Trace Metals Analysis: Strategies to Minimize Your Analytical Blank

How to minimize contamination from the labware used during elemental analysis process, as well as technologies that can lower prep blank, improve data quality, and maximize lab efficiency.

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INTRODUCTION

New regulations, fundamental research needs, and QA/QC requirements are all driving trace metals laboratories to achieve ever lower levels of detection. As such, the transition to more sensitive analytical instrumentation has been necessary. Most commonly, inductively coupled plasma mass spectrometry (ICP-MS) is utilized for this purpose. Given the higher sensitivity of this technique, minimizing interference from the analytical blank has become absolutely crucial. Fortunately, there are straightforward ways to minimize contamination from the labware used during the elemental analysis process, as well as several technologies that can lower the prep blank, improve data quality, and maximize lab efficiency.

Numerous factors can impact the quality of an analytical blank, including airborne contamination in the laboratory environment and the method of sample preparation, such as open vessel digestion versus microwave. In addition, the materials with which the sample comes in contact throughout the analytical process and the purity of reagents can significantly affect the results. For trace and ultra-trace metals analysis, the method of cleaning labware components between runs is absolutely critical. Analysts also play an important role in the level of contamination.

MATERIALS USED FOR TRACE LEVEL ANALYSIS

Labware for trace metals analysis comes in a variety of different material types. Glass is probably the most common and certainly the least expensive, however it is the worst choice for trace metals analysis because it has the highest concentration of trace metal impurities. Hydrocarbon polymers such as polypropylene and polyethylene are typically an improvement

Figure 1: Extractables from fluoropolymers.

- Measurement of the total extractable metals from the fluoropolymer surface
  - *TFM is a modified PTFE
- Piece of each material placed in a solution of 2% HNO_3/1% HF
  - Solution Temp: 50°C
  - Period: 2-weeks
- Solution analyzed by ICP-MS
- PFA /FEP significantly cleaner than PTFE/TFM for all elements analyzed
  - PFA **lowest total impurities**

	PFA pg/cm^2	FEP pg/cm^2	TFM pg/cm^2	PTFE pg/cm^2
B	5	1	<20	<20
Ca	5	8	60	50
Fe	4	9	90	80
Zn	1	1	8	30
Na	2	2	40	30
Mg	1	1	30	10
Cu	<1	1	30	10
Pb	<1	<1	1	<1
Al	4	2	90	50
K	<1	<1	<30	<30
Cr	1	3	8	6
Ni	4	8	30	20

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over glass, but they are still not pure enough for low level measurements. Although their cost is higher, fluoropolymers are ideal materials for trace metals analysis due to their very low levels of impurities.

Polytetrafluoroethylene (PTFE), like all fluoropolymers, is chemically inert, has a low coefficient of friction, and is very temperature resistant, with a working range of -73 °C to 260 °C. Unfortunately, it is opaque and can suffer distortion, making it less amenable for labware use. The biggest challenge with PTFE, however, is that it cannot be molded; PTFE parts must be machined or pressed together. Thus, relative to other fluoropolymers, PTFE tends to have the highest levels of trace metal impurities. In addition, because of how parts are manufactured, PTFE also tends to have a very rough surface, which means that it can be difficult to clean, thereby leading to the potential for carryover of contaminants to subsequent runs.

Perfluoroalkoxy (PFA) is a copolymer derivative of PTFE and is similar to PTFE in many ways. One of the biggest differences is that it is melt processible, allowing it to be injected or blow molded. These types of manufacturing minimize the level of trace metal impurities and give the parts very smooth surface finishes, thus minimizing the potential for memory effect between samples. It is almost transparent and offers a working range of -270 °C to 260 °C. A less common fluoropolymer, fluorinated ethylene propylene (FEP) is another very clean material for trace metals analysis. Its properties are very similar to PFA, however its working temperature range of -270 °C to 200 °C is limited at high temperatures. Thus, for heated applications, PFA is the best material.

The total extractable metals from the surface of different fluoropolymers were measured after soaking pieces of PFA, FEP, PTFE, and TFM (a modified PTFE) in dilute acid solution at 50 °C for two weeks (1). The ICP-MS results tabulated in FIGURE 1 show that PFA and FEP had much lower levels of extractables than TFM and PTFE. In terms of total impurities, PFA exhibited the highest purity of all the fluoropolymers that were tested.

