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# RECENT RESULTS OF THE INVESTIGATION OF A MICROFLUIDIC SAMPLING CHIP AND SAMPLING SYSTEM FOR HOT CELL AQUEOUS PROCESSING STREAMS

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*A Fuel Cycle Research and Development project has investigated an innovative sampling method that could evolve into the next generation sampling and analysis system for metallic elements present in aqueous processing streams. Initially sampling technologies were evaluated and microfluidics sampling chip technology was selected and tested. A conceptual design for a fully automated microcapillary-based system was completed and a robotic automated sampling system was fabricated. The mechanical and sampling operation of the completed sampling system was investigated. In addition, the production of a less expensive, mass produced sampling chip was investigated to avoid chip reuse thus increasing sampling reproducibility/accuracy. The microfluidic-based robotic sampling system's mechanical elements were tested to ensure analytical reproducibility and the optimum robotic handling of microfluidic sampling chips.*

## I. INTRODUCTION

Sampling and analysis of nuclear fuel recycling plant processes are required to both monitor process efficiency while ensuring Safeguards and Security goals are met. In addition, environmental regulations lead to additional sampling and analysis to meet licensing requirements. The volume of samples taken by conventional means can restrain productivity while samples are analyzed, require process holding tanks that are sized to meet analytical issues rather than process issues (creating a larger facility footprint), or, in some cases, overwhelm analytical laboratory capabilities. These volumes can also provide a significant radiation dose to analytical personnel and equipment. These issues only grow when process flow sheets propose new separations systems and new byproduct material for transmutation purposes. A novel means of streamlining sampling and analysis was evaluated to increase efficiency while meeting all process information requirements.

## II. SAMPLING SYSTEM DESIGN

### II.A. Initial Sample Chip Design

Microfluidic chips (also known as lab-on-a-chip) are used in commercial industry for the handling and manipulation of microliter amounts of fluids.[1-4] These chips were envisioned as a means of sampling reprocessing solutions through the use of capillary action when the chip is contacted (using robotics) with the solution to be sampled. The initial chip design consisted of a 16mm by 30mm quartz chip as seen in Fig. 1 made by Dolomite Microfluidics. It contained eight capillary channels. Four were straight with a volume of 2 µl and four were serpentine with a volume of 10 µl. With these chips, eight samples were taken each time a sample was collected. The sample chips were fabricated from two quartz-glass wafers with one half of each capillary etched into each wafer. The wafers were then pressed together such that the channels maintain an oval cross section. The chips cost approximately $300 each.

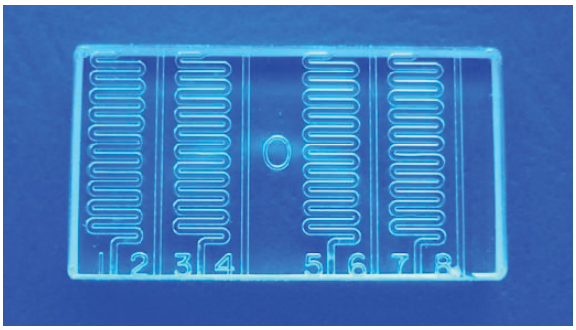


Fig. 1. Initial microliter sample chip.

