Aluminum Contamination of Nickel Tubes Used in NCD Construction

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Introduction

The cylindrical bodies of the NCDs are made from ultra pure nickel. This purity is achieved by depositing from nickel carbonyl vapor onto a 2-inch diameter mandrel. The mandrel is aluminum with an anodized surface. When the desired thickness is achieved, the process is stopped and the system is cooled, allowing the two materials to separate. Imperfections in the anodizing of the mandrel map into raised patches or "splotches" on the inside nickel surface. When separation occurs, some material is also taken from the mandrel, causing the imperfections to worsen. As additional tubes are made on a given mandrel, the surface splotch density increases and the appearance of the tubes deteriorate. Of considerable concern is that that these splotches may be harboring high concentrations of aluminum, a material known to contain thorium at the 1-10 ppm level. Since we require the nickel to be < 10 ppt Th, aluminum becomes a concern at the 1-10 ppm level.

SEM Study

Scanning Electron Microscopy (SEM) reveals the shape and chemical makeup of these splotches. A beam of 20 kV electrons, 60 Angstroms wide, scans across the sample, imaging the surface. The color of the image is an indication of the surface roughness. Flat features are dark and rough features appear as various shades of gray. White typically indicates the boundary of an object. Elemental abundances are determined from the scattered x rays, averaged over a depth of approximately 2 μm.

Fig.1 shows a small area on the inner surface of tube T-180. The left side of the picture shows a badly splotched region, while the right side is relatively free of splotches. A broad 1 mm^2 scan of the clean region revealed the spectra shown in Fig. 2. With this broad scan, no aluminum was detected to within a sensitivity of approximately 0.5%. A broad scan of the splotched region revealed traces of aluminum (not shown) and prompted a closer look at some smaller features.

Figs. 3A and 3B show two close ups. A keen eye should be able to pick these features out of Fig. 1, in the middle of the picture and at the center-bottom. There appear to be

