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Is the Proof *REALLY* in the PUDDING? UHP COMPONENTS PREPARED BY ACID LEACHING

SCOPE

During our childhood we've all heard the phrase, "The proof is in the pudding", meaning that if a cook has a good pudding recipe, and the cook adds the listed ingredients in the proper order, stirring all the ingredients for just the right amount of time and then cooking the mixture at the correct time and temperature, the finished "pudding" will be a delicious culinary delight.

Each year the need for stricter cleanliness levels for Ultra High Purity (UHP), parts are discovered. In the semiconductor industry, while the need for UHP processing equipment is becoming increasingly evident, cleanliness guidelines for equipment manufacturers have been slow in coming. While waiting for finite specifications, a few UHP manufacturers have established their own cleaning and testing procedures. This paper will apply the "pudding" principle to focus on the right cleaning and testing "*recipe*" for UHP components comprising McMillan's microturbine flow sensors and controllers, designed specifically for semiconductor processes. The "*proof*" will be demonstrated by comparing purity levels of units cleaned with deionized water to those that are processed in a special acid cleaning "*recipe*". Comparative measurements will be amount of metallic (ppt), contaminants and cumulative particles generated at ≥ 0.05 -micron levels.

INTRODUCTION

Metallic ion contamination and particle generation continue to have increasing impacts on semiconductor fabrication. Trace metal contamination can detrimentally affect performance of the electronic devices on the wafer. While components that are installed during wafer fab construction may have time to be flushed with acid solutions to remove as much metallic contamination as possible, components installed as upgrades or replacements once the fab is in production must be clean when installed to prevent costly downtime.

Circuits in state-of-the art electronics are sensitive to many different types of contamination during the manufacturing process. In particular, trace metal contamination can affect the semiconductor property of gate oxide, change dielectric strength of insulating layers or cause silicate formation where not desired. All can detrimentally affect the performance of the electronic circuit resulting in lower reliability or component failure.

By taking certain steps during production, UHP component manufacturers can ensure that their products are cleaned and ready for installation in any process. This is accomplished through a series of ultrasonic and acid extraction cleaning steps, including exposure to HF and HNO₃ solutions. These acids aggressively extract undesirable metallic contaminants present in polymers. [1]

LABORATORY TESTING CAPABILITIES

In order to meet and exceed increasing demands for higher purity in semiconductor industries using liquid flow measurement and control, all UHP flow sensor components are acid leached and tested for particles and metals in a dedicated Class 100 clean room.

Measuring particle and metal contaminants after acid leaching insures thorough cleaning of all UHP flow sensor components. Successful cleaning of UHP flow control units equals to zero particle generation and baseline ultra low/trace (ppt) metal contamination, measured by state-of-the-art laboratory equipment:

1. Particle analysis is performed per PMS Model HSLIS M-50, Liquid Optical Particle Counter, allowing online particle counting down to 0.05 μ (.05 micron) levels. (Serial # 39521).
2. Metals analysis is performed per Agilent Model 7500ce ICP-MS (Inductively coupled plasma mass spectrometer). The Agilent Model 7500ce is specifically designed for optimal analysis of trace metals at low ppt levels in high matrix samples using (ORS), Octopole Reaction System technology. (Serial # JP14101021).

CLEANING "RECEIPE"

All McMillan UHP flow sensors and controllers are cleaned by a three-part system consisting of component sonication, acid leaching and deionized water rinsing.

Step 1-Ultrasonic Extraction

Ultrasonic cleaning can be used for almost any material in just about any shape or size. The principle involved is to immerse the part in a bath containing some type of aqueous cleaning fluid. The bath has transducers bonded to the surface, which produce ultrasonic energy into the cleaning fluid forming cavitation events. The formation and collapse of cavitation events scrub the faceted surface of the parts - the ultrasonic energy imparts significant cleaning power to the surface of the part which is very effective in removing particles, even strongly bonded ones. Because the extraction force is constant, more

reliable and repeatable particle removal can be obtained [2]. This method is particularly effective in removing smaller sized particles, where the presence of contamination is more critical to the product's yield, such as in the semiconductor industry.

Ultrasonic Cleaning-Method

1. All components of UHP flow-sensors/controllers are placed in a specifically designed solution for optimal particle removal and sonicated for one hour.
2. UHP components include PFE bodies, micro-turbine wheels and all internal wetted parts excluding sapphire shaft and bearings.
3. Sonicated components are rinsed again with ≥ 18.0 um deionized water.

