24	81.±14.
29	A1a	586 ±38	950.	5.15	0.62 ±0.04	290.	3.32 ±0.21	644.±41.
31	A1a+A1b	657 ±34	590.	5.02	1.11 ±0.06	290.	5.98 ±0.31	588.±31.
33	B	297 ±35	790.	16.44	0.38 ±0.04	290.	2.02 ±0.24	123.±15.

3 Results

The results of the γ-ray counting are shown in Table 1. The sample labelling is as follows: ALL indicates the full sample; this was divided into subsamples A and B; subsample A was divided into A1 and A2; A1 was divided into A1a and A1b. "Std. rate" indicates the count rate of the standard source. Most of the samples have had repeated measurements, as shown in the table.

The thorium mass, determined for each sample, is given again in Table 2, where each column corresponds to set of measurements done at the same time. Unbracketed numbers indicate independent measurements. Numbers in parentheses () have been deduced. Some measurements are shown more than once in the table, in which case the repeated value appears in square brackets []. The errors indicated are statistical only. It can be seen that some of the measurements do not repeat well, and this is probably due to geometrical efficiency problems. In particular, the measurements for samples A1a + A1b $\equiv$ A1, in columns 3 and 4, show less thorium than either of the constituent samples, A1a and A1b. With the exception of these two columns, the overall agreement between measurements is not too bad, and gives an average of 7.7±0.5 ng. An independent measurement of the total sample at CRNL gave 8.9±1.6 ng which is in agreement.

4 Discussion

The last column of Table 1 shows large variations in the thorium concentration from one sample to another. This variation is independent of such variables as the standard, handling of the samples, and the neutron flux. The division into subsamples, in effect, took place inside the sealed container during the neutron irradiation, (*i.e.*, it was during the irradiation that the sample fractured into a powder). After irradiation there is no more production of ^{233}Pa, and so contamination of the samples after the container has been opened is unlikely.

Table 2: Thorium content (ng)

	1	2	3	4	5	6	7
A1a	3.0±.2	3.3±.2					
A1b	2.8±.4	(2.7±.4)					
A1a+A1b	(5.8±.3)	6.0±.3	2.7±.2	1.9±.2			
A2	[0.5±.2]	[0.5±.2]	0.5±.2	[0.5±.2]			
A1+A2	(6.3±.4)	(6.5±.4)	3.2±.3	(2.4±.3)	7.1±.4		
B	1.3±.2	2.0±.2	0.7±.1		1.3±.1		
A+B	(7.6±.5)	(8.5±.4)	(3.9±.3)		(8.4±.4)	7.9±.2	6.0±.2

Many of the measurements of acrylic that have been made in the past have shown large fluctuatations from sample to sample, and it has been difficult to show that the variations were due to the material rather than due to contaminations, or problems with procedure. The results of the present experiment point to heterogeneity as a plausible reason for the fluctuations.

5 Conclusions

Variations in the local concentration of thorium in acrylic have been found to range over a factor of 6 within a 37g sample. This is strong evidence that thorium has a heterogeneous distribution in acrylic.

April, 1990

Alpha Spectrometric Report, SNO

In addition to carrying out further analyses for direct comparison of alpha spectrometric and mass spectrometric measurements, my work in the past quarter has concentrated on improving the reproducibility of radium recovery and counting efficiency.

A full elemental analysis by neutron activation of 395 grams of acrylic, performed at Guelph in 1988 but only recently brought to my attention, has indicated that Ba may exceed Ca in this material by a factor of 6. Even if a large error is assumed, this is still a most surprising discovery given the usual ratio of these two elements in nature. The likelihoood of ^{226}Ra contamination in excess of its parent ^{238}U is consequently much enlarged. A recent analysis by myself of spec-pure BaCO$_3$ has shown this compound to contain as much as 0.13 dpm ^{226}Ra/100 μg. This information puts a considerably higher priority on obtaining reliable Ra data.

Several analyses of spiked acrylic have been performed in such a way as to identify the procedures causing substantial losses.