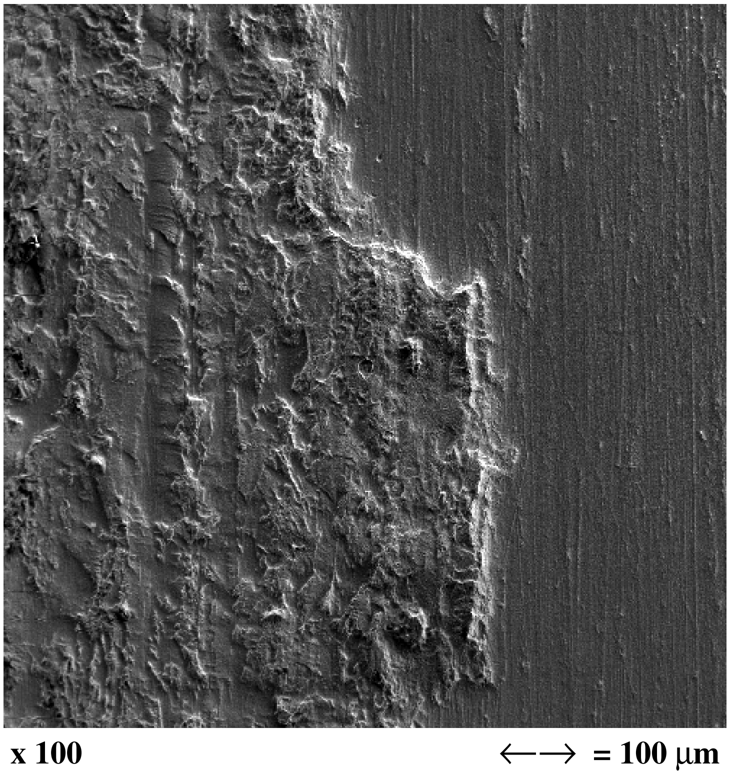


Figure 1: A badly splotched region of tube T-180

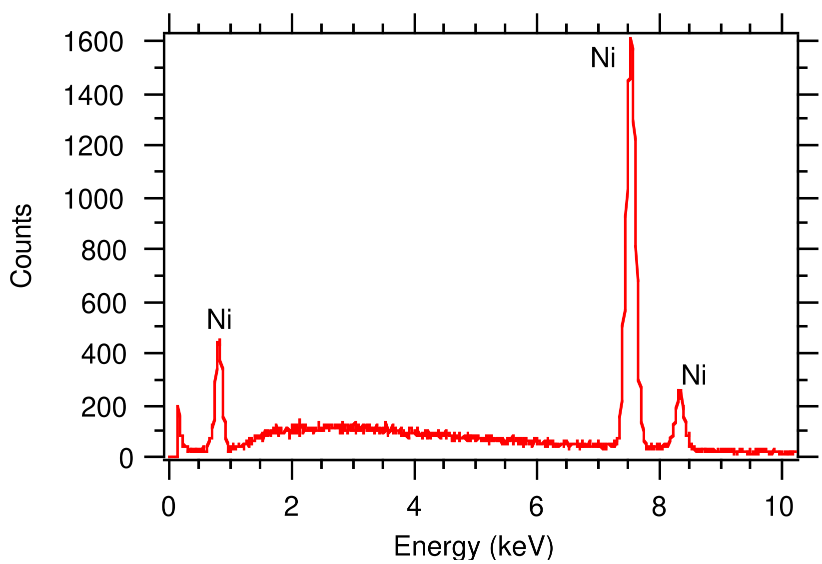
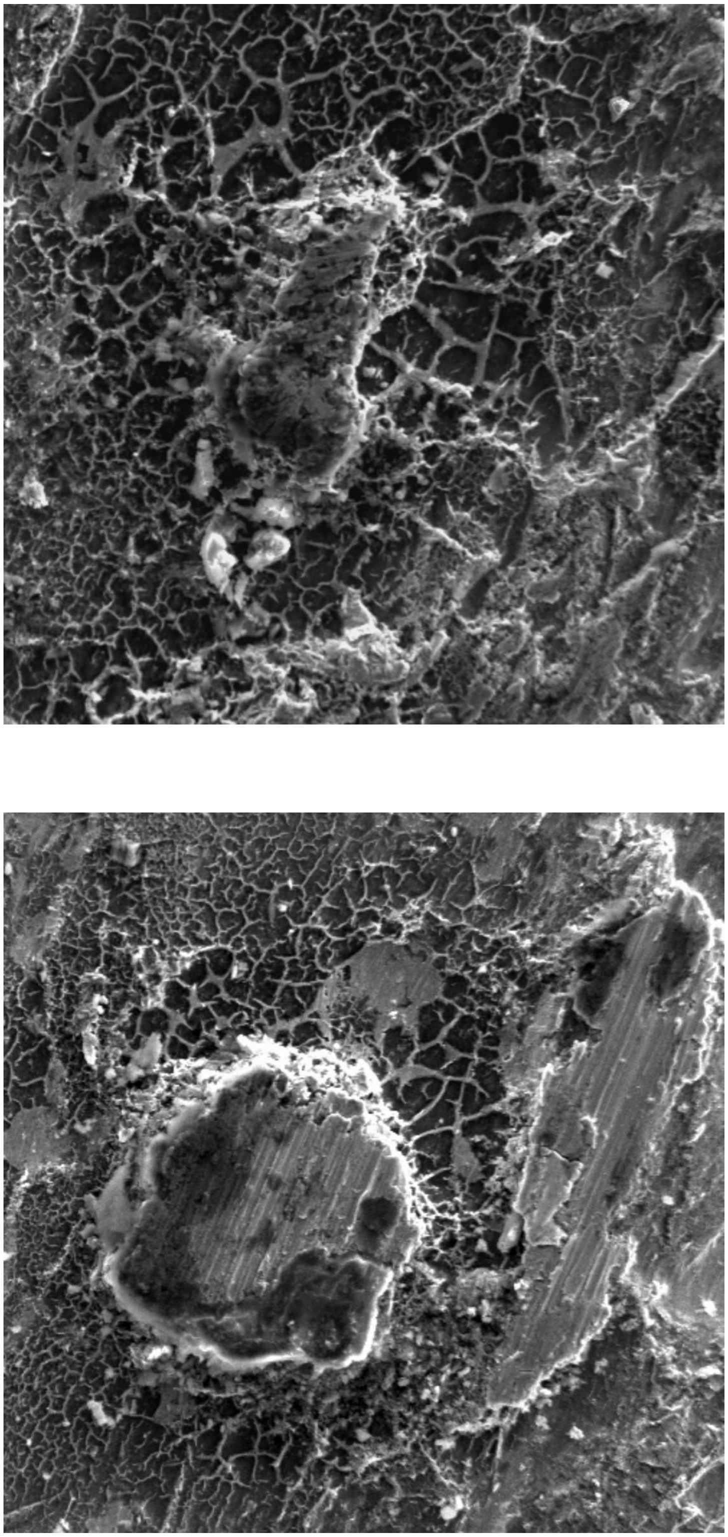


