TECHNIQUES FOR IMPROVED ICP-OES AND ICP-MS ANALYSIS

Achieving the Lowest Possible Detection Limits with ICP-OES and ICP-MS by Minimizing Contamination in Sample Preparation

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The increasing demand for lower and lower detection limits is a major consideration for any laboratory performing trace metals analysis. The development of sophisticated instrumentation, such as ICP-OES and ICP-MS, provides the capability to achieve multielement limits of detection previously unobtainable by other atomic spectroscopy techniques. However, the analytical instrument is just one component in achieving the lowest limits of detection using plasma spectrochemistry. The other critical area that puts significant demands on a laboratory's overall detection capability is to ensure that the sample preparation procedure does not contribute any additional sources of contamination. Several factors must be considered when looking to minimize contamination and reduce blank levels while preparing samples for analysis by plasma spectrochemistry. These factors include laboratory cleanliness, reagent choice and purity, quality of materials used, and the digestion procedure itself.

Before we evaluate these sample-handling factors, let's first examine how detection limits are measured so we can better understand the impact of background (BG) levels on the overall analytical method detection capability.

DETECTION LIMITS

The detection capability of an instrument can be defined by several different criteria including instrument detection limit (IDL), method detection limit (MDL), limit of quantitation (LOQ), and background equivalent concentration (BEC). Each of these terms is defined a bit differently, but all four are affected by the analyte signal, the BG intensity, and the BG noise. Let's take a look at instrument detection limit (IDL), which is broadly defined as the concentration of the analyte that generates a signal intensity of three times the standard deviation (SD) of the BG noise of the calibration blank at the analyte mass/wavelength. IDL is typically calculated using the following equation:

$$\text{IDL} = \frac{3 \text{ x SD of BG noise of blank x analyte conc.}}{\text{analyte signal - BG signal of blank}}$$

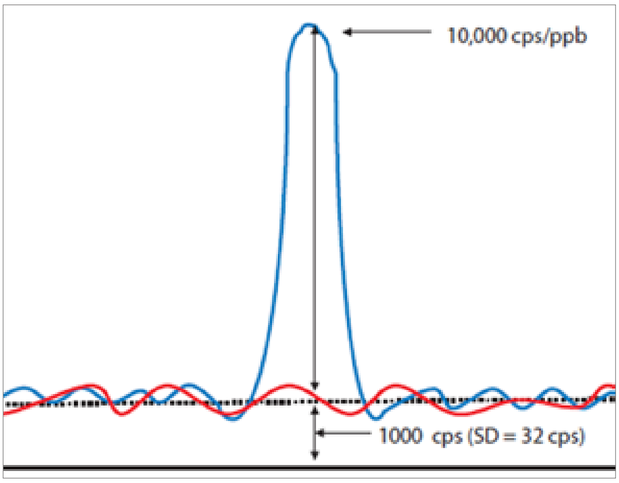

Figure 1 - The importance of the background signal/noise of the blank (red) compared to the analyte intensity (blue) when measuring detection limit.

Where the BG noise is expressed as the square root (√) of the BG signal of the blank and SD is usually based on 7–10 replicates of the blank, depending on the methodology used.

Figure 1 exemplifies the importance of the blank's BG signal (red line), and whether it is either structured spectral BG or due to a contaminated blank. It can be seen that a concentration of 1 ppb analyte (blue) produces a signal of 10,000 counts per second (cps), while the intensity of the blank signal is 1,000 cps. If we apply the above equation, we get an IDL of 0.011 ppb as shown below:

$$\text{IDL} = \frac{3 \text{ x } \sqrt{1{,}000} \text{ x 1 ppb}}{10{,}000 - 1{,}000} = 0.011 \text{ ppb}$$

However, if the BG signal was 10 cps instead of 1,000 cps, the IDL would be 0.0009 ppb, approximately 12x lower, as shown by the equation below:

$$\text{IDL} = \frac{3 \text{ x } \sqrt{10} \text{ x 1 ppb}}{10{,}000 - 10} = 0.0009 \text{ ppb}$$

Clearly, the BG level and noise have a direct impact on the achievable detection limit using plasma spectrochemical techniques. For that reason, anything that can be done to reduce the sources of contamination will have a beneficial effect on improving the method detection capability. With that in mind, let's examine the "Clean Chemistry" tools available from Milestone that can reduce contamination in every stage of the sample preparation process for trace element analysis.