A. Purification

1) Ignition Tube washout and removal of uranium and thorium on anion exchange resins......total loss <5%

2) Separation from interfering ions remaining in solution:
   i) Coprecipitation with BaSO$_4$

If substantial amounts of barium are present in the sample, then a coprecipitation step will provide the necessary decontamination from other elements in solution. Tests with 100-200 μg Ba carrier showed good reproducibility of radium recovery (~90%). Unfortunately in order to obtain good energy resolution , Sill (1987) has recommended that no more than 100 μg of Ba be present: quantities in excess of 400 μg would be considerably too large for good source preparation.

   ii) Uptake of Ra on MnO$_2$-coated beads.

This procedure is considered to be highly specific for radium in the presence of Na, Ca, etc in seawater concentrations. However recent tests using 100-200 μg Ba and ^{133}Ba tracer have shown that uder the conditions chosen (very low ionic strength, pH>7 and 4 hour contact time) barium is also strongly adsorbed by the beads and/or the test tube walls. Since losses of radium during this step were averaging ~35%. and Ra -

Ba separation was slight, this procedural step is of little benefit.

iii) Cation Exchange Separation

Since Ba and Ra are very closely related in the periodic table, any procedure designed to separate these 2 elements quantitatively should provide adequate decontamination from the remainder of the residue. The cation exchange step already in place in our radium procedure has been given further study to optimize this separation. Column size was increased somewhat to handle potentially larger quantities of Ba than previously anticipated, and trial runs were carried out using ^{133}Ba tracer. The best conditions determined to date are as follows: the sample is dissolved in 0.01M NaEDTA at pH 6.4, and transferred to a column already prepared in that form. Ba is eluted at pH 8.5, and NaEDTA is washed from the column with 0.5M HCl until no residue remains in the dried effluent. Ra is subsequently eluted in a small volume of 3M HNO_3. Recovery of Ra through this step has averaged 82%.

Average recovery through 2 anion and 1 cation exchange separations..............77%

B.Source Preparation

i) Precipitated Ba(Ra)SO_4, mounted on a 0.1 micron filter.

These sources show good peak resolution, though losses due to self absorption reduce counting efficiency to ~ 25%. However a much more serious consideration is the substantial increase in background introduced by the Tuffryn filters used. despite overnight soaking in dilute acid (0.024 dpm in the region of interest). Other possible filters should be investigated. though the anticipated variability in barium from sample to sample makes this procedure less attractive as a routine method.

ii) Dried Source Preparation

While it is possible to prepare an almost massless source by drying a tracer solution directly on a counting disc, it seems to be extremely difficult to do so once the solution has been transferred from one container to another, even in a Class 100 fumehood. This situation is further compounded by passing the acid solution through a small cation exchange column immediately prior to source preparation. Consequently some energy degradation seems inevitable. However by flaming the disc following drying, it is possible to achieve a counting efficiency of 26% on a routine basis.

iii) Electroplating

This technique provides an excellent source, with very good peak resolution and correspondingly small background correction. Unfortunately recoveries have proved to be extremely sensitive to the presence of other ions in solution. However I have recently found that repeated refluxing of the final column eluate with HNO_3-H_2O_2 has sharply reduced this problem, and further improvement beyond the 65% plating yields recently obtained are anticipated.

In summary, then, recent recoveries for a full separation procedure: a) -obtained with dried source..........77%
(counting efficiency 26%)

b) -obtained with electroplated source.. 49%
(counting efficiency 30%)

Recent Results

The last two large samples vapourized have been subdivided, following ignition tube washout, with approximately 95% being used for alpha spectrometric measurement, and 5% used for mass spectrometry. Agreement in both cases has been well within 2σ error.