Figure 2: X-ray spectra from a general scan of the clean area of Fig. 1. The nickel K-α, K-β, K-γ peaks are seen on a continuous background.

two materials present, one dark and smooth and the other rough and gray. Elemental abundances for each of these materials were determined by holding the electron beam in place, rather than scanning it.



x 720 ⟷ = 20.00 μm

Figures 3A, 3B: Close ups of Fig. 1

The light gray material of Figs. 3A and 3B proved to have a spectrum identical to that shown in Fig. 2, indicating that it was at least 99.5% nickel. The black material (looks like cracked paint) was also analyzed, giving the spectrum shown in Fig. 4. One sees a significant fraction of aluminum. The visual appearance of this material suggests that it is in fact aluminum oxide (which is expected because the mandrel was anodized). The additional Ni peaks in this spectrum are expected from the surrounding nickel while the trace elements of Si, S, Cl, Ca appear to be associated with the aluminum oxide. One possible explanation for their appearance is the polishing compound used to finish the mandrel.

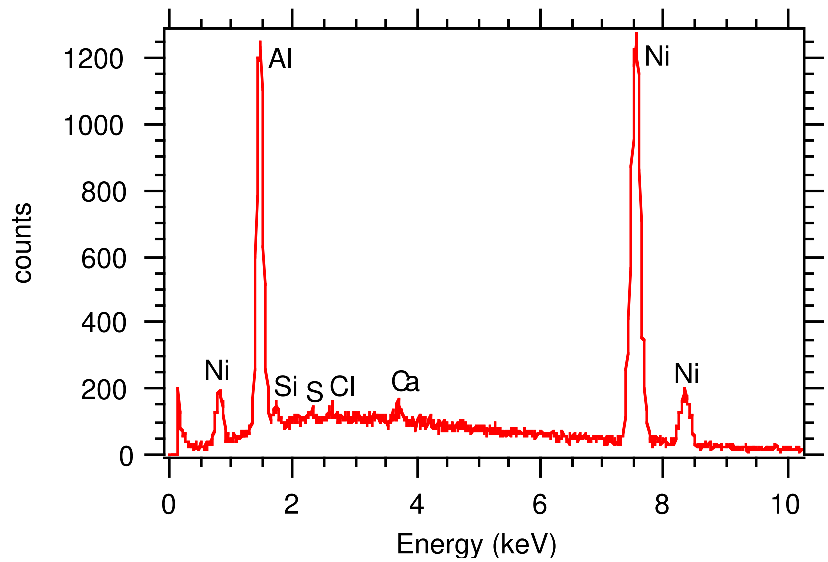


Figure 4: Spectrum from the black "cracked paint" seen in Figs. 3A and 3B.