STRATEGIES FOR REDUCING SAMPLE PREPARATION CONTAMINATION

Overall cleanliness in a laboratory is important to prevent contamination and analytical errors resulting from high or inconsistent blank levels. Contamination can come from several sources, but two basic areas to monitor are reagents and materials used in the analysis process. In a typical trace metals laboratory, acids are used throughout—cleaning, preparing standards and blanks, and digesting samples. Different grades of acid are available for purchase, but careful consideration is required when selecting the appropriate grade. The detection limit and analytical requirements will dictate the necessary acid grade, but as the contaminant levels go down, the cost of the acid can increase quite dramatically. One way to address this problem is to invest in technology such as the duoPUR sub-boiling distillation system to purify lab-grade acids and reagents in-house, so contaminant levels are more in line with higher purity reagents, without requiring the laboratory to purchase significantly higher-priced acids.

Additional sources of contamination can also come from glassware and plastic containers that are used for sample preparation, particularly in high-throughput labs that are processing large numbers of samples. If the containers and vessels are not cleaned thoroughly, they can contribute to contamination resulting in high blank levels. For that reason, technology such as the fully automated traceCLEAN closed-vessel acid reflux cleaning system is well-suited for the demands of a high throughput ICP-OES/ICP-MS sampling environment.

Finally, one major consideration is the sample digestion procedure itself. It is important that the samples be completely dissolved and all elements of interest be available in solution, without risk of contamination. For many sample types, heating in an open vessel, such as hot plates or hot blocks, is insufficient to provide a consistent dissolution due to the modest temperatures achieved. These digestion methods are also very time-consuming, labor-intensive, and suffer from high contamination risks. With the introduction of closed-vessel digestion techniques—such as those used in modern microwave sample preparation systems—high temperatures can be achieved using elevated pressures within the vessels. Additionally, the combination of elevated temperatures and pressures using microwave heating provides shortened sample preparation cycles, all in a sealed vessel that eliminates exposure to cross-contamination. Advanced microwave digestion systems such as the ETHOS UP and the ultraWAVE provide excellent sample preparation for trace metals analysis and help to minimize contamination from sampling components and cross contamination between samples, which is extremely challenging for other microwave digestion systems.

Let's examine the various approaches offered by Milestone that are used to minimize sample preparation contamination, including acid purification, acid reflux cleaning, and the advanced microwave digestion sampling components and accessories.

ACID PURIFICATION

The chemical reagents used during the analysis are an important source of the analytical blank. Sub-boiling distillation such as the duoPUR has been demonstrated

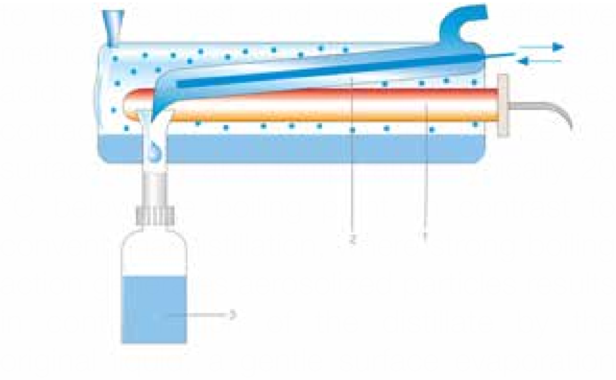

Figure 2. duoPUR acid purification system

during sub-boiling distillation prevents the formation of spray or droplets and yields a very high-purity acid.