Supplier	TIMS ($pg.g^{-1}$)		ALPHA SPEC. ($pg.g^{-1}$)	
	Th	U	Th	U
CY/RO	4.7	8.3	(232)7.0±1.0	(238)6.7±.79 (234)
			(228)6.0±1.0	(230)0.5±.15
				(226)0.22±.22
Stores	2.8	0.98	(232)3.2±.53	(238)0.71±.17
				(234)2.0±.28
			(228)3.0±.49	(230)0.38±.09
				(226)0.82±.29

Report on INAA of Acrylic

27/4/90

Physics Department, University of Guelph

A number of samples of acrylic have been neutron activated in McMaster University's reactor. Nine samples of Rohm and Haas, Canada, acrylic were cut from different places on a single sheet 3/4" thick. This acrylic had paper on two sides. After cutting to size they were cleaned in alcohol. In addition, pieces of acrylic from Polycast (P2) and Cyro, supplied by Ted Clifford, were irradiated in a second irradiation. Irradiations generally last for two hours at a flux of about 10^{13} n/cm^2-s. The samples are sealed in aluminum canisters containing a small piece of $A\ell$ foil as the flux monitor. The $A\ell$ foil has been standardized for its Th and U content by comparison with geological rock standards. The $A\ell$ foil is found to be constant in Th and U to at least 10%.

Results

Table 1 shows the results for Th in the Rohm and Haas samples, and a few results for U. (The Np had decayed away in many samples before we could count them.) The results for Th are fairly constant, with two, apparently high samples, no's 3 and 5. An interesting correlation occurs, however, when we plot the total spectrum count rate of the sample (all have approximately the same weight, 8 to 9 gms.) versus the time at which it was counted, fig. 1. It is clear from this figure that sample #3 contains an excess of a long-lived element. An examination of the spectrum shows that it contains large excess of ^{59}Fe (x23) ^{60}Co (x20), and ^{65}Zn (x7) compared to the other acrylics. If we leave this sample out, then the average Th level in this acrylic is 31 ± 4 pg/g, with a χ^2 of 9.4 for 7 degrees of freedom, an acceptable fit. However we do not know whether the contamination observed in no. 3 is picked up from our laboratory or indicates inhomogeneities in the acrylic. We have examined the relative intensities of the ^{51}Cr, ^{59}Fe, ^{60}Co and ^{65}Zn lines in the $A\ell$ foils and it is clear that we are not contaminating the sample with aluminum.

Table 2 gives the results for P2 and two Cyro samples, as reported in Sudbury. The cause of the high U in P2 is not known. It is hard to see how it could have been contaminated in our laboratory since we do not use uranium.

We are still investigating the anomalous fission products, in particular ^{132}Te, seen in the samples. We will report on this later.

J.J. Simpson.