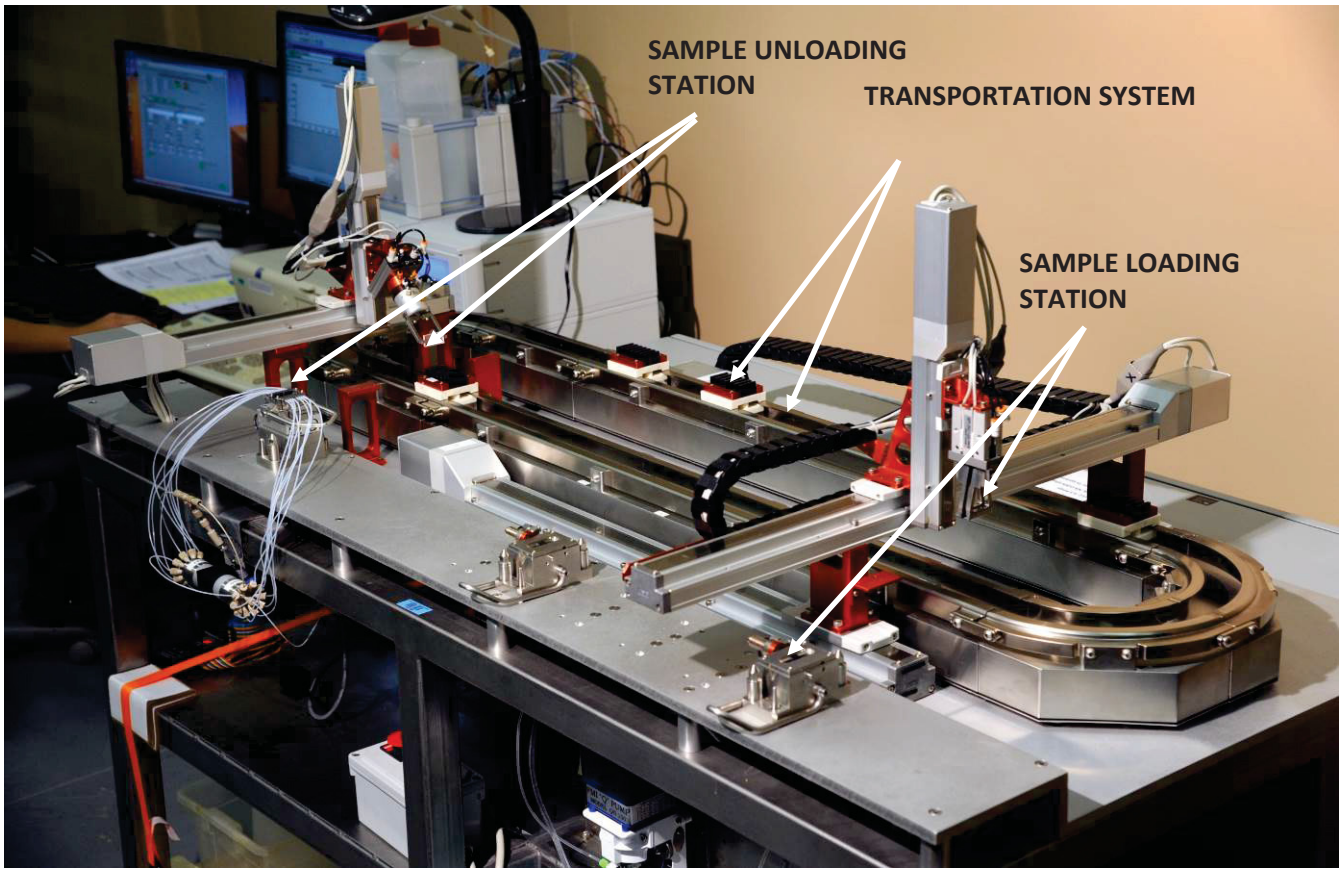

Fig.2. Robotic system for taking microfluidic samples

**II.B. Robotic Sampling System**

The robotic system designed and fabricated for testing of the microfluidic sampling concept included a sample transportation system, sample loading station, and sample unloading station (Fig.2).[5-7]

The sample transportation system included a linear electric-motor based conveyer system and a small carrier fitted with a magnet that enabled movement on the small continuous track. The carrier had a sample chip holder mounted on it (Fig. 3). A short (2.3 meter) track was used for this system; however, tracks over a kilometer in length have been used in commercial applications.

A pick-and-place robotic arm was programmed to pick up the sample chip from the carrier and take it to the sample loading station. The sample loading station included a reservoir chamber through which the sample solution was recirculated. This chamber included a sliding valve that opened to allow the robotic arm to lower the chip into the solution where it was filled by capillary action.