Step 2-Acid Leaching

Since all McMillan UHP flow sensors and controllers use fluorinated polymers, Kal-Rez and sapphire wetted parts; they can be cleaned in aggressive acids that have been proven to be very effective in leaching the most trace metal contaminants from plastics. Several studies have shown that 49% HF is the most aggressive acid for leaching trace metals from PFA, followed by 70% HNO₃ [3]

Acid Leaching Methods – Dynamic and Static

UHP flow sensors or controllers having 1/8" to 3/8" PTFE Flare-Tek connections are dynamically acid leached:

Dynamic Acid Leach Procedure

1. Prepare a 1000 ml PFA beaker soaked overnight in an acid solution consisting of 10% Optima Grade HNO₃ mixed with 2% HCl, then rinsed under continuous stream of ≥ 18.0 megohm deionized water for 20 minutes. [4]
2. Pour an acid solution consisting of TAMA or OPTIMA brand purity HNO₃ and HF into cleaned 1000 ml PFA beaker.
3. In hood area using double containment for safety, connect flow sensors to appropriate PTFE tubing and circulate acid solution from 1000 ml beaker through flow sensors for one hour.
4. After an hour of acid leaching, using appropriate PTFE tubing, connect flow sensors to a rinse station and rinse with .04 um filtered ≥ 18.0 Meg ohm deionized water for one hour. Repeat steps 3 and 4 as necessary to insure zero (background) contaminants.

Static Acid Leach Procedure

1. Larger UHP volume flow sensors having $> 3/8$ " connectors are statically leached with acid solution for one hour then rinsed with ≥ 18.0 um deionized water for an hour.
2. Cleaning cycle is repeated until testing shows zero (background) contaminants.

Step 3 – Deionized Water Rinsing

After all flow-sensors have completed acid leach cycles, using PTFE connections; they are hooked to a ≥ 18.0 meg-ohm Di water outlet and rinsed for a minimum of one hour.

NOTE: Particle levels of deionized rinse water are continuously monitored. Rinsing cycle will only begin if rinse water background particle levels are cumulative ≤ 2 particles/ml at 0.05 um.

COMPONENT PARTICLE TESTING – 1st “PROOF”

Once McMillan’s UHP flow sensors have been subjected to the acid leach - deionized water cleaning system, they are particle tested for purity. Cleaned units are placed inline ultra pure > 18 Meg ohm deionized water stream and particle tested per HSLIS PMS M-50. See Figure 1.

The PMS M-50 HSLIS Flow sensor measures particles going through the instrument cell window at 100 ml/minute. Bypass flow is set to half of maximum rated flow-sensor volume. Flow sensors are installed for particle measurements after baseline (cum ≤ 2 particles/ml); levels at 0.05 μm for deionized water have been achieved. Data collected from first few minutes of shedding by the flow sensor were discarded because particle counts reflected disturbances caused by the installation procedure (ex. - air bubbles), that were superimposed on particle shedding from installed flow sensor.

NOTE: All component acid leaching, particle testing and metals analysis was performed in a Class 100 clean room.