P. Jagam.

Table 1

Rohm and Haas (Canada) Acrylic

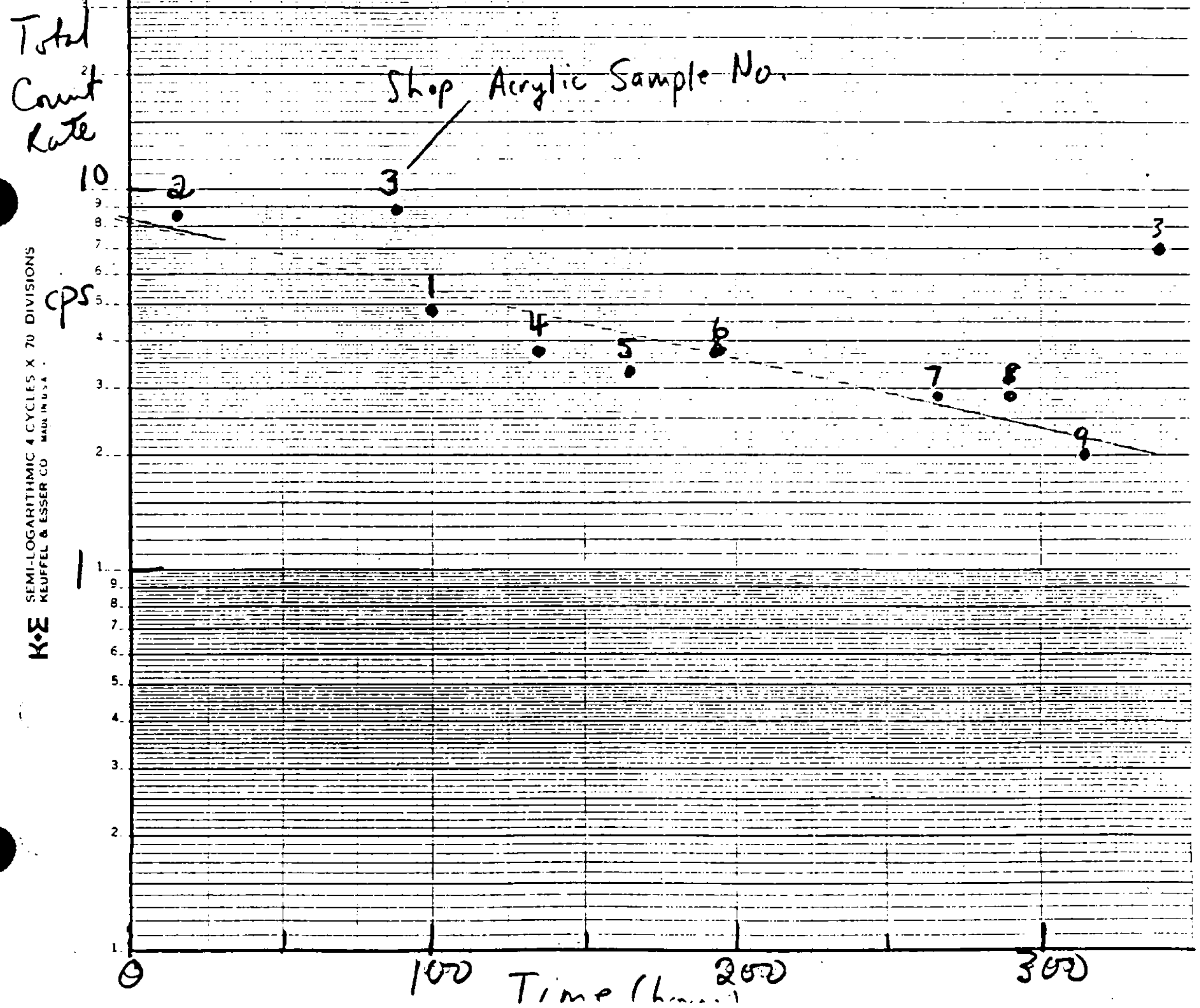
Sample no.	Th (pg/g)	U
1	54 ± 18	44 ± 16
2	33 ± 14	< 27
3	139 ± 43	74 ± 54
4	27 ± 9	< 100
5	74 ± 18	
6	28 ± 13	
7	34 ± 15	
8	18 ± 10	
9	26 ± 11	
Average (omitting #3)	31 ± 4	
	$\chi^2 = 9.40/7$	

Table 2

Acrylic

Sample	Th (pg/g)	U (pg/g)
P2	15 ± 6	1720 ± 130
Cyro #1	23 ± 7	58 ± 18
Cyro #2	29 ± 6	240 ± 40

Total Spectrum Counting Rate in Rohm & Haas' Acrylic, vs Time of Counting



Chemical Processing of Acrylic Samples for U and Th + Determination.

M. M. Fowler and J. B. Willhelmy
Group INC-11, Mail Stop J514
Los Alamos National Laboratory

Neutron Irradiation of the Acrylic Samples.

Samples of acrylic are machined, using either tungsten carbide or high speed steel cutting bits, so that they will fit into plastic pneumatic carriers. The finished samples are about 1 cm diam. by 3 cm long and weigh about 3.5 g. The samples are ultrasonically washed with HCl, HF, and water prior to insertion into the plastic carriers. Irradiations are made using the INC-5 Omega West reactor which has a neutron flux of about $1\text{x}10^{13}$ n/cm^2/s. The total irradiation fluence is typically $2.4\text{x}10^{17}$ n/cm^2.

Volatilization of the Acrylic.

