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Author(s):	Havrilla, George J.
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Preliminary Study of Microfluidic Chip as Sample Containment for Quantitative hiRX Measurements

Kathryn McIntosh and George J. Havrilla
Los Alamos National Laboratory
Los Alamos, NM 87545

Abstract:
This is a preliminary report on the development and testing of a microfluidic sample chip for the hiRX prototype instrument test slated for FY14. We used an in-house manufacturing laser-based tool at LANL. This allowed us to change experimental parameters rapidly and generate desired features as needed. The finished product was not a polished commercial grade specimen; however we were able to make these relatively easily and quite rapidly. The performance of these handmade devices was surprisingly good with about 5% RSD for a 1 microliter sample volume.

Results:
The first efforts in this development involved testing various materials for acid resistance. Since spent fuel solutions are primarily nitric acid, we used both 25% and 75% HNO_3 for testing. A 1 microliter droplet of nitric acid was placed on samples of acrylic polymer, polycarbonate, silicone and Kapton. The only specimen to exhibit any degradation after 24 hours was the

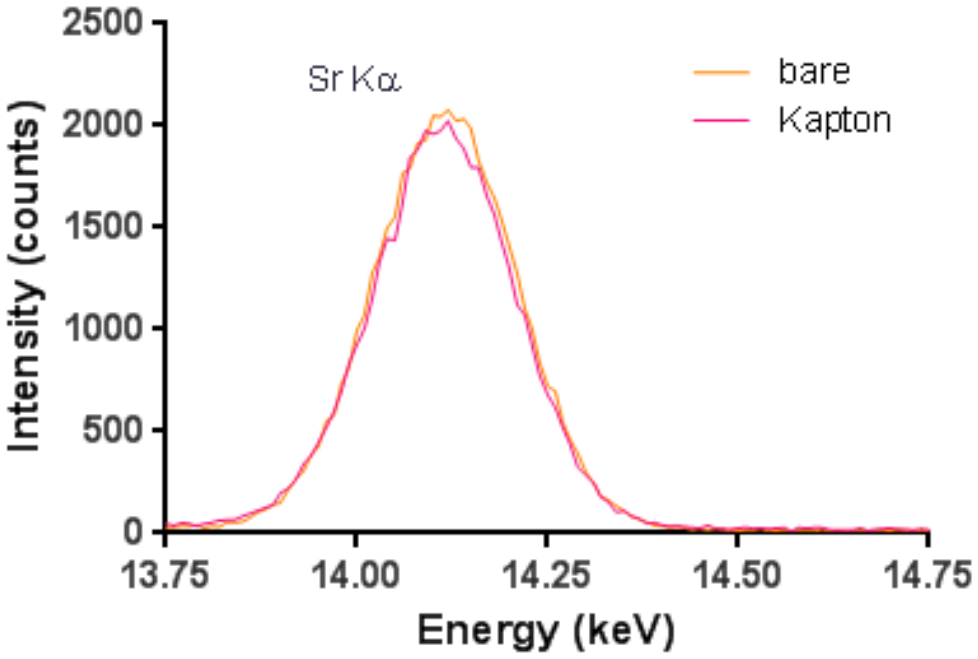

Figure 1. Comparison of SrKa signal for bare sample and one with 40 micrometer Kapton covering.

acrylic. The following testing used Kapton since this is known to have excellent chemical resistance and good compatibility with X-ray irradiation.

The first test was to determine if and how much signal decrease we might encounter with Kapton sample cell materials. Figure 1 shows two SrKa line spectra for a bare sample and one with a 40

micrometer Kapton cover. There is a modest, ~5% decrease, in the SrKa signal intensity. This result demonstrates that for a thickness of 40 micrometers of Kapton we will experience a very slight decrease in signal intensity. The Kapton will be an acceptable top surface covering for our microfluidic sample cell. The microfluidic design is very simple with 2 ports for input and output, 2 channels to transport the fluid into and out of the sample volume and the sample volume compartment. The prototype microfluidic chip is shown in Figure 2. The channels, sample ports and the sample volume were ablated using a UV laser cutter. The sample volume is approximately 1 microliter, with dimensions of 1 x 1 x 1 millimeters. A diagram showing the assembly of the different layers and the layout are shown in Figure 3. The prototype microfluidic sample cell consists of the following layers: a 240 micrometer base of Kapton, 25 x 25 mm; a silicone adhesive 50 micrometers thick, with a 500 micrometer thick polycarbonate layer, another silicone adhesive layer with a top layer of 500 micrometer polycarbonate followed by