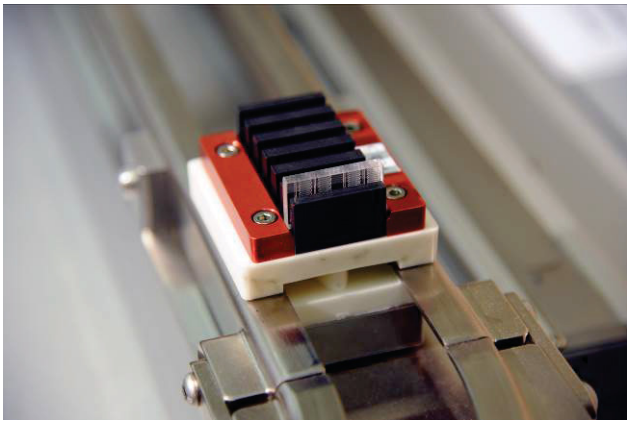
Fig. 3. Sample carriers/holders.

After the chip was filled, the robotic arm placed it back into the sample carrier and it was transported to the sample unloading station (Fig. 4).

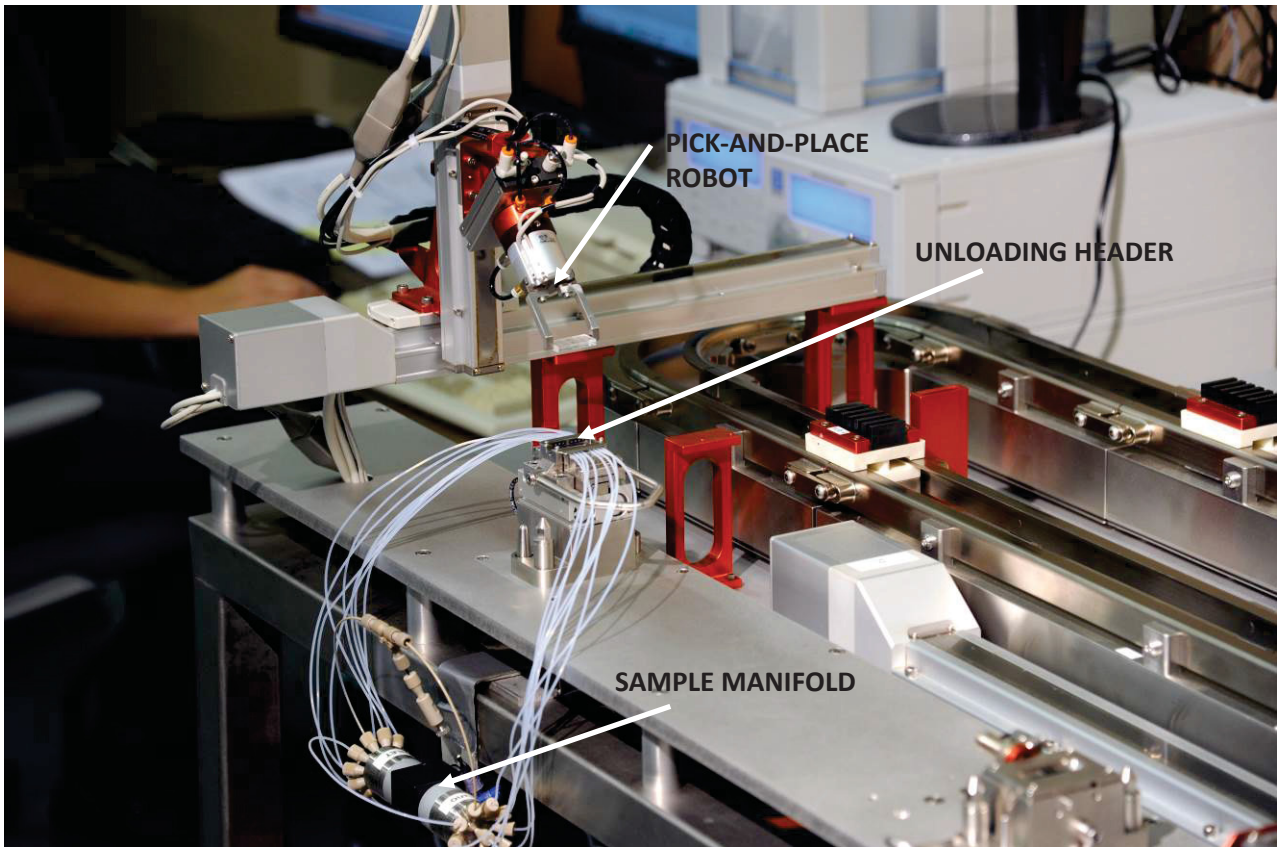

Fig. 4. Sample unloading robotic arm and station.