FIGURE 1 – Flow Path of Fluid System

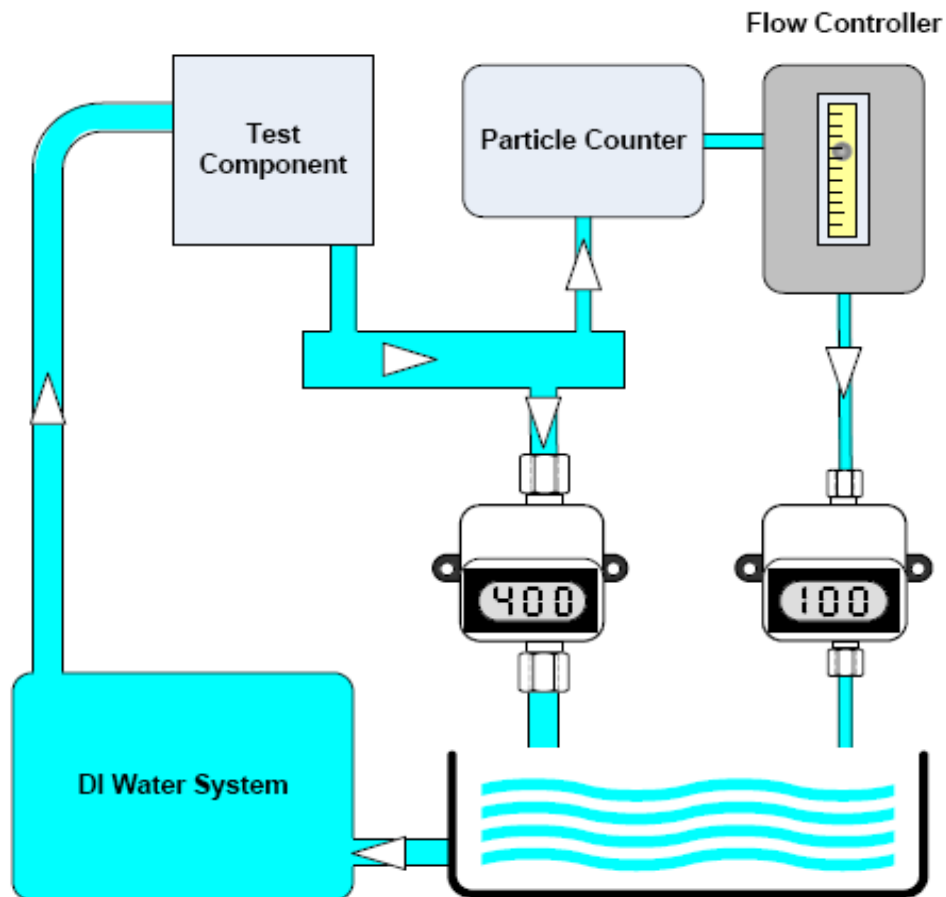
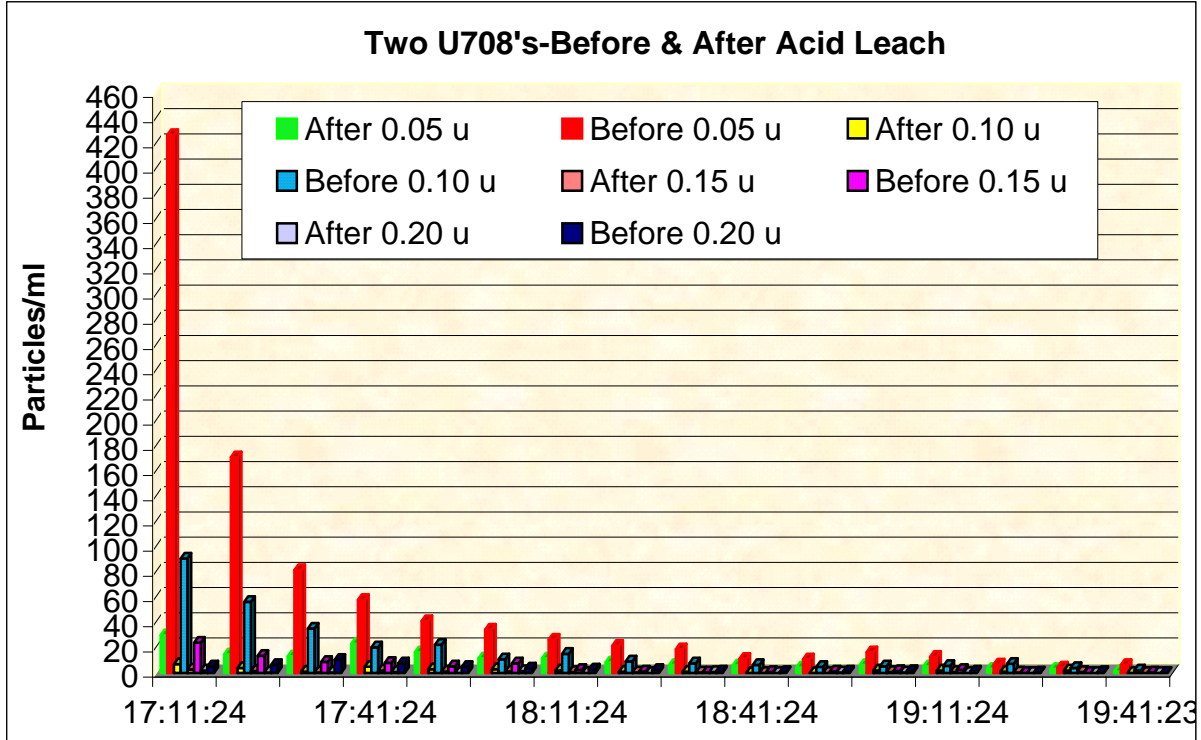