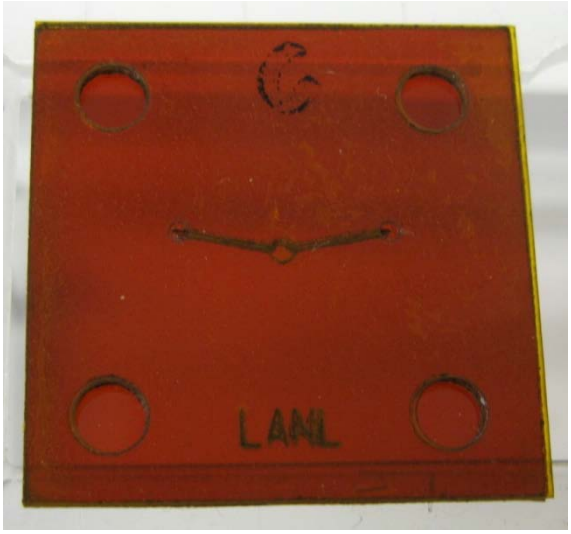

Figure 2. Picture of prototype microfluidic hiRX sample cell.

another silicone adhesive layer. This produces our 1 mm thick sample compartment thickness. The topmost layer is the analytical surface of 40 micrometer thick Kapton layer with the input and output ports. The channels and sample compartment volume are cut into the polycarbonate, but not into the base Kapton layer.

Five microfluidic prototype chips were produced. Each one was filled with 2 microliters of 10,000 ppm Sr aqueous solution. The channels and sample volume of each cell were mapped using the EDAX Eagle III micro X-ray Fluorescence instrument at 30 kV, 600 μA, a dwell time of 200 msec and a matrix of 64 x 50 pixels, an X-ray spot size of ~50 micrometers. Figure 4 shows the SrKa elemental maps of the prototype microfluidic cells with the Sr solution filling the channels and sample volume.

Once the center of the sample well was determined from the elemental maps shown in Figure 4, spectra were collected for 100 live seconds, with 10 repeats for each microfluidic chip. The average net SrKa intensities for each chip are plotted in Figure 5. The bar chart shows the reproducibility among the 5 chips was around 5%. While this is not the ultimate target of 0.1%, this is quite good for our initial attempt at fabricating multiple microfluidic sample chips. We expect to have a performance of 1% or better for commercially produced microfluidic chips due

to better laser precision and quality control of the fabrication processes. Another aspect of these measurements is the X-ray spot size is around 50 micrometers (we were using the EDAX Eagle III for the MXRF measurements), compared to the sample well diameter of around 1 mm. Even the hiRX would have a significantly smaller probe area of around 200 micrometers compared to the sample compartment diameter of 1000 micrometers. Hence, we are sampling only a very small area of the sample well. Collecting the net intensity of one microfluidic chip repeatedly 10 times, produced a precision of 1% RSD. This result seems to indicate the variations among the chips are production based and could be significantly improved with tighter manufacturing control.