After irradiation, the samples are taken out of the plastic carrier and placed in a volatilization tube along with ^{231}Pa and ^{235}Np for chemical yield determination. The volatilization tube, 25 mm diam. by 75 mm long, has a 12 mm diam. connection tube 100 mm long terminating in a 14/35 standard taper joint. The tube is connected, through a glass trap cooled in liquid nitrogen, to a vacuum pump. The system is evacuated to less than 0.01 torr and the tube is heated in a small furnace. Initially the temperature is held at 200-220 °C. until the sample melts and quits degassing. During this period the pressure will often increase to greater than 1 torr. When the pressure again drops to less than 0.05 torr, the temperature is the gradually raised to 400-420 ° + C. as the acrylic distills away. This process takes about 3-4 hrs and depends somewhat on the type of acrylic sample. At the end of the volatilization the tube is cooled to room temperature while still under vacuum. In most cases, there is only a small amount of carbonaceous material left in the tube. The tube is removed from the trap then the joint and upper end of the connection tube are cleaned to remove vacuum grease and any soluble high boiling material that may have condensed near the joint.

Digestion of the Residue.

Next 0.5 mℓ of conc. HNO_3 and 0.5 mℓ of conc. $HClO_4$ are added + to the tube. The tube is then heated to boil the acid mixture. More nitric acid is added as it distills from the tube. After most of the carbon is washed from the walls the last of the nitric acid is distilled off and the perchloric acid destroys the carbon yielding a pale green clear solution. The perchloric acid is the distilled down to near dryness, 0.5 mℓ nitric acid is added and distilled off to near dryness. Next 1 mℓ of conc. HCl is added and + distilled off. This is repeated until no more NO_2/N_2O_4 fumes are evolved. The solution is then transferred along with 1 mg of Fe^{+3} to a centrifuge tube and $Fe(OH)_3$ is precipitated with conc. NH_4OH. The $Fe(OH)_3$, carrying the Np and Pa activities, is centrifuged down and the supernant is discarded. The precipitate is then dissolved in conc. HCl, reprecipitated with conc. NH_4OH, and centrifuged. Again the supernant is discarded and the precipitate is dissolved in 0.5 mℓ conc. HCl.

Ion Exchange Separation of Np and Pa.