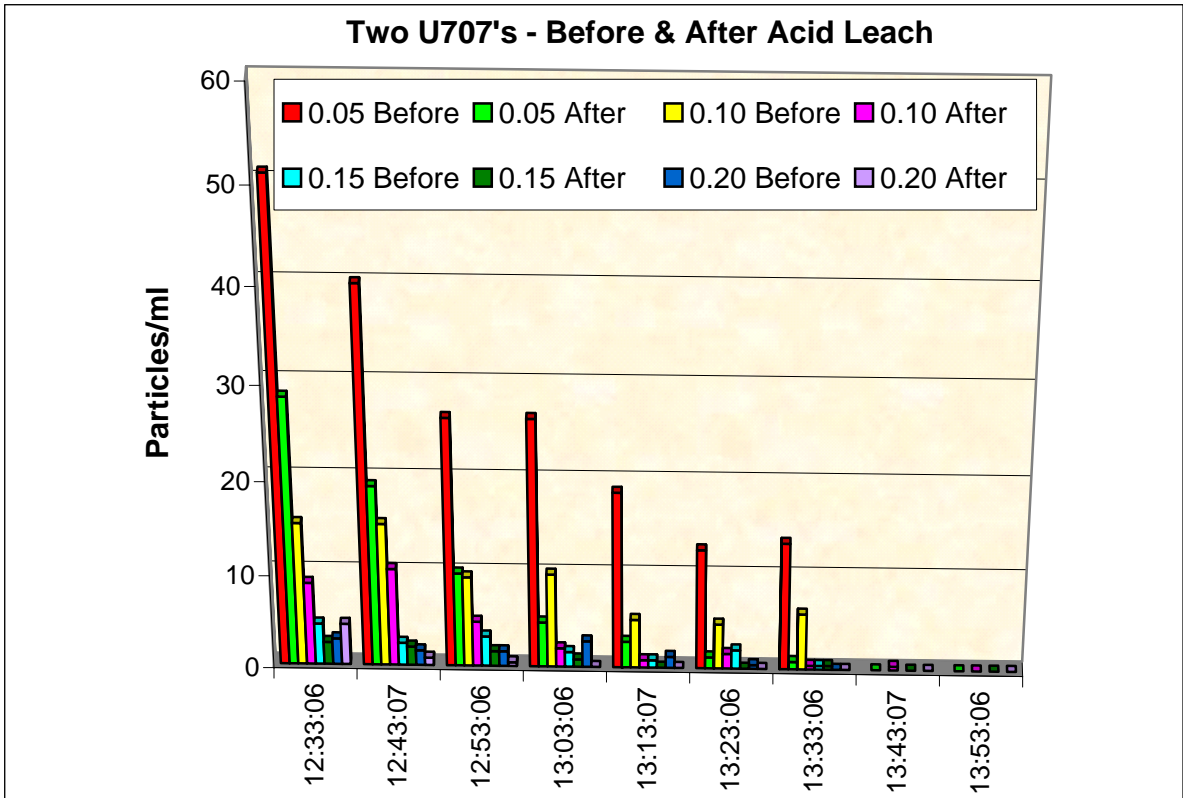
Figure 1

“Pudding Proof” Particle Results

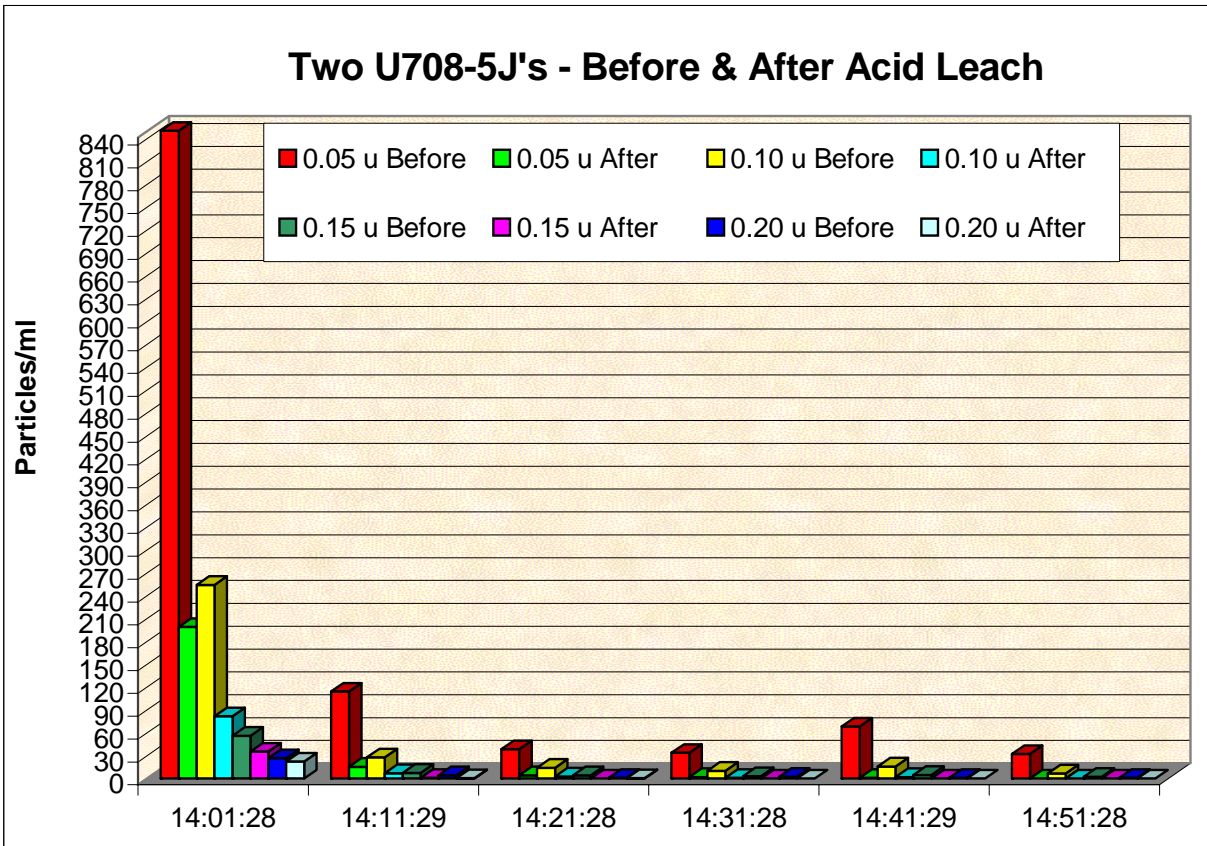
The first way acid-cleaning effectiveness was measured was by comparative particle testing. Seven sets of UHP flow sensors were collected over several months’ production time, consisting of different models with varying range sizes and flow configurations, each set however; being identical. Example: Two UHP Model 708’s, range 5J were tested. These seven units were comparatively tested: one UHP unit was acid cleaned and the other was only rinsed in deionized water before particle testing. Here are some of the test results:



In this U708 UHP model, particle cleanup time to achieve ≤ 0.4 Particles at $0.05\mu\text{m}$, was reduced by a factor of 2.8 in acid cleaned flow sensor -2.5 hours vs. 7 hours in non-acid cleaned flow sensor.