The duoPUR sub boiling distillation system shown in Figure 2 consists of two quartz distillation units. Each unit contains two infrared heating elements (1), a water-cooled condenser (2), a high-purity PFA collection bottle (3), and a fully automated acid loading/ discharge system. The vaporized liquid is collected on the inclined water-cooled condenser and drips into the collection bottle. The double distillation process is microprocessor-controlled, allowing the user to set the distillation time and power allowing for a distillation rate up to 200 mL per hour, depending on the power setting and the temperature of the cooling water.

The purification capability of the duoPUR system is exemplified in Table 1, which compares trace element results from two labs carrying out the double-distillation of reagent-grade nitric acid with that of Ultrex II nitric acid from J.T. Baker. It can be clearly seen that duoPUR data shows comparable results to the ultra-high purity acid.

Milestone also offers the subCLEAN, an acid purification system that is made of high-purity fluoropolymers instead of quartz, which is

	Customer 1	Customer 2	Baker Ultrex® II
Element	Concentration (ppt)	Concentration (ppt)	Concentration (ppt)
Ag	16	<5	<10
Al	<10	119	<20
As	19	<1	<20
Au	38	–	<20
B	<10	–	<10
Ba	<10	2	<10
Be	22	<0.5	<10
Bi	25	–	<10
Ca	<10	–	<10
Cd	<50	<1	<10
Co	<10	<1	<10
Cr	<10	3	<10
Cu	<10	10	<10
Fe	<10	<65	<10
Ga	<10	–	<10
Ge	<50	–	<10
In	<10	–	<1
K	<10	32	<10
Li	<10	–	<10
Mg	<10	19	<10
Mn	12	2	<10
Mo	22	<1	<10
Na	<10	–	<10
Nb	<10	–	<1
Ni	<10	9	<20
Pb	31	2	<10
Pd	<50	–	<20
Pt	<50	–	<20
Re	<10	–	<10
Rh	<10	–	<10
Ru	<10	–	<20
Sb	18	<1	<10
Sn	11	6	<20
Sr	<10	–	<10
Ta	<10	–	-
Ti	<50	6	<10
Tl	<10	<1	<10
V	<10	<1	<10
W	<10	–	<10
Zn	<10	12	<10
Zr	14	–	<10

Table 1. Comparison of contamination levels of double-distilled HNO_3 using the duoPUR with that of Ultrex II (J.T. Baker) ultra-high purity nitric acid.

suitable for the purification of HF, as well as for HNO_3 and HCl. The acid is automatically loaded into the distillation container, where it is gently heated below its boiling temperature as previously described. In addition, the subCLEAN does not require cooling water or a chiller, as acid vapors rapidly condense into a collection bottle by forced air cooling.

It's also worth pointing out that there are significant cost savings when using the duoPUR, compared to purchasing high purity reagents. This is demonstrated in the following example (all costs provided as estimates for example purposes only): If a laboratory processes 200 samples per month using 30 mL of ultra-pure nitric acid (J.T. Baker Ultrex II) per sample, it will use 6 L of ultra-pure acid at a cost of approximately \$5,500 per month or \$920 per liter per month. Six liters of reagent-grade acid (Sigma Aldrich) would only cost approximately \$250 per month or \$40 per liter per month. By distilling this lower grade acid, \$5,300 would be saved every month, which translates to the duoPUR paying for itself in less than four months. This is demonstrated in Table 2, which shows the cost saving for both nitric and hydrochloric acid.

Mineral Acid	Ultra Pure Grade per Liter (J.T. Baker Ultrex II)	Reagent Grade per Liter (Sigma Aldrich)
Nitric Acid	\$920	\$40
Hydrochloric Acid	\$890	\$40

Table 2: Comparison of approximate cost per liter between ultra-pure grade nitric and hydrochloric acid (J.T. Baker Ultrex II) and producing it from-grade reagents (Sigma Aldrich) using the duoPUR sub-boiling distillation system.