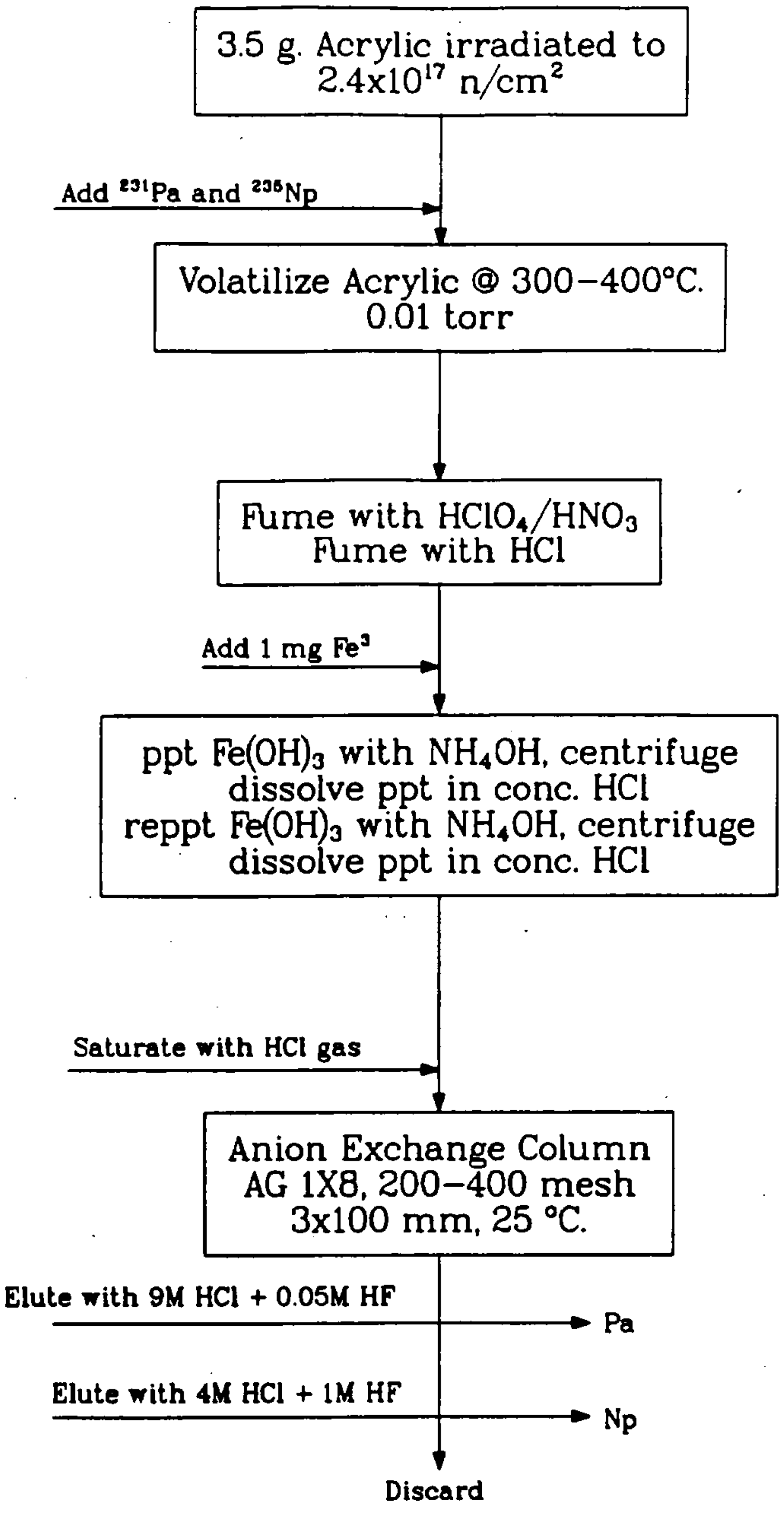
^{239}Np and ^{233}Pa are separated on a small column with AG 1X8 anion exchange resin (200-400 mesh). The column is a plastic tube 3.5 mm diam. and + 100 mm long that holds 1 cm^3 of resin. The column is pretreated with water then with 3 m +*ell* of conc. HCl. The solution from the digestion step is saturated with HCl gas the transferred to the column with 4 washes of 0.5 mℓ of conc. HCl. The Pa activity is eluted from the column with 3 mℓ of 9M HCl that contains 0.05M + HF. After the Pa is collected, the Np activity is eluted with 2 mℓ of 4M HCl containing 1M HF. Both the Pa and Np are collected directly in small counting vials. The chemical yield has been improving with time and is now about 70% for both Np and Pa.

Counting of the Np and Pa Activities.

The activities are measured with a well type intrinsic Ge detector. The detector is made with low background components and has a NaI(Tl) compton suppression shield. The background of the detector is about 3 c/hr/keV at 300 keV. With our sample sise and irradiation conditions, 1 ppt of U in the acrylic gives a counting rate of 10.7 c/h while 1 ppt of Th gives a counting rate of 1.7 c/h assuming unity chemical yields.

In our irradiation conditions, with a poor cadmium ratio, the formation cross section for ^{233}Pa is about 9 barns while that for ^{239}Np is about 13 barns. Both of these effective cross sections are quite a bit larger than for the (n,γ) reactions with thermal neutrons. (7.4 & 2.7 b)

The Th is estimated from the intensity of the 312 keV transition associated with the decay of ^{233}Pa and the U concentration comes from the intensity of the 228 keV transition in the decay of ^{239}Np.


3.5 g. Acrylic irradiated to
2.4x10^{17} n/cm^2
Add ^{231}Pa and ^{236}Np
Volatilize Acrylic @ 300–400°C.
0.01 torr
Fume with $HClO_4/HNO_3$
Fume with HCl
Add 1 mg Fe^3
ppt $Fe(OH)_3$ with NH_4OH, centrifuge
dissolve ppt in conc. HCl
reppt $Fe(OH)_3$ with NH_4OH, centrifuge
dissolve ppt in conc. HCl
Saturate with HCl gas
Anion Exchange Column
AG 1X8, 200–400 mesh
3x100 mm, 25 °C.
Elute with 9M HCl + 0.05M HF
Pa
Elute with 4M HCl + 1M HF
Np
Discard