Savillex's unique supply agreements with both of the world's leading suppliers of

fluoropolymer resin allow them to offer a wide range of PFA labware. All of their products are made from PFA and are molded from virgin high-purity PFA resin. No regrind material (waste fluoropolymer arising from production) is used, nor is any additive or release agent. This ensures maximum purity of their products.

For cleaning PFA labware between uses, nitric acid works well for nearly all applications. Heated cleaning with high concentrations of HCl or HNO_3/HCl mixtures can cause white deposits to form on PFA, which is likely Cl ions replacing F ions on the surface of the polymer, and the material's properties are not impacted. It should be noted that scoring or marking the inside surface of PFA labware should be avoided, as any marks or indentations can trap contamination from the previous digestion and make cleaning difficult.

Acid cleaning is more critical for labware that is used in heated applications (i.e., sample digestion) because it has a tendency to swell and trap contaminants during cool down. Removal of the contaminants requires long periods of soaking or a heated cleaning method. The level of a cleaning method's aggressiveness is determined by the necessary blank levels for the measurement. For example, geochemists work at extremely low levels of detection, possibly even sub-ppt. Such applications require aggressive cleaning methods to ensure there is no crossover contamination between uses and that the lowest levels of detection can be achieved.

REAGENT PURITY

It is very important that the acid used in trace metals analysis has elemental concentrations that are well below the levels present in the sample. This is because the amount of acid used for digestion is significantly greater than the amount of sample being digested. As such, high-purity acid is required for ultra-trace metals analysis. There are three different grades of acid available. Reagent, or ppm grade, is the least expensive but the least pure. Trace metal grade, which may be referred to as ppb or 1 ppb grade acid, contains fewer impurities, but is nonetheless not pure enough for trace metals analysis. Ultra-trace or high purity, 10 ppt grade acid has the highest purity, that is necessary for quantification of trace metals. However, its cost is considerably higher, often as much as ten-fold that of lower grade acids. Moreover, high-purity acids are easily contaminated during repeated opening of the container.

It is very important that the acid used in trace metals analysis has elemental concentrations that are well below the levels present in the sample.

High-purity acid is made from a process of sub-boiling distillation, a simple process in which the acid is gently heated to produce vapor. The vapor is extremely high purity and is collected to produce the high-purity acid. However, in sub-boiling distillation, as the name implies, the heating must be very gentle. If the acid boils, aerosols can be created and contamination in the acid reservoir can be transferred to the vapor itself.

For chemists who would like to save money and purify their own acid, Savillex has a series of acid purification systems called the DST Series. These systems are made from all PFA components, avoiding the potential for contamination from the system. As self-contained units, no external cooling source is required. The DST Series purifies trace metal (1 ppb) grade nitric acid, HCl and HF. In a

Figure 2: Purification of trace metal grade nitric acid in the DST-1000 in a single distillation.

- Customer in semiconductor industry
- Trace metal grade HNO_3 purified in DST-1000
  - Temperature setting of "HI"
- Single distillation
- Analysis by Agilent 8800 ICP-MS
- HNO_3 purified in the DST-1000 was equivalent to, or in some cases better than, commercially available high purity HNO_3 (10 ppt)

Analyte	Detection Limit	High Purity HNO3 (10 ppt	DST Produced HNO3
Li	1	<1	<1
Na	1	1	<1
Mg	1	2	<1
Al	1	1	<1
K	1	5	<1
Ca	1	7	<1
Cr	1	7	1
Fe	1	6	4
Ni	1	<1	<1
Cu	1	<1	<1
Zn	1	<1	<1
W	1	<1	<1
Mn	1	<1	<1
Ti	1	<1	<1
Co	1	<1	<1
Sb	1	<1	<1
Ag	1	<1	<1
Au	1	<1	<1
Pt	1	<1	<1
In	1	<1	<1
Mo	1	2	<1
Be	1	<1	<1
V	1	1	1
As	1	2	2
Cd	1	<1	<1
Cs	1	<1	<1
Ba	1	<1	<1
Pb	1	<1	<1

single distillation, trace metal grade acid can be purified to levels as good as, if not better than, commercially available high-purity acid. In addition to acids, the DST systems can also be used to purify water. The systems are user friendly, self-serviced, and have a high return on investment (ROI), paying for themselves in just a few months.