ACID REFLUX CLEANING

Cleaning various items used in ultra-trace analysis work is a critically important laboratory routine. To minimize contamination, traditional cleaning methods require soaking items in hot acids, often for several hours. To be effective, large volumes of acid are consumed and need to be changed regularly. There is also a substantial risk of exposure to hot acids and acid vapors using traditional soaking techniques. This is particularly the case when trying to achieve high-quality blanks when using microwave digestion procedures, as pre-cleaning the vessels is critically important. However, it is not sufficient to simply wash or soak vessel liners in dilute acid. The surface of PTFE is porous and will take up trace amounts of digest solution at elevated temperatures, especially as it "ages" with continued use. Running a blank in a vessel previously used to digest a sample, without thorough cleaning, will lead to serious blank contamination.

To circumvent issues associated with acid soaks, and to more thoroughly clean microwave digestion vessels, labs may choose to perform a separate cleaning run (with blank acid) in the microwave prior to each sample digestion run. The downside is that this significantly reduces the sample processing capacity of the microwave system and impacts the vessel lifetime. So in order to address these issues, Milestone has developed the traceCLEAN, a fully automated, self-contained, acid steam cleaning system that can not only be used for cleaning microwave digestion sample vessels and containers, but also for other accessories, glassware and components that are used with the ICP-OES and ICP-MS instrumentation.

So how does the system work? The items to be cleaned are placed in the traceCLEAN, where freshly distilled acid vapors continuously reflux within the sealed unit, thoroughly leaching any metal contaminants from the items. Various holders are available for vials, microwave digestion vessels, flasks, glassware, and ICP sample introduction components, such as torches, nebulizers, or spray chambers. Steam cleaning with nitric acid vapors is a highly effective cleaning method for preconditioning and routine cleaning of containers and apparatus. The component to be cleaned is placed over a PTFE-coated glass rod. Acid in the lower reservoir is heated, and purified acid vapor travels up through the glass rod and condenses on the container, removing surface contamination as shown in Figure 3.

> “The items to be cleaned are placed in the traceCLEAN, where freshly distilled acid vapors continuously reflux within the sealed unit, thoroughly leaching any metal contaminants from the items.”

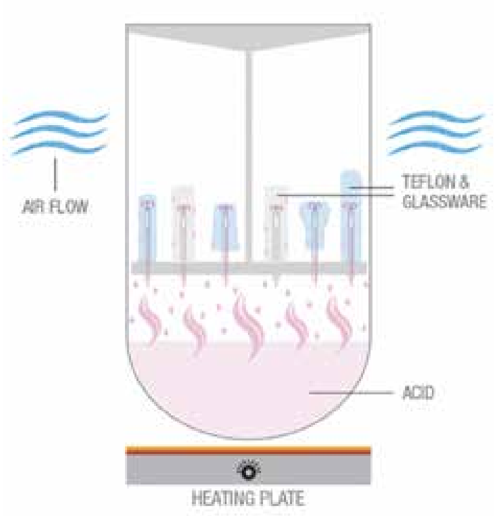

Figure 3: Schematic of the traceCLEAN acid reflux cleaning system

MICROWAVE DIGESTION COMPONENTS

Traditional, state of the art closed vessel microwave digestion instruments, such as the ETHOS UP and the ultraWAVE Single Reaction Chamber (SRC) system have all been designed with “Clean Chemistry” technology in mind. Digestion vessel material is a key consideration for clean chemistry sample preparation. Milestone engineers all its digestion vessels from either glass, quartz or TFM, a high-density and thermally resistant form of PTFE, which can withstand higher temperatures (up to 300 °C). TFM is chemically inert to most dissolution reagents and provides a non-contaminating environment for ultra-trace metals analysis. All ETHOS UP rotors including the SK-15 high-pressure rotor and the MAXI-44 high throughput rotor also feature vessels with liners manufactured from high-purity TFM, minimizing absorption of vapors and liquids over time, which can negatively impact the digestion blank. In addition, smaller TFM inserts can be used inside the standard 100 mL TFM vessels to accommodate smaller samples or to minimize the dilution factor and the contact surface.