		Th (ppt)		U (ppt)		
		count	chem	count	chem	
Reynolds	①	26 ± 6	15 ± 4			(noted a geometry effect here)
	②	21 ± 2				– before going in reactor clean ultra in DDD.
		(4 ± 2)				irradiated sampled cleaned with ultra pure HCl/HF
Polycast.			0.9 ± 1.4		0.09 ± 0.15	
Swedlow.	Ⓐ		19 ± 3			
	Ⓑ		16 ± 4			
	Ⓒ				15 ± 18	
	Ⓓ		93 ± 9			
	Ⓔ		11 ± 3		11 ± 2	
Quartz Suprasil		7 ± 1		3 ± 1		

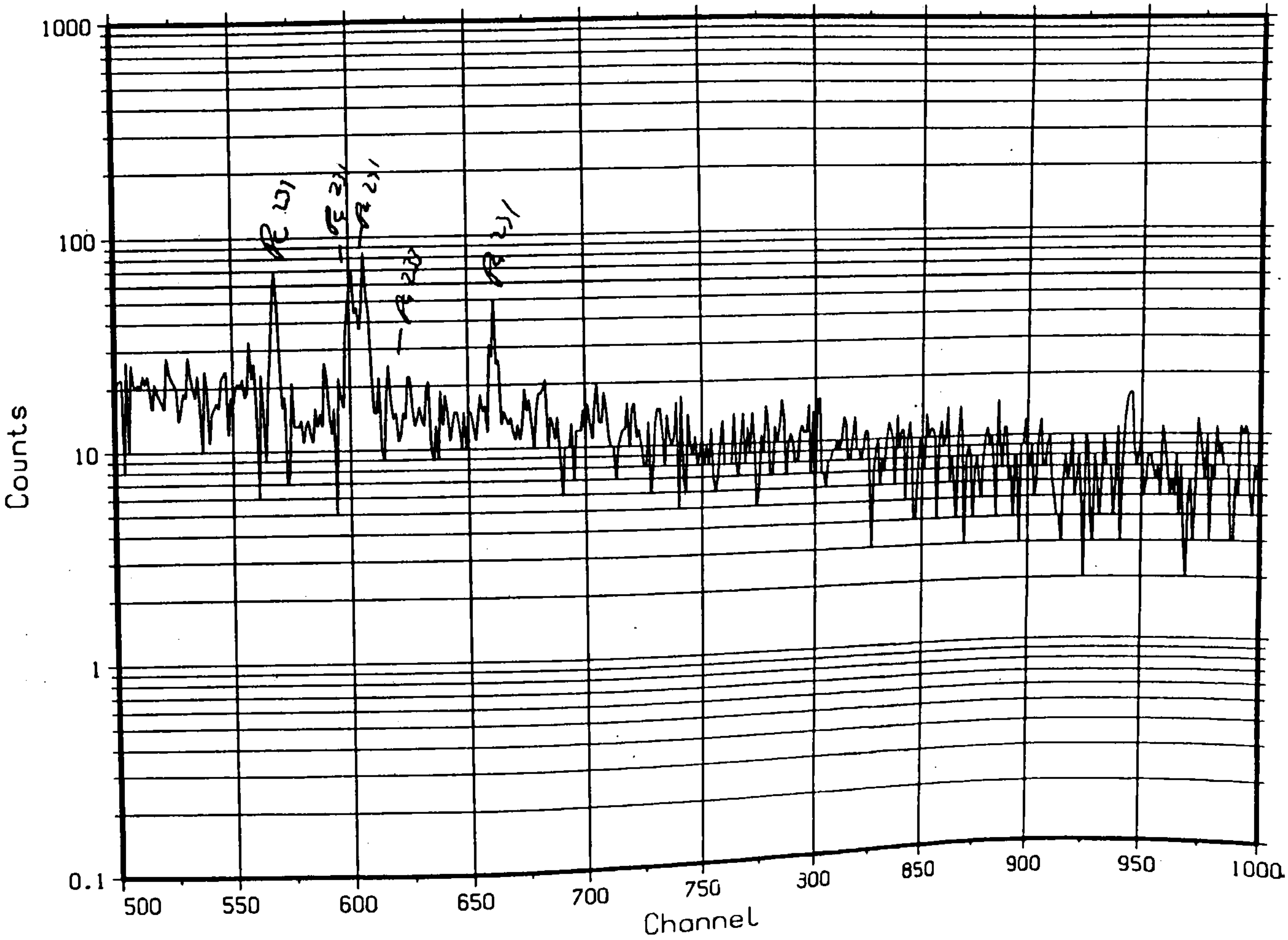
@ t = 0 ; ey = 1 ; 3.8 gm sample ; 7 hr irradiation
(2.4×10^{17} n/cm^2)