The DST series comprises two models: the DST-1000 and the DST-4000. The systems are very similar, with just a few small differences. The DST-1000 is a 1-liter fill whereas the DST-4000 has a 4-liter capacity. The distillation rate on the DST-1000 is about 500 mL of high-purity acid in 12 hours. The DST-4000 production rate is double that, approximately 1-liter of high-purity acid in 12 hours. Moreover, while the DST-1000 has a simple temperature controller, the DST-4000 features a very precise digital temperature controller. The DST-4000's automatic shutoff sensor allows for completely unattended operation as well. Both systems offer easy acid addition and removal with conveniently located front fill tube and stopcock.

A Savillex customer in the semiconductor industry compared the performance of the DST-1000 with commercially available high-purity acid. Using the "HI" temperature setting, trace metal grade nitric acid was purified in the DST-1000 in a single distillation. As shown in FIGURE 2, the purity of the resulting acid was better than or equal to the purchased high-purity acid. The cost savings associated with buying and purifying lower grade acid rather than procuring expensive high-purity acid is significant. A calculation of the ROI for the DST-4000 in a large laboratory using 5 L high-purity nitric acid per month at an expense of $500 per liter has been compared to using the DST-4000 to purify trace metal grade acid at $40 per liter. Implementation of the DST-4000 in this case would save $73,000 over the first three years, after the unit pays for itself in only 4.5 months.

In addition to their cost effectiveness, the DST instruments are easy to use and ready to distill right from the box with no need for factory trained engineers for installation or

maintenance. Because the systems facilitate on-demand production of high-purity acid, laboratories using them always have access to freshly produced, high-purity acid. This is in contrast to purchasing costly high-purity acids, which begin to degrade immediately after opening. The lower expense afforded by the DST series allows chemists to use high-purity acid for other applications as well, including cleaning.

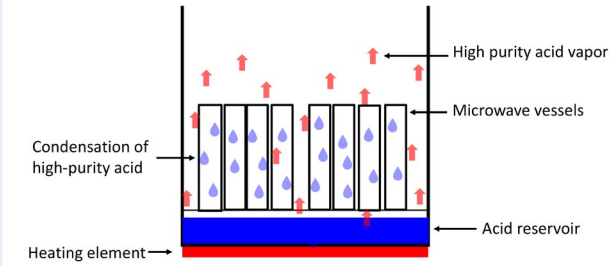
ACID CLEANING MICROWAVE DIGESTION VESSELS

Microwave sample preparation is a commonly used method for digesting samples before ICP-MS analysis. This preparation technique offers several advantages, including very high digestion temperatures which enable the digestion of even the most difficult sample types. In addition, it works with sealed vessels, thereby eliminating the potential for airborne contamination as well as accommodating very small acid volumes for lower blanks. Typically made from PFA or PTFE, a single microwave digestion vessel will be used to digest many hundreds of samples over its lifetime. Therefore, effective acid cleaning is required to eliminate the possibility of cross contamination. As previously mentioned, heated applications require more aggressive cleaning procedures.

The three primary cleaning methods for microwave digestion vessels are acid soaking, microwave cleaning, and acid vapor cleaning. Although inexpensive, acid soaking is labor intensive and low throughput. Safety is a factor as well, since the operator is directly exposed to large acid volumes. Finally, the cleaning solution itself can become a source of contamination.

Microwave acid cleaning is a popular, effective method for cleaning microwave vessels. The vessels are simply filled with 10–12 mL of acid and heated in the microwave, enabling the higher temperatures to provide more efficient cleaning than acid soaking. The process takes 2–2.5 hours. Microwave cleaning is not without its drawbacks, however. It significantly decreases microwave capacity as it is only being used for processing samples 50% of the time. Also, the expensive vessels are being exposed to high temperatures and high pressures, which shortens their lifetimes.

Figure 3: Acid vapor cleaning of vessels.