QUARTZ INSERTS

However, the ultimate vessel material for producing low-digestion blanks is quartz. Quartz is available with very low levels of metal impurities, does not absorb vapor or liquid, and is easy to clean. The high-pressure SK rotor is often used with 35 mL quartz inserts that fit inside the standard TFM vessels. The sample is weighed into the quartz insert and acid is added. Due to the smaller volume, less digestion acid can be used (only 2–4 mL), which reduces the

digestion blank. Since the sample is digested in the quartz insert, the TFM vessel does not need to be cleaned and lasts longer. An additional benefit of using quartz inserts is the ability to use higher weights of organic samples. The insert sits in 10 mL of a water/H_2O_2 mixture. During the heating cycle, H_2O_2 reacts with the gases CO_2 and NO_x produced during digestion, greatly reducing pressure buildup in the vessel. This allows higher weights of organic samples to be digested, especially with complex matrices such as oil and coal samples.

All ETHOS UP rotors can accommodate high-purity quartz vessels which are ideally suited for ultra-trace analysis. The benefits of lower acid volume, elimination of vapor and liquid absorption by the vessel walls, and easy cleaning all apply equally well to the different rotor configurations, as all vessels have indirect temperature control via an IR sensor (Milestone's easyTEMP), and because quartz is transparent and has excellent heat-conduction properties, IR temperature monitoring is both very accurate and fast.

SINGLE REACTION CHAMBER (SRC) MICROWAVE DIGESTION VIALS

Clean Chemistry technology has been incorporated in the ultraWAVE through the design of its sample vials. Unlike rotor-based closed vessel digestion where samples are digested in individually pressurized vessels, the ultraWAVE's Single Reaction Chamber itself is the pressure vessel. Samples are weighed into simple autosampler-type vials available in glass, TFM, or quartz and placed in a rack. The rack is lowered into the chamber, and all samples are digested together. The benefit of glass is that it is disposable, but for the lowest digestion blanks, TFM or quartz should be used, both of which give extremely low blanks. Digestion acid volumes of only 1-4 mL further reduce the digestion blank. Since the pressure in the vials is the same as the main chamber, absorption of vapor or liquid by the walls of the TFM vial is virtually eliminated. It should be noted that the ultraWAVE vials have loose-fitting TFM caps which allow for very easy handling. This is possible because the larger vessel which holds the vials is pre-pressurized with 40 bar of nitrogen prior to the start of the microwave program. This nitrogen load acts as a "gas-cap" and keeps all the vials independently closed. As the pressure builds, equilibrium is achieved both inside and outside the individual vials. As a result, a variety of vial types including disposable glass, quartz, TFM, or any combination thereof, can be used.

The extremely low digestion blank of TFM is exemplified in Figure 4, which shows ultraWAVE digestion blanks (4 mL high-purity HNO_3 diluted to 20 mL with DIW) obtained for 26 elements in glass, quartz and TFM vials. All digestions and measurements were performed in non-cleanroom conditions using an Agilent ICP-MS system. The trace metal content of the digestion blank can arise from impurities in the acid and/or water, contribution from the vials, airborne cross contamination, or from the ICP-MS sample introduction system. Only four elements were found to be greater than 1 ppb. The highest levels were for B and K, which were present in both vials, suggesting the source is not the vial material.