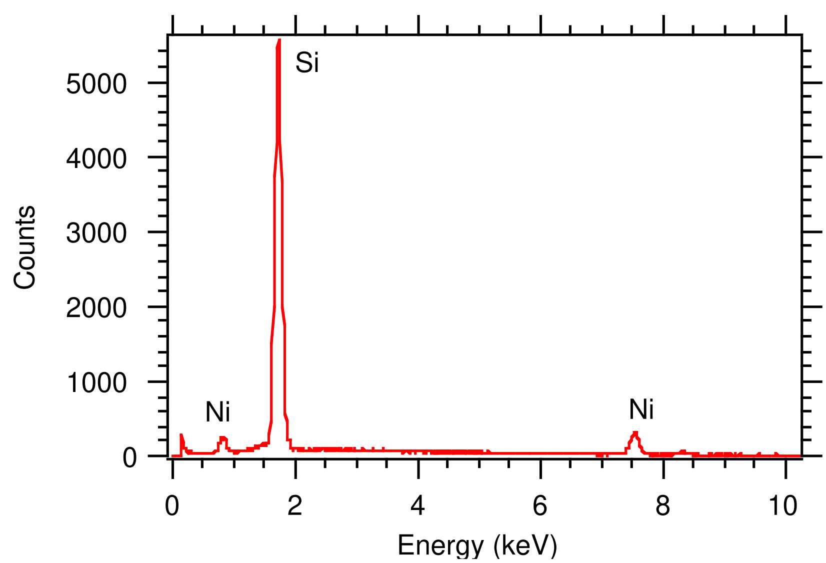
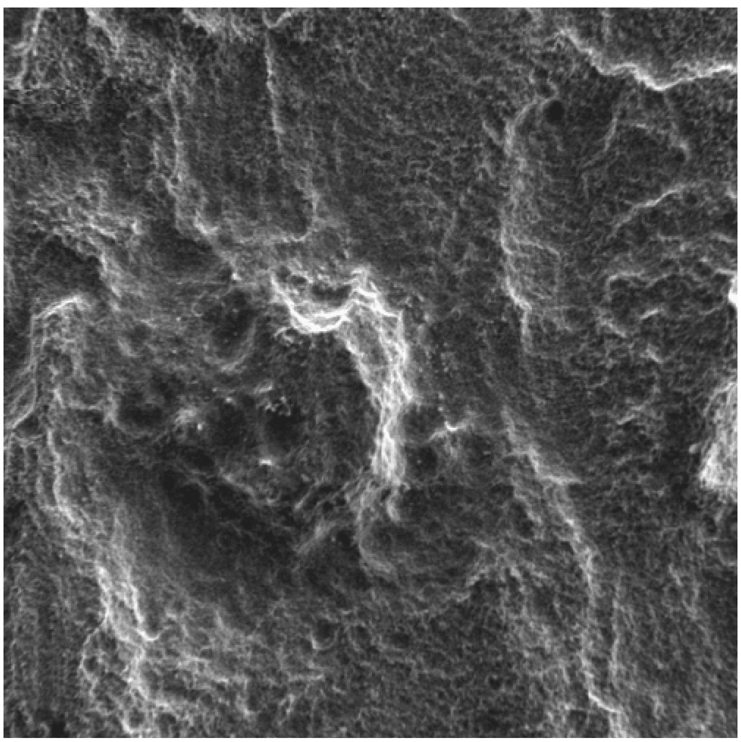


Figure 5: Silicone rich region seen in Fig. 3B

Almost all features had a spectrum similar to Figs. 2 or 4, showing various concentrations of Al and Ni. There was one notable exception. A small dark spot, almost in the center of figure 3B, proved to be rich in silicone (Fig. 5). Again ,this is suspected to be a grain from the polishing compound used on the mandrel. This was not investigated further.

Etching

The section of T-180 under study was subsequently etched for 10 minutes in a solution of 4M nitric, 0.2M HF acid. The various regions were re-imaged with results like that shown below. Figure 6 is a re-image of figure 3B after etching. The sharp features have disappeared and the material appears to be uniform in composition. The spectra showed no signs of aluminum or any material other than nickel.   Note that the sensitivity of the spectral analysis is approximately 0.5%. Thus a more sensitive technique is required to address the issue of aluminum contamination.



x 720 $\longleftrightarrow$ **= 20.00 μm**

Figure 6: Re-image of the region shown in Fig. 3B after etching

ICP Mass Spectrometry

Seeking a higher sensitivity for aluminum, the problem was pursued using Inductively Coupled Plasma Mass Spectroscopy. ICPMS works by vaporizing a fluid sample and drawing it into a plasma torch. After the sample is ionized, it is accelerated and electrostaticly steered, so to identify the various mass components.