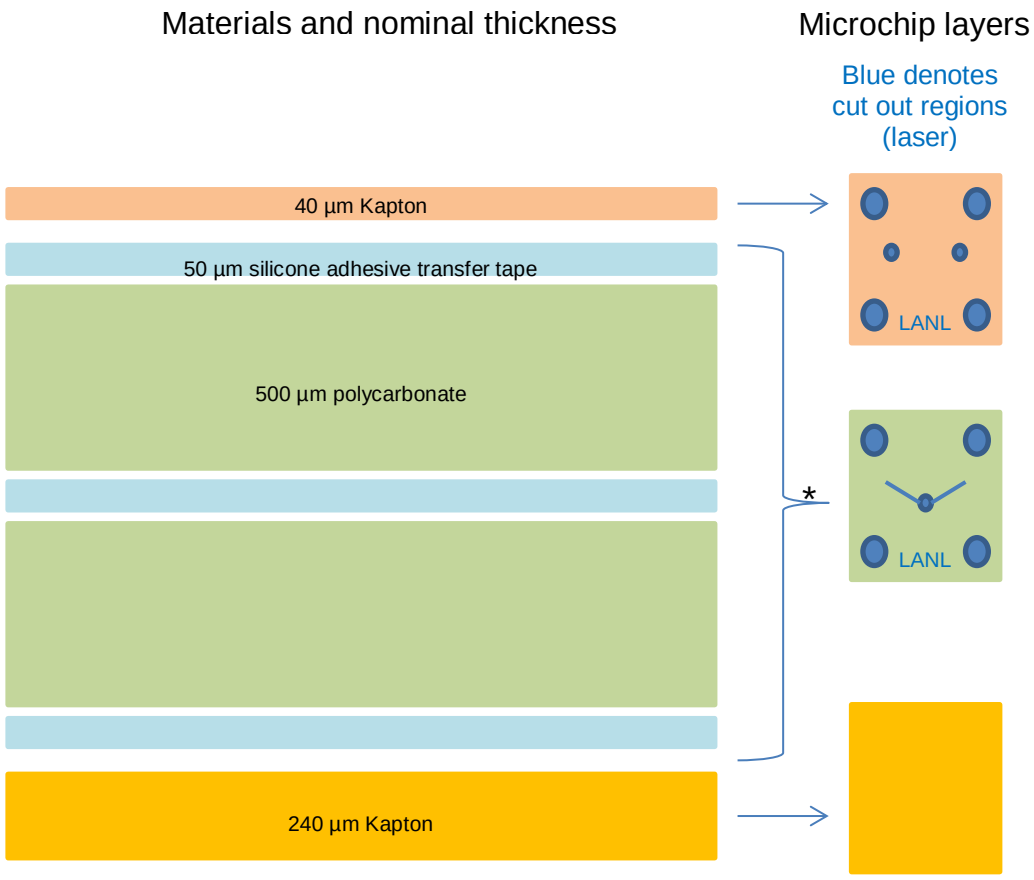

Figure 3. Diagram of prototype microfluidic chip for hiRX sample cell.

The final demonstration of the microfluidic chip performance is shown in Figure 6, which is a plot of the net SrKa intensity versus Sr concentration for 50 to 1000 µg/mL. The linear correlation of 0.997 demonstrates that even this hand-built microfluidic sample cell could be used for quantitative analysis. Concentrations from 5,000 to 10,000 µg/mL were nonlinear and are not shown. The nonlinearity of these higher concentrations is most likely an indication of saturation. Further development work in these high concentration ranges will help elucidate the underlying cause for the apparent nonlinearity.

These results are very encouraging for the home built prototype microfluidic sample chips. Commercial production should improve precision significantly where greater control over the

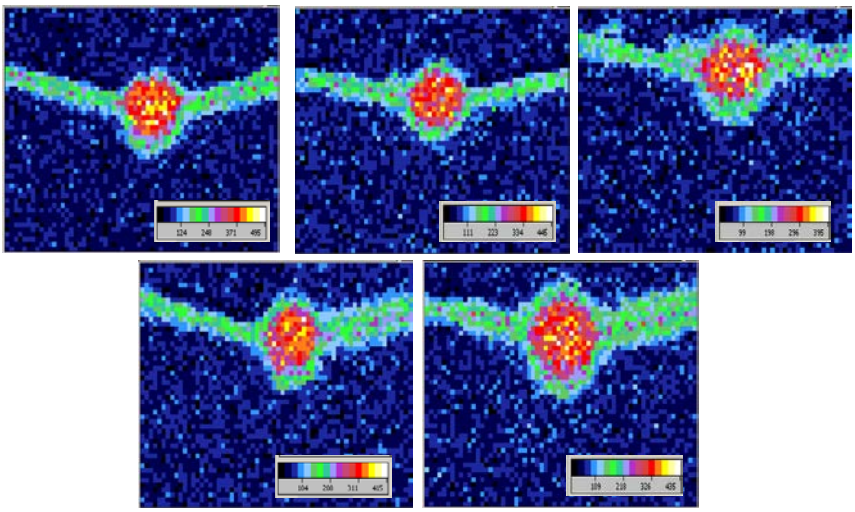

Figure 4. Elemental SrKa maps using the EDAX Eagle III instrument, showing the channels and sample well filled with Sr solution.

material removal to create the channels and sample volume will result in more reproducible sample wells. We are in discussions with several vendors regarding pricing and design of the next beta-prototype microfluidic sample cell.