In this set of U707's, acid leached flow sensor went to baseline in 1 hour, 20 minutes; vs. non-acid leached flow sensor that went to baseline in 4 hours, 20 minutes.



In this set of U708-5J units, cleanup time was reduced from 2 hours 40 minutes to 50 minutes.

COMPONENT METALS ANALYSIS – “2ND PROOF”

A second way of measuring acid cleaning effectiveness is by metals analysis. A comparison of metal contamination was performed on a total of 40 flow-sensors, before and after acid cleaning. The 40 flow sensors were collected over several months' time consisting of varying models, flow configurations and range sizes.

Metals-Sample Procedure

1. Samples collected for metals analyses were from 40 flow-sensors ranging in size from 100 ml/minute to 50 L/minute after ultra pure >18 Meg ohm deionized water rinse. A second series of samples were collected from the 40 flow sensors after they had been acid cleaned then rinsed with ultra pure > 18.0 Meg ohm deionized water.
2. Samples were collected in duplicate and consisted of 10 ml of >18.0 Meg ohm UHP water that had been rinsing through cleaned units for one minute.
3. Samples collected in 15 ml PTFE vials that had been thoroughly cleaned in acid solution and rinsed under a continuous stream of >18.0 Meg ohm deionized water.

Metals-Instrumentation

Metals analysis was performed per Agilent Model 7500ce ICP-MS, equipped with the Shield Torch System and an inert PFA sample introduction system. The Agilent 7500ce is an ideal instrument for metals analysis due to its Octopole Reaction System (ORS) technology, designed for analysis of trace metals in high matrix samples, with nine orders of dynamic range. The 7500ce uses collision reaction cell (CRC) technology in the form of the ORS to remove polyatomic interferences, allowing detection of Si, V, As, and Se in one Multi-Tune analysis [5].

The inert PFA sample introduction system from Elemental Scientific, Omaha, NE, USA, consists of a PFA-100 self-aspirating micro flow nebulizer, 35-mm PFA end cap, 35-mm PFA spray chamber, 2-mm O-ring free Platinum injector and quartz torch.

Metals-Analysis Procedure

1. All flow sensor samples were analyzed directly without dilution or pretreatment, thus avoiding sensitivity loss due to dilution and potential contamination.
2. Samples were analyzed using a Multi-Tune method consisting of H₂, He, normal and cool plasma conditions. Since this method features fully automated switching from one analysis mode to the next, all elements of interest are analyzed in a single acquisition, reducing the risk of contamination from further sample handling.
3. Samples were aspirated at an uptake rate of 100ul/min
4. Multi element calibration standards [6] were prepared with 2% Optima grade HNO₃, 2% Optima grade HCl and trace Optima grade HF, at concentrations ranging from 250 to 10,000 ppt (parts per trillion).

Metals-Detection Limits

1. Both instrument and method detection limits were calculated from calibration data generated during this study. Instrument detection limits or (IDL's), are a measure of an instrument's sensitivity, run at optimal conditions. Three sigma instrument detection limits for this study were calculated using the standard deviation of 10 UHP blank replicates as follows [7]:

$$\text{IDL (ppt)} = \frac{(3 \times \text{Blank Standard Deviation Counts} \times 10,000 \text{ ppt Standard Counts})}{(10,000 \text{ ppt Mean Standard Counts} - \text{Mean Blank Counts})}$$

2. Method detection limits or (MDL's), are defined by the EPA as “the minimum concentration that can be determined with 99% confidence, that the true concentration is greater than zero” [8]. The MDL is different from the IDL in that it takes into account sample matrices, interferences, methodologies, analysts, etc. MDL's were calculated similar to 40 CFR 136. Ten replicates of a calibration standard were analyzed; the standard deviation of replicates calculated and the MDL was determined by the following formula:

$$\text{MDL} = \text{Student's } t \times \text{Standard Deviation of Replicate Analysis}$$