Nickel segments, cut from tube T-180, were etched in 4M nitric, 0.2M HF acid baths and the left over solution was analyzed. In principle, one could measure both the aluminum and nickel intensities on the ICPMS, dividing to give their ratio. However, the Al/Ni ratio is typically so small, that one can not be sensitive to aluminum without saturating in the nickel window. A different approach was taken, measuring the nickel content by weighing the nickel samples before and after etching, leaving the ICPMS to be tuned to just aluminum.

Before etching in a particular bath, a sample was drawn from the acid solution. These blanks were subsequently treated identically to post-etch samples and were also counted using the ICPMS, thus measuring the background contamination of the acid solution. In addition, standard solutions were prepared containing known quantities of aluminum. These were run on the ICPMS, giving a measure of the machines response to aluminum and its fluctuations in efficiency, thus allowing errors to be estimated. Further discussion of how these various measurements were analyzed and compared can be found in [1]

The presence of HF acid in the etching solution was a serious complication. HF acid easily leaches aluminum from plastic containers and hence produces a background in the measurements. Also, HF acid was unacceptable for running through the ICPMS as it would attack quartz components in the machine, damaging it and leaching contaminants into the test solution. However, it was necessary to include this acid to accurately simulate the etching solution used in NCD production, where HF acid is used particularly for its properties to disolve aluminum and heavier metals. To solve this problem the etch baths had to be dried down and reconstituted with dilute nitric acid. Further discussion of this technique and the subsequent mitigation of background contamination can also be found in [1].

Table 1 shows a subset of all results. Not shown are results for which the background levels were the major contribution to the signal. The first column is the label that was attached to each bath for identification. Sometimes the same nickel segment was etched in subsequent etch baths, although a number of segments were used to get the full set of results. These various segments were all cut from a heavily splotched region of tube T-180 and their overall surface splotch density varied by about 20% between samples.

Table 1: Results from various etches

Bath	Area of nickel (cm^2)	Etch time (mins)	Mass etched (grams)	depth range (μm) (1 sided)	Average depth (μm)	Al/Ni ratio (ppm) (both sides)
1A	79.3	0-10	0.370	0.0-2.6	1.3	9250 ± 2090
1B	68.5	10-20	0.285	2.6-5.0	3.8	510 ± 120
2A	53.9	0-20	0.498	0.0-5.2	2.6	4320 ± 1170
2B	53.9	20-30	0.250	5.2-7.8	6.5	90 ± 26
2C	53.9	30-40	0.226	7.8-10.2	9.0	70 ± 30
3A	89.4	0-20	0.776	0.0-5.0	2.5	not tested
3B	89.4	20-30	0.450	5.0-7.9	6.4	111 ± 13
3C	89.4	30-40	0.464	7.9-10.8	9.3	31 ± 5

The area of the sample was measured to within a fraction of a percent and the mass etched was measured by weighing the nickel sample before and after, again to within a fraction of a percent. These numbers allow one to calculate how deeply the nickel was etched. Quoted above is the depth etched from a *single* side, assuming that both sides of the sample were etched equally deep. In addition, one can calculate the nickel concentration of each bath after etching by simply dividing the mass etched by the volume of the bath.

Samples from the various etch baths were subsequently dried down, reconstituted, and analyzed for aluminum. Blanks were treated identically. Large uncertainties were introduced by fluctuations in the machine's efficiency. These were measured by including the known standards in the ICPMS run sequence. Smaller but still significant errors arise from the Poisson statistics of counting and these two sources of error were combined in quadrature. The background contamination was measured from the blanks and subtracted from the etch bath results. The additional error that this produces was again added in quadrature.

In the final column, one simply forms a ratio of the aluminum to nickel concentrations, thus getting the Al/Ni ratio by mass. This ratio includes the nickel etched from *both* sides of the nickel segment so that the actual surface contamination is approximately a factor of two higher than the numbers quoted (since we expect the outer nickel surface to be essentially free of aluminum).

These results are also shown in Fig. 7. The vertical error bars are the uncertainties in the Al/Ni ratio. The horizontal bars are not errors but rather represent the range over which the sample was etched.