An excellent alternative to microwave cleaning is acid vapor cleaning, which leaves the microwave 100% available for sample preparation and minimizes wear on the microwave vessels. Based on the principle of sub-boiling distillation, acid vapor cleaning uses high-purity acid vapor from trace metal grade acid to clean digestion vessels at elevated temperatures. While the total cleaning time is 3-4 hours, much of that time is unattended so the analyst is free to perform other tasks. Since contaminants stay in the acid reservoir at sub-boiling temperatures, the acid can be reused. Exposure of the operator to concentrated acids is minimized as well. Although it is commonly used for cleaning microwave digestion vessels, it can also be used to clean other types of labware.

The acid vapor cleaning process depicted in FIGURE 3 shows a reservoir of acid being heated to produce extremely pure vapor. Vapor travels up the inside of the cleaning chamber, condenses on the inside and outside walls of the microwave vessels, and then fall back into solution. This results in a constant refluxing of high-purity acid vapor that efficiently rinses the vessels and accessories.

There have been several acid vapor cleaning systems on the market for many years. While effective, they all have faced the same challenges. Adding and draining acid is difficult and they have all been manufactured using metal components to some degree. In addition, they can be cumbersome to load and to unload, and their capacity tends to be quite small. The systems are relatively expensive, and most require factory-trained engineers for installation and maintenance. To address these issues, Savillex developed the VC Ultra, which was specifically designed for acid cleaning microwave digestion vessels. All wetted surfaces are manufactured from PFA or PTFE. Its large cleaning chamber accommodates up to 40 microwave vessels. The user-friendly system makes it easy to load and unload vessels and caps, and the front fill tube simplifies addition of acid. Easy drainage is through the front of the unit as well.

In the VC Ultra, high-purity acid vapor generated from trace metal grade HNO^3 cleans labware with unattended operation. The system's flexible configuration allows it to clean various types of microwave vessels. Additionally, a variety of cleaning racks are available to accommodate microwave vessels from the most popular microwave manufacturers. The system can also be easily configured to clean general labware, including beakers, vials, flasks, even ICP components with the Universal Labware Cleaning Kit. The kit is composed of a PFA grid with posts that can accommodate labware of different sizes. The VC Ultra also includes two removable shelves that are located on the top of the system. These shelves are perfect for microwave covers and plugs or any small components.

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Table I: Processing time—Savillex VC Ultra versus microwave

	VC Ultra (minutes)	Microwave (minutes)
System Loading	5	40
Cleaning Time	240	30
Cool Down	30	30
Unloading system	5	30
Rinsing Vessels	15	15
Total Processing Time:	**4 hours, 55 minutes**	**2 hours, 25 minutes**

- Microwave cleaning is faster than VC Ultra but note operator time needed: 25 min with VC Ultra vs 85 min for the microwave
- VC Ultra can be set to run overnight - simply unload and rinse vessels next morning

The VC Ultra uses an external color touchscreen controller which features 1-Click Start. Operators simply turn the system on, press the button on the screen, and the cleaning begins. The typical cleaning profile in the VC Ultra is anywhere from 3 to 4 hours. There are preloaded cleaning methods that range from 1 hour to 4 hours and a status indicator light on the controller displays the progress of the cleaning cycle. There is a manual cleaning mode as well. At the end of the cleaning run, the microwave vessel cleaning racks are removed from the system. A convenient vessel transport case allows the chemist to easily transport the cleaning rack from the system to a cleaning station while minimizing the potential for exposure to concentrated acid or fumes.

TABLE I compares cleaning times of the VC Ultra acid vapor system to microwave cleaning. At first glance, microwave cleaning appears to be less time consuming. However, the 25 minutes of operator time needed for the VC Ultra is far less than the 85 minutes required for microwave cleaning. Another advantage of the VC Ultra is that it can be set to run overnight; operators can simply unload and rinse vessels the next morning.