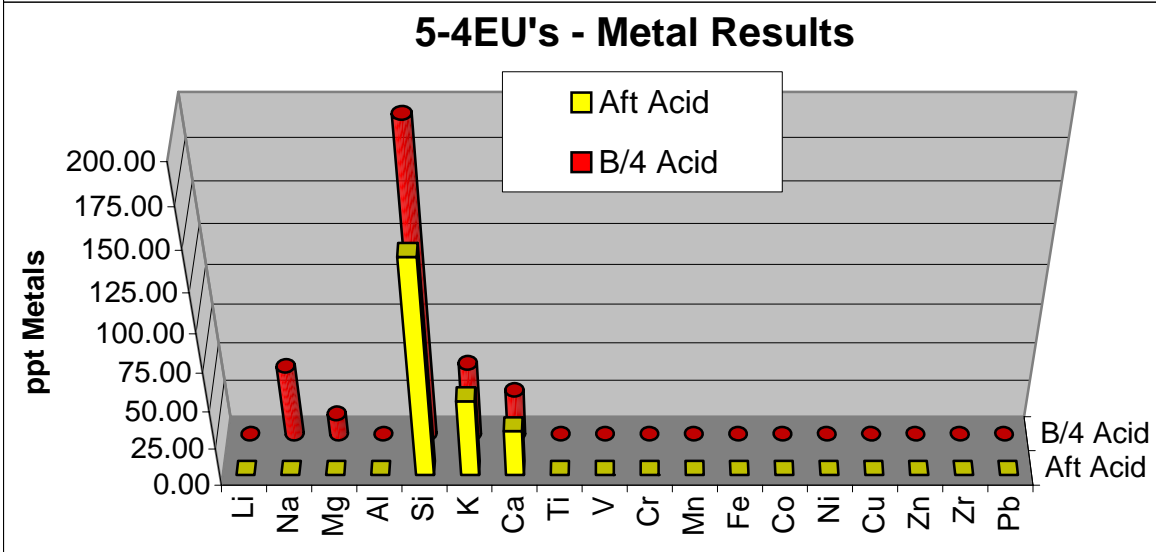
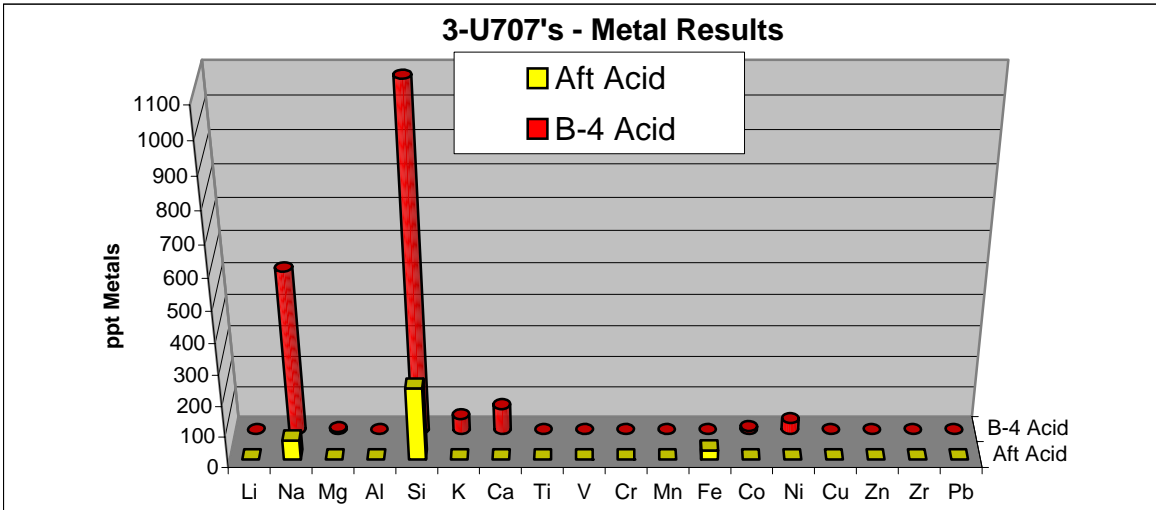
3. Calculated instrument detection limits and method detection limits are shown below:

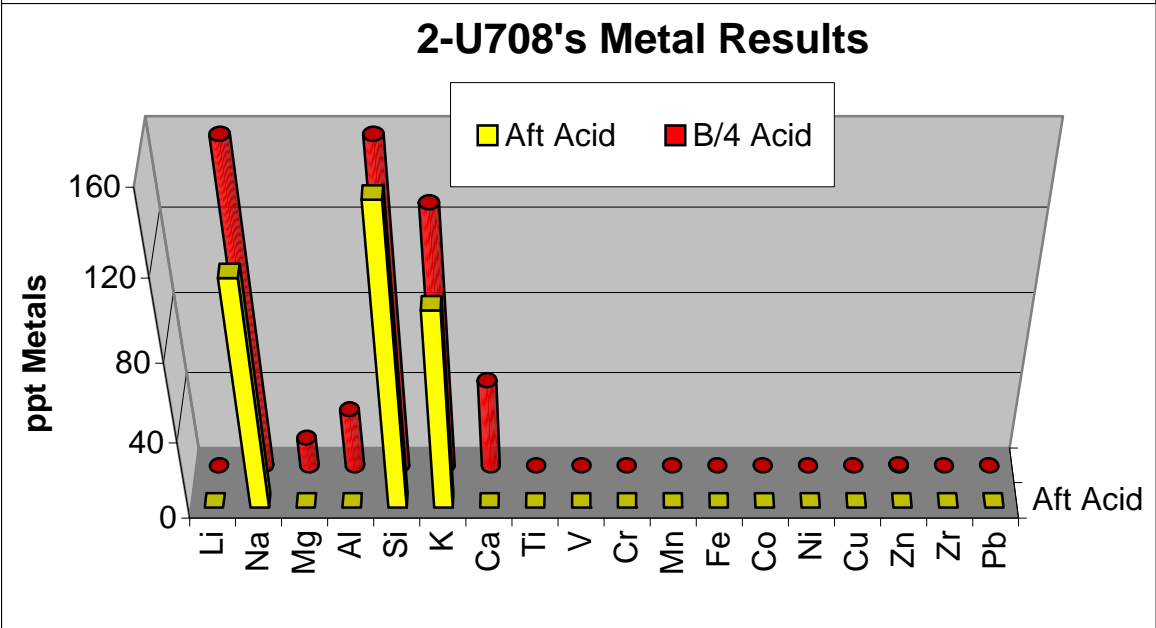
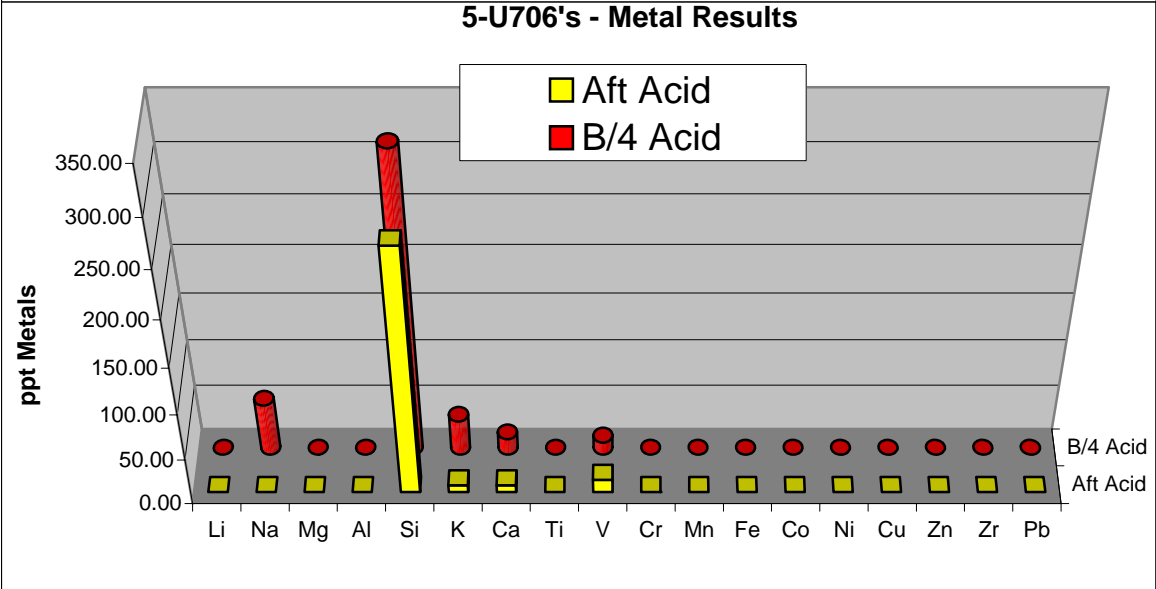
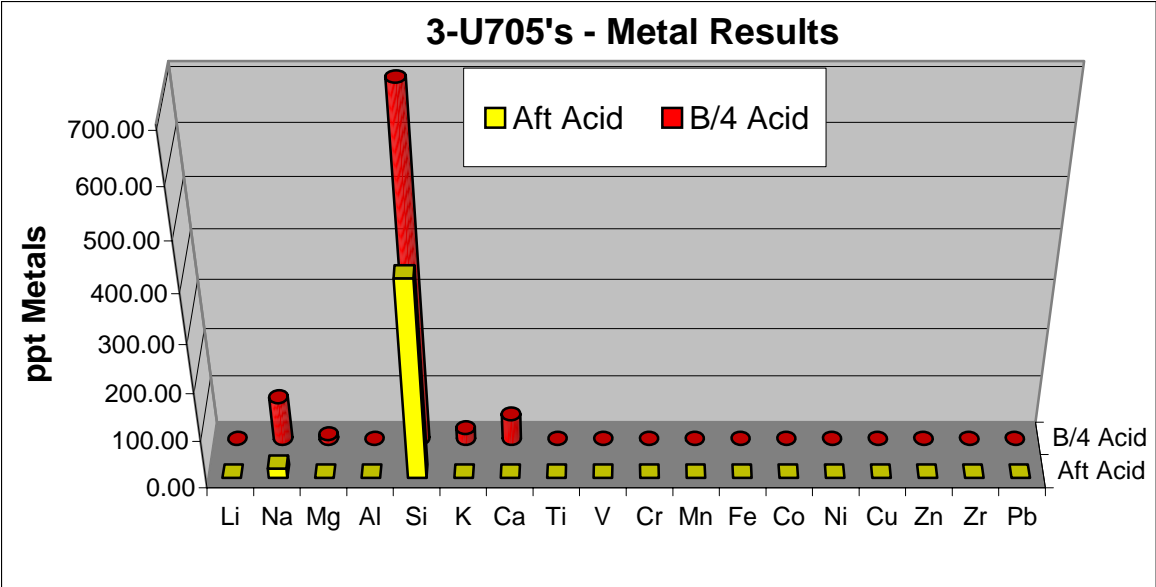
(ppt) Instrument Detection Limits and MDL's