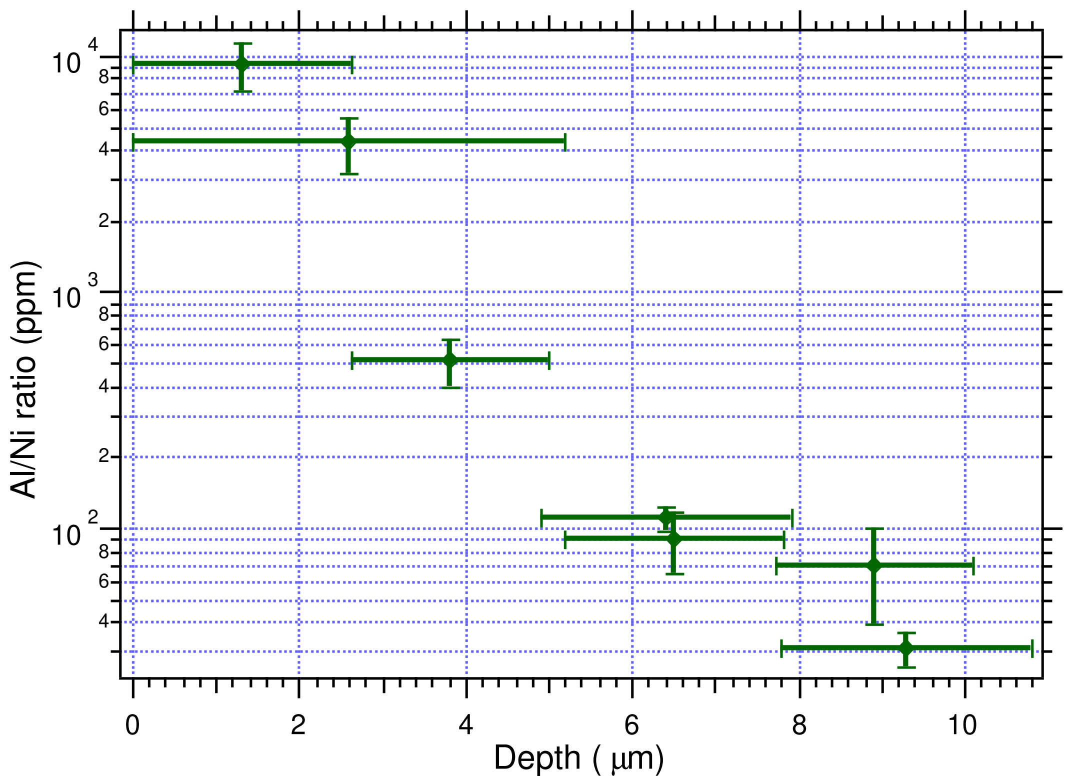


Figure 7: Aluminum contamination as a function of depth

Note: The second point on the graph (bath 2A) is quite different to the other data points. All other results are for 10 minute etches, while bath 2A was a 20 minute etch. In fact, we should expect bath 2A to have approximately half the aluminum content of 1A since it was etched twice as deeply yet received most of its aluminum during the first few minutes of etching. The ratio of results from bath 2A and 1A yields 0.47 ± 0.16, as expected.

Interpretation and Discussion

One immediately sees that the aluminum content falls off with depth; a not particularly surprising result. If one does a linear extrapolation of the last four data points, one finds an intercept of 10.6 ± 2.2 μm as shown in Fig. 8. This result should be taken somewhat loosely, as we have made no argument for a linear fit and the data points do not represent the aluminum contamination at particular depths but rather the integrated contamination over a given depth range.