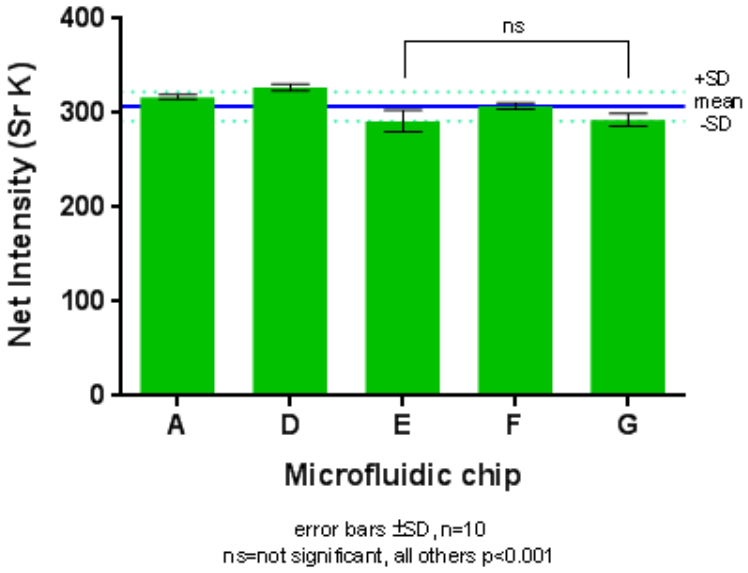

Figure 5. Bar chart of net SrKa intensities for an average of 10 spectra collected at the center of the sample wells for 5 different microfluidic sample wells.

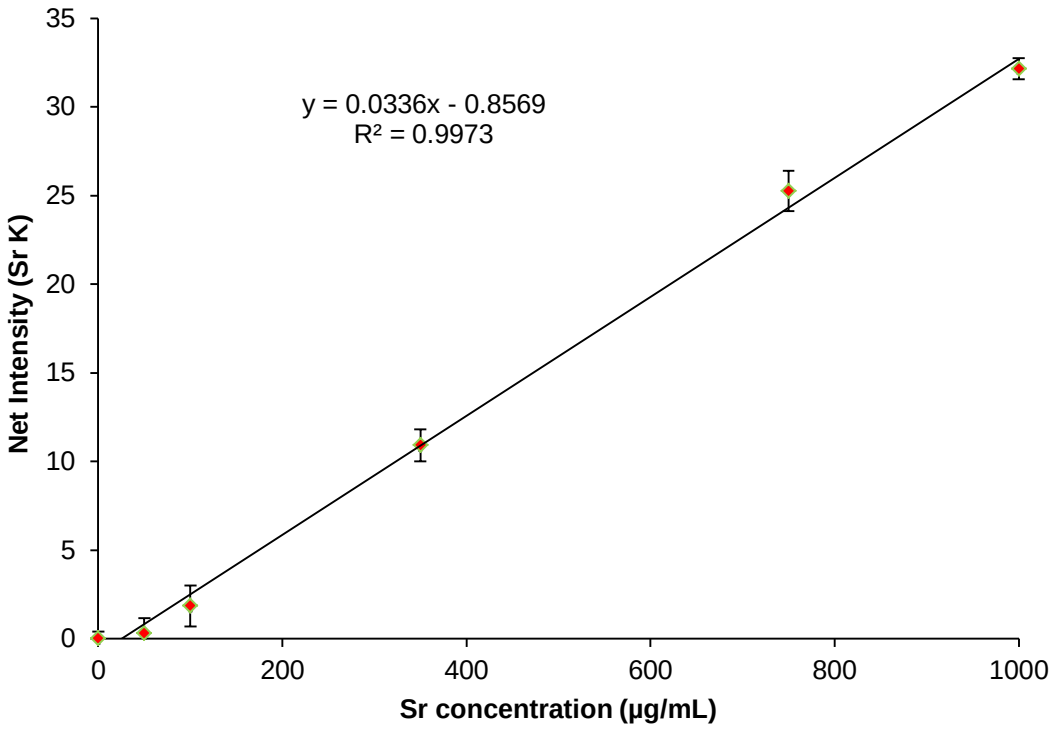

Figure 6. Calibration plot for Sr concentration and measured net SrKa intensities.