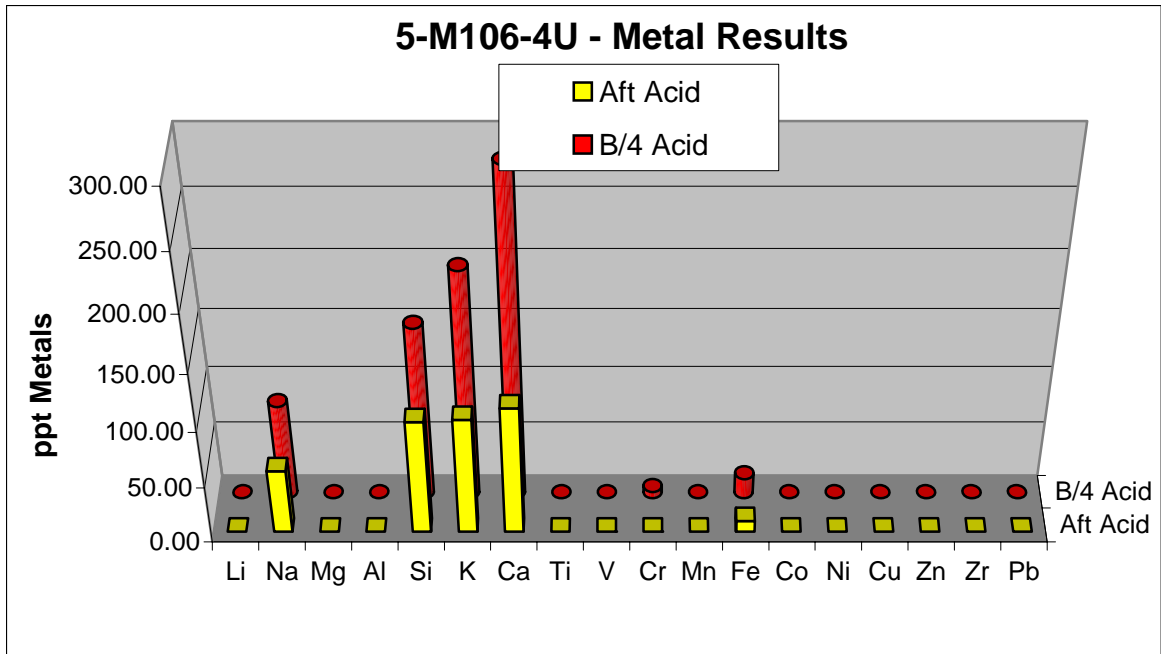
Element	Mass	Tune	ppt IDL	ppt MDL'S
Li	7	Cool	0.12	104.50
Be	9	He	0.10	127.20
Na	23	Cool	8.28	395.97
Mg	24	Cool	0.79	244.06
Al	27	Cool	1.85	290.35
K	39	Cool	1.13	241.86
Ca	40	Cool	9.09	247.76
Cr	52	He	2.75	357.36
Mn	55	H2	1.14	279.31
Fe	56	Cool	5.53	357.28
Co	59	Cool	0.42	246.91
Ni	60	He	2.54	146.21
Cu	63	He	2.59	118.07
Zn	66	He	2.24	232.89
Ga	69	Cool	0.3	247.01
Rb	85	Normal	0.6	267.73
Sr	88	Normal	0.2	155.98
Ag	107	Normal	0.7	100.70
Cd	111	Normal	0.6	193.36
Sn	133	Normal	4.16	281.57
Ba	137	Normal	0.5	263.95
Pb	208	Normal	0.3	218.4
Si	28	H ₂	323	484.39

“Pudding Proof” Metal Results

Comparative metals analyses were performed on 40 flow-sensors: Before and after acid cleaning. Results reported in ppt, minus blanks. Here are some of the test results:







“PUDDING PERFECTION”- SUMMARY

The McMillan cleaning recipe of 1) sonication, 2) acid leaching and 3) deionized water rinsing produces a flow-sensor that is UHP cleaned to “pudding proof” perfection:

- Average particle cleanup time was reduced by **32.8%** to a baseline of ≤ 2 (cumulative), particles/ml at 0.05 um. This is well below SEMI F63-0701 [9] and SEMI E49.3-0298 [10], particle contribution guidelines.
- Averaged acid cleaned flow-sensor metal results show deionized water baselines of ≤ 0.1 ppb contaminants/flow-sensor. This is also well below SEMI F63-0701 [9] and SEMI E49.3-0298 [10] guidelines, proving acid leaching with HNO₃ and HF, to be highly effective in removing both metallic and particle contaminants.
- McMillan’s UHP flow-sensors are ready for installation in any UHP semiconductor application, thus saving manufacturers expensive cleaning or rinsing downtime before installation.

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