Table II: DST 1000 – Savillex Acid Purification System

	Al 167.019 nm ppb	As 188.980 nm ppb	B 249.772 nm ppb	Ba 455.403 nm ppb	Be 234.861 nm ppb	Cd 214.439 nm ppb	Co 228.615 nm ppb	Cr 205.560 nm ppb	Cu 213.598 nm ppb	Fe 238.204 nm ppb
Distilled Avg	-0.11653	0.077767	-0.01207	-0.0017	0.0001	-0.0021	0.007167	0.021033	-0.0043	-0.0409
Reagent Grade Avg	1.15785	0.1473	0.1992	0.00845	0.0002	-0.0021	-0.00185	0.01085	-0.01715	-0.0319

	K 766.491 nm ppb	Mg 280.270 nm ppb	Mn 257.610 nm ppb	Na 588.995 nm ppb	Ni 216.555 nm ppb	Pb 182.143 nm ppb	Sr 216.596 nm ppb	V 292.401 nm ppb	Zn 202.548 nm ppb
Distilled Avg	-0.0098	-0.08607	-0.00437	-0.04363	0.002333	0.007	-0.0075	-0.025	-0.0402
Reagent Grade Avg	0.00535	0.15905	-0.00315	0.5404	0.0041	-0.0074	0.07855	-0.015	-0.0194

Data generated using ICP-OES

USER EXPERIENCE WITH DST-1000 AND VC ULTRA

CEM, a world leader in microwave digestion, employs the Savillex DST-1000 and VC Ultra accessories for optimal lab efficiency. The DST-1000 is used in their labs to purify reagent grade acid, which is the lowest grade with the highest level of impurities. In one distillation run, the system reaches very low ppb levels of all the various elements. TABLE II compares the concentrations of impurities for purified and reagent grade acids. In this case, data was generated using ICP-OES. This purification saves considerable expense by avoiding the purchase of high-purity acid. An ROI calculation revealed that the system paid for itself in just over six months, with more than $21,000 saved in the first three years, after allowing for the cost of the system. Due to its efficiency and high ROI, CEM has added another DST-1000 to their analytical laboratory.

A blank experiment was performed by CEM to evaluate the VC Ultra acid vapor cleaning system. The study involved the digestion of NIST SRM 1575 pine needles, which contains high levels of metals. After digestion, the vessels were quickly rinsed with deionized water, placed in the cleaning system, and then cleaned overnight. Subsequently, 10 mL nitric acid was added to each vessel, digested, diluted, and run as a blank by ICP-OES. The blank was treated as a full digested sample under rigorous conditions to see if any contaminants from the pine needles could be extracted from the vessels. As tabulated in TABLE III, very low ppb levels were observed as well as levels below the detection limit, thereby demonstrating the success of the VC Ultra. The laboratory later discovered that 4-hour cleaning runs were just as effective, and now uses the VC Ultra for the majority of their vessel cleaning.

CONCLUSION

Detection limits and data quality are heavily impacted by the cleanliness of labware, reagents, and other factors. Clean sample

CEM, a world leader in microwave digestion, employs the Savillex DST-1000 and VC Ultra accessories for optimal lab efficiency.

Table III: Cleaning Study Results

As 188.980 nm ppb	B 249.772 nm ppb	Ba 455.403 nm ppb	Be 234.861 nm ppb	Cd 214.439 nm ppb	Co 228.615 nm ppb	Cr 205.560 nm ppb	Cu 213.598 nm ppb	Fe 238.204 nm ppb
0.0227	0.165	0.00217	nd	nd	0.0096	0.0256	0.0065	0.0675

K 766.491 nm ppb	Mg 280.270 nm ppb	Mn 257.610 nm ppb	Na 588.995 nm ppb	Ni 216.555 nm ppb	Pb 182.143 nm ppb	Sr 216.596 nm ppb	V 292.401 nm ppb	Zn 202.548 nm ppb
0.551	0.153	nd	0.587	nd	0.128	0.00673	nd	0.354

Data generated using ICP-OES

preparation techniques are essential for minimizing impurities in the analytical blank, while the materials used for labware and equipment play a significant role as well. Available from Savillex, labware made from PFA has the lowest levels of impurities and are recommended for all trace metals analyses. Also critical is the use of high-purity acids, which can be very expensive. Savillex's DST Series of acid purification systems allows chemists to easily purify less costly, lower grade acids to generate high-purity acid at a fraction of the price. In addition, since microwave digestion vessels typically see hundreds of samples, their thorough cleaning is vital in order to avoid cross contamination. The VC Ultra is a highly effective option for unattended acid cleaning of vessels and a variety of other labware. With these means of achieving maximum cleanliness, laboratories can now confidently face the challenges of ever decreasing detection limits for trace metals analysis.

Image Courtesy of Savillex

REFERENCES

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