At the unloading station, the chip was picked up by a second pick-and-place robotic arm, rotated 90 degrees and placed into the unloading header for introduction into the analytical instrument. After placement, the header clamp was actuated by applying instrument air to the header clamp piston causing the chip to by physically clamped and sealing the eight sample channels. The unloading header was connected by tubing to a sample manifold. To empty a channel and send the sample to the analytical instrument, the proper position of the sample manifold was selected by the controller allowing a solution (water, acid, etc.) to flow through the tubing and channel to push the sample volume (in plug flow) to the instrument. Each channel was emptied sequentially. After unloading, the chip was unclamped, the robotic arm picked it up and placed it as directed.

The system controller was a standard desktop computer running National LabVIEW™ which provided various sequences of command sets specifically designed to operate the system.

## III. SYSTEM TESTING

A series of tests were performed to evaluate the mechanical operations and handling of the chips. The chips were manually loaded into the sample carrier. Flow to the sample loading station was started, and the automated sampling sequence was initiated using the LabVIEW™ control system. The operation of the sampling sequence was visually observed to identify and correct any leaks, programming flaws, abuse to the sample chips, reproducibility issues, or other improperly performed functions.

Sampling sequences were performed for single and multiple chips. As the analytical equipment available for use was a single channel ultraviolet-visible spectrophotometer (UV-VIS), the solutions used for testing consisted of 1 g/L and 100 g/L holmium nitrate. The initial programming included a dipping time (holding the chip in the solution) of 10-13 seconds while the solution flowed through the sample loading station at 0.087 mL/sec. The programming also included a channel flush time in the unloading station of 90 seconds for the low concentration solution and 300 seconds for the high concentration solution with the flow rate of the solution of 1 ml/min. As testing proceeded, changes were made to the system programming, sample recirculation flowrate and sample transport flowrate as necessary to improve system performance.

A second set of tests were conducted by filling the chips by flowing the solution through a chip placed in a header by hand and placing this chip in the sample carrier then having the robotic system unload the chip to the UV-VIS.

## IV. ALTERNATIVE CHIP INVESTIGATIONS

Due to the difficultly in cleaning the capillary channels on the expensive glass chips, less expensive, one time use, plastic chips were investigated. An injection molded sample chip made from thermoplastic was pursued for this purpose. Materials testing was conducted on three Grilamid TR™ moldable polyamide plastics (TR90, TR90 LX, and TR55 LX) in acid (5M $HNO_3$), base (5 M NaOH), and organic (30% tributyl phosphate in Isopar L) at room and elevated (50°C) temperatures. These tests showed that for these solutions the TR90 LX showed the greatest chemical resistance.

Fluid to solid interface contact angles were also measured for the acid, base and organic on the three types of Grilamid TR™ plastics as well as on stainless steel to verify the length and diameter of the channel in a chip made of these materials would be sufficiently filled by capillary action. A smaller contact angle provides greater capillary fill action. TR90 had the smallest contact angle of the plastics for these solutions. .

It was decided to procure several prototype chips made out of the TR90 plastic; however, after further design investigation the subcontracted commercial fabricator found they could not meet the specifications on the channel diameters with these plastics. Therefore, this plan of action was terminated.

An alternative design was then pursued which included a chip made of plastic with embedded stainless steel channels enabling taking of six 2µl samples at one time (Fig.5). Six prototype chips were made. The stainless steel channels were small enough to allow the chips to fill by capillary action. An estimate of $12-$15 each was given on making these chips in bulk.