for 1 pg/g Th 312 keV U 228 keV
1.7 cts/hr 10.7 cts/hr.

LANL results

Tungsten sample.

Shot:2001 Jug: 1 Mass: [illegible] Counter: 49 ROT: 101.6263
Count-length: 507 mins Zero-time: 99.4806(90)
Start-time: 101.2744(90) Zero: 0.1154 Gain: 0.5002
TAPE: CR-900411.101 SN: 101-056 USER:47



Bkg – 3.3 cts/hrs/keV.

SNO3

	Th pg/g	U pg/g	^{235}U (equiv nat U) pg/g
CY/RO #1	23 ± 7	58 ± 18	1700
CY/RO # 2	29 ± 6	240 ± 40	4000
P2	15 ± 6	1720 ± 130	2400

Guelph measurements
Apri '90

May 4, 1990

Hi Davis:

I thought I should send you an update of our radioactivity efforts. Below is a table of our latest results for samples we have studied. The results are basically the same as presented in Sudbury, but some of the samples were counted for longer times and therefore the statistical errors were improved.

Supplier	ID	Th		U	
		No Chem	Chem	No Chem	Chem
Reynolds	1301	26.2 +/- 5.5	14.8 +/- 3.6		
	2149	21.3 +/- 2.8			
(after acid cleaning		4.5 +/- 2.4)			
	1302	3.4 +/- 2.7			
Polycast	2001		0.8 +/- 0.9		0.09 +/- 0.15
	2002				
Swedlow A	1503		19.2 +/- 3.3		
B	1603		16.8 +/- 2.1		1.7 +/- 0.8
C	1703		26.2 +/- 7.3		2.2 +/- 0.6
D	1802		93.0 +/- 8.7		
E	1901		10.1 +/- 4.8		
	1902		12.1 +/- 2.8		
Suprasil	2301	6.8 +/- 0.9		3.2 +/- 0.9	

A few notes on the table: The Reynolds sample 1302 was the one I told you in Sudbury that we had irradiated and were letting cool before counting. We had hoped to see a reasonable amount of Th and then use this as a certification for our vacuum distillation technique. Unfortunately (for the purposes of this test anyway) the sample was found to have a very low Th content. Before irradiation it was treated with our ultra pure acid, ultrasonic cleaning technique. The first two Reynolds samples were not cleaned in this manner and gave higher values. However, when we cleaned sample 2149 after the irradiation the Th content was greatly reduced (to a value more in line with the new 1302 results). This may mean that the Reynolds samples were not too bad once the surface is treated.

We have now irradiated the second polycast sample you sent me (2002) and I will pick it up from the reactor today and start it counting.

I have been in contact with Swedlow and they will try to make us some minimum ingredient Acrylic. Mac Fowler and I are proposing to go out to Swedlow next week and talk to them about the process. We are trying to develop techniques for analyzing large samples and have talked to some of our plastic people. We have a small amount of 229Th which we would like to use as a tracer in some plastic which we will cast. We are looking into building a larger vacuum evaporation system which will allow us to process several hundred grams at once. We would reflux this evaporator with nitric and perchloric acid to extract the Th. With the traced samples we will be able to determine the recovery yield.

Best regards
Jerry Wilhelmy