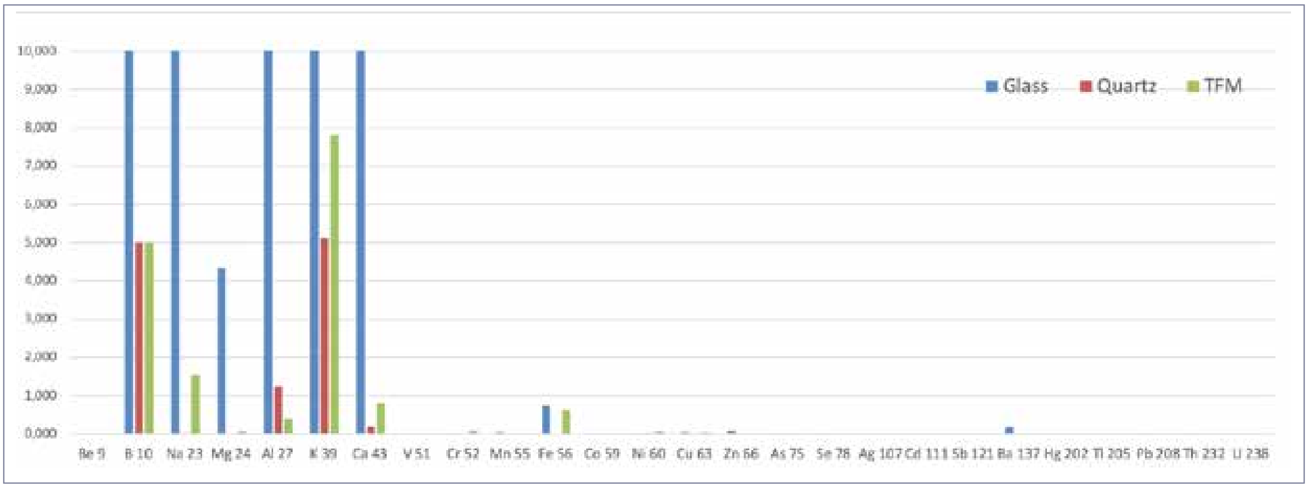

Figure 4: ultraWAVE microwave digestion blanks (4 mL high-purity HNO_3 diluted to 20 mL with DIW) obtained for 26 elements in glass, quartz and TFM sample vials, clearly showing the benefits of using TFM to carry our ultra-trace analysis (all data generated with an ICP-MS system)

FINAL THOUGHTS

It is widely accepted that sample handling and preparation must evolve and improve to meet the same high standards as plasma spectrochemical instrumental techniques. Several external factors can critically impact the quality of the data, including reagent purity, sample preparation methodology, materials used to prepare the sample, the environment in which the samples are prepared, and sample to sample cross contamination. The significant role of the analytical blank in the determination of trace metals therefore cannot be overemphasized, which means that sample preparation procedures must be at least as sophisticated as the instrumentation used in the measurement process.

This study has demonstrated that ultra-trace analysis is as dependent on minimizing contamination and controlling the analytical blank as it is on the accuracy and precision of the instrument carrying out the analysis. When working at ppb and ppt levels using ICP-OES or ICP-MS, the higher the blank and the worse the BG noise, the poorer the detection capability. To address these issues, Milestone has developed a wide range of products, accessories, and consumables to support clean chemistry sample preparation and address the multitude of challenges faced by the modern analytical laboratory when carrying out ultra-trace elemental analysis.

Robert Thomas is the principal of Scientific Solutions, a consulting company that serves the application and writing needs of the trace element user community. He has worked in the field of atomic and mass spectroscopy for more than 40 years and has written over 90 technical publications including a 15-part tutorial series on ICP-MS. He recently completed his fourth textbook entitled Measuring Elemental Impurities in Pharmaceuticals: A Practical Guide. He has an advanced degree in analytical chemistry from the University of Wales, UK, and is also a Fellow of the Royal Society of Chemistry and a Chartered Chemist. He has led the heavy metals, plasma spectrochemistry task force on the ACS Committee on Analytical Reagents.