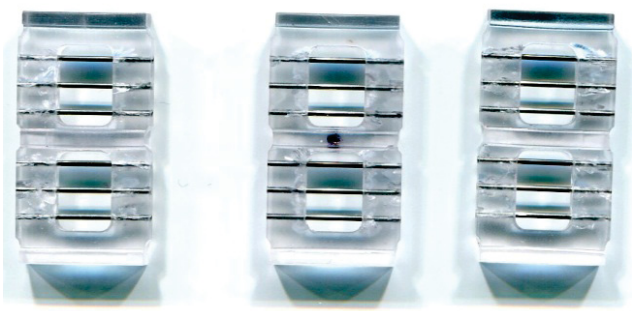

Fig. 5. Plastic chips with stainless steel microchannels.

Based on the system test results previously mentioned, it was determined that filling the chips by capillary action (i.e., dipping) resulted in many channels not filling completely. The chip channels were more consistently filled by flowing the solution through the channels. At these small volumes, any variation in the fill amount can drastically affect the sample accuracy and variability. In general, it was found that a 10 µl channel gave less relative standard deviation of the results. Therefore, as a potential future path forward, two potential chip designs with a minimum of a 10 µl volume and with diameters sized to hold the solution by surface tension but not fill by capillary action were recommended. This would require some redesign of the robotic system sample loading/unloading stations.

## V. SYSTEM TEST RESULTS

The following observations and system adjustments were made during the course of testing:

- The flowrate of solution through the sample unloading station to the analytical equipment was reduced to 0.75 mL/min to reduce the pressure in the small sample lines.
- To minimize cross contamination from the sample carrier, the rate the chip was withdrawn from the sample loading station was decreased to allow solution to drip from the sides of the chip prior to it being placed in the carrier.
- The time the chip was dipped into the sample loading station was increased to 30 seconds, dip depth increased by 2mm, and sample recirculation rate increased to 0.118 mL/sec to increase the success in completely filling all capillaries in new glass chips (although this did not significantly improve the filling of used chips).
- To decrease leaks at the unloading header, the tubing was cut to ensure it laid flat against the chip, tubing position relative to the gasket was adjusted, the robotic system was directed to release the chip prior to clamping, and the air pressure to the clamping mechanism was increased. These modifications provided a better seal between the header and the chip, although leaks still occurred on blocked channels.
- It was found that evaporation of the sample prior to unloading can be significant.[8] The 2 µl channels lost 8-11% of their volume in 15 minutes and more than 23% in one hour. The 10 µl channels lost up to 5% of their volume in one hour. Therefore the time between loading and unloading the chips must be minimized.

- Cross contamination from the sample unloading manifold was evaluated by running a chip unload program twice in a row. A significant amount of contamination was not found to be held up in the manifold.
- Cross contamination from the gasket/tube/chip interface in the chip was tested by running the unload program on a filled chip, flipping the chip over and running the unload program a second time. This did not find significant amounts of cross contamination.
- Air bubbles, probably formed at the ends of the channels when the chip was placed in the unloading header, caused significant problems with results on the UV-VIS.

Uv-VIS results from the recent glass chips testing and previous chip testing done using an inductively coupled plasma mass spectrometry (ICP-MS) by Idaho National Laboratory (INL), Argonne National Laboratory (ANL) and Los Alamos National Laboratory (LANL) are compared in Tables I and II. These results eliminated the data from the channels that were visually observed as not being completely filled. The % error (difference in concentration of measured versus actual) on the UV-VIS analyzed samples was not calculated due to wide variability in the results during calibration of the UV-VIS. Therefore, the Relative Standard Deviation (RSD) was used to compare the uncertainty between different measurements. The RSD is the sample standard deviation divided by the mean value of the sample data set.

TABLE I. Results on 2µl channels.

| | INL ICP-MS | ANL ICP-MS | LANL ICP-MS | INL UV-VIS |
|---|---|---|---|---|
| % error | 16.5% high | 31.5% low | ~10% low | - |
| % RSD | 10.3% | 65.2% | 15-20% | 13.2% |
| # channels | 12 | 16 | 6 | 20 |

TABLE II. Results on 10 µl channels.

| | INL ICP-MS | ANL ICP-MS | LANL ICP-MS | INL UV-VIS |
|---|---|---|---|---|
| % error | 3.5% high | 3.7% low | 2% low-1% high | - |
| % RSD | 5.0% | 13.9% | 3.5-5% | 2.8% |
| # channels | 12 | 15 | 6 | 20 |