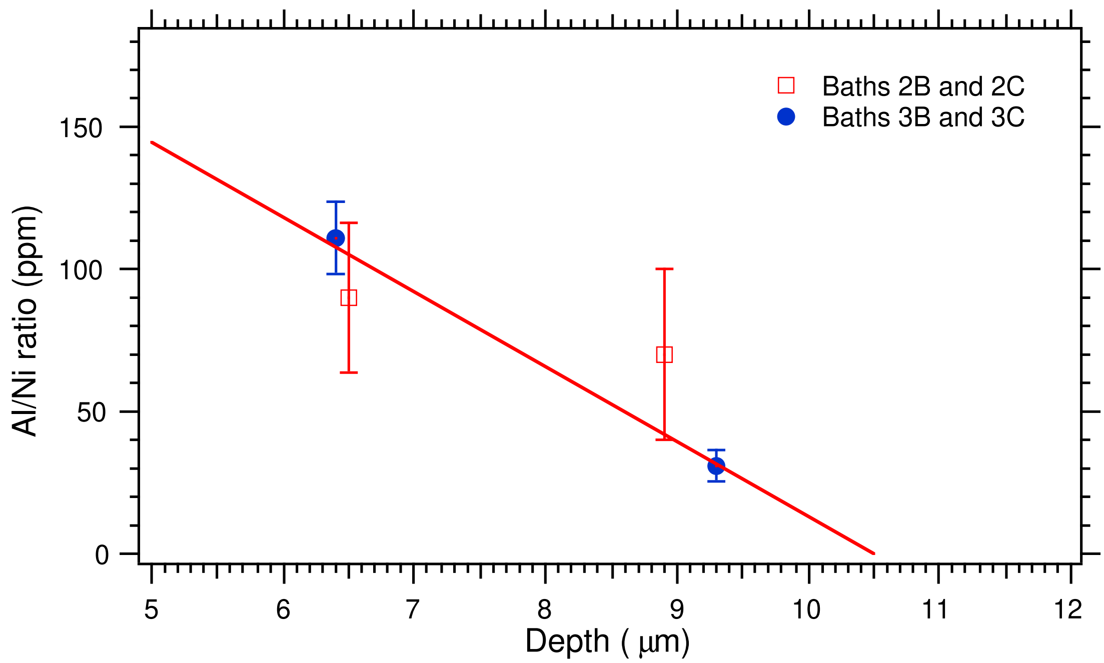


Figure 8: Extrapolation of the last 4 data points

However, this result still proves useful in defining the depth required for mitigating aluminum. Prior to this study, tubes were being etched for only 10 minutes, removing approximately 2 μm of nickel from each side. As a consequence of this work it was decided that significantly more nickel needed to be removed from the inner surface of the tube. A procedure was implemented for electropolishing the inner surface to a depth of approximately 20 μm. This is followed by an etch which removes an additional 2 μm from each side, thus removing a total of approximately 22 μm of material from the inner surface [2], [3].

Even if this linear fit is incorrect, one can still argue that the total aluminum contamination is less than 1 ppm. As the SEM photographs showed, the contamination is in the form of aluminum oxide flakes. Tube T-180 was deposited onto a mandrel that had a 25 μm anodized layer and so one expects the contamination to go no deeper than this. The last data point is 31 ± 5 ppm (at 9 μm). Tubes are typically 15 - 20/1000th inch thick. In a *worst case scenario*, if this contamination extended uniformly all the way to 25 μm and we remove 22 μm from electropolishing and etching, one would get an aluminum contamination of 0.2 - 0.3 ppm, averaged over the entire nickel. This is an extreme upper limit.

We have analyzed small segments of one tube (T-180) and must consider if this is representative of the whole array. Firstly, one should note that these segments were heavily splotched. In general, the splotching on a given tube is localized and typically averages out to be considerably less than that studied here.

Tubes T-172 to T-185 were deposited using the same mandrel. Tubes T-168 to T-171 were deposited onto a mandrel that had a 2.5 μm anodized layer, much less than T-180. All other tubes were deposited onto an anodized layer 38 μm thick [4]. Thus most of the aluminum contamination is by aluminum oxide flakes that are potentially 50% thicker than those studied here. One might then expect that the depth profile of Fig. 7 to scale accordingly. If so, the linear fit to the tail of this profile would extend the contamination to around 16 ± 3 μm. The *worst case scenario* argument would give an upper limit of 0.9 – 1.5 ppm, averaged over the entire nickel.

References

[1] Quantifying the Aluminum Contamination of Nickel Tubes to Be Used In NCD Construction (Internal NCD report), Smith
[2] NCD Electropolish Log book, Elliott *et al*.
[3] NCD Etch Logbook, Elliott *et al*.
[4] Private Communication (from Mirotech to S. Elliott)

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