As noted, these Tables do not include information from chips incompletely filled. On the INL UV-VIS testing for the single chip runs, up to 21.8% of the channels were eliminated primarily due to incomplete channel fill. For the multichip runs, this increased to 63%, partially due to the increase in evaporation in the channels. Therefore, some additional testing was completed by flowing solution through the channels to fill them. These tests were conducted on both the glass and plastic/stainless steel chips. These resulted in completely filled chips except for some meniscuses and similar standard deviations to those obtained after elimination of the questionable data from the "dip fill" runs (Table III). These results continue to show significant RSDs (12-79%) for 2 µl channels even when they appeared completely filled. The 10 µl channels show similar RSDs as the capillary filled ones in Table II; however, in Table II a large percentage of the channels were eliminated prior to the calculation and in Table III all of the channels were analyzed as all were full.

Table III. Comparison with Flow Filled chips

| 100 g/L solutions | Flow Fill Glass 2µl | Flow Fill Glass 10 µl | Flow Fill SSplastic 2µl | Dip Fill SSplastic 2µl |
|---|---|---|---|---|
| % RSD* | 12.6% | 6.7% | 14.8% | 79% |
| # channels | 12 | 12 | 36 | 36 |

## VI. CONCLUSIONS

A microfluidic based robotic sampling system was fabricated, configured, tested. Its mission was twofold: testing extremely low volume microfluidic based sample chip technology applied to elemental analysis and at the same time demonstrating the application of currently available technology to address the issues associated with sampling spent nuclear fuel processing aqueous solutions. The overall goal is to significantly reduce sample volume thus reducing the sample waste streams and at the same time reducing radiation exposure to humans and analytical instrumentation.

The system's mechanical elements were tested through visual inspection of both single chip and multiple chip runs to ensure reproducibility and the optimum safe handling of microfluidic sampling chips. Some general observations/recommendations made during chip testing and analyses include:

- The 10µL channels generally produced data that had much smaller relative standard deviations than the 2µL channels as would be expected as even a tiny variation in the smaller channel is a much higher percentage difference overall.
- Chip loading is an issue. Filling with capillary action requires a very small diameter and is contingent upon the solutions sampled and the materials used for the chips. Through modification of dipping depth and time, the system was able to routinely fill the glass chips completely. Even with complete filling there

may be some variation between channels due to the formation of meniscuses.

- Once a full chip is placed in the sample unloading header, there will be a small air bubble at each end of the channel that could affect analytical results with instruments like the UV-VIS. This shouldn't be an issue when using the ICP-MS.
- Leaking due to channel blockage reemphasizes the need for clean chips and solutions that are free from particulates.
- Adjustments were made to the lines to mitigate leaking; however, on occasion the lines would need to be readjusted. Implementing a header with permanently attached lines would eliminate leaks associated with changes in tube positioning and sealing.
- Evaporation from the chips is an issue especially with the 2 µL channels. Therefore, the present design which enables loading several chips at one time and taking them to one unloading station is not recommended. The point is to minimize the time between chip loading and chip unloading.
- Relying on the capillary action of the microfluidic chip channels is not the optimum method for filling the chips. Active flow is better (i.e., filling the channels in a chip holder by flowing fluid through the chip). This would minimize surface contamination issues from "dipping" the chips, ensure that each channel is sufficiently purged with a representative sample, and ensure that the channel is completely filled. It would potentially allow plastic chips with a slight larger channel diameter to be used.
- The tiny volume of the 2µL samples amplifies any fill volume errors and causes the results to have a high % RSD in general. One possibility is to focus on a chip that would fill with pumping that could contain several 10 µL samples instead of 2 µL samples to increase the accuracy of the results.
- One of the design changes identified is the need to integrate automated decontamination measures to clean the sample transportation pucks and sample unloading station to prevent cross contamination. One possibility would be to clean them with a system that integrated carbon dioxide pellet/ice crystals with a vacuum system which would remove and capture contamination without leaving any liquid waste.[9]

## ACKNOWLEDGMENTS

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