CLEAN CHEMISTRY TOOLS

WHAT IT TAKES TO ACHIEVE THE LOW ANALYTICAL BLANKS NECESSARY TO PRODUCE GOOD ICP/ICP-MS DATA

by Tim Michel and Don Potter

In recent years there have been continued developments in instrumentation for trace metals analysis—particularly in ICP-OES and ICP-MS. Current ICP-OES instruments are capable of ppt level detection limits for many elements, while the development of collision/reaction cells (CRCs) in ICP-MS has greatly reduced spectral interferences, enabling ICP-MS to be applied to the most complex sample types and to a wider range of digestion acids. Both of these developments have, in turn, placed greater demands on the sample preparation step, especially on microwave digestion, which is being used more widely as a sample digestion technique for ICP-MS. The greater sensitivity of ICP-MS in particular means that the quality of the analytical blank is critical to generating high-quality data. The application of instruments and strategies to reduce the sample prep blank is often called the application of Clean Chemistry techniques. This article highlights the factors impacting blank quality, in particular when microwave digestion is used, and reviews some Clean Chemistry products and technologies designed to help the analyst generate superior analytical data.

"The significant role of the analytical blank in chemical analysis of trace metals cannot be overemphasized. Sensitive instrumentation such as ICP-MS, ICP-AES, and GFAA requires that sample preparation be at least as sophisticated as the instrumentation used in analysis. ... Trace analysis is as dependent on control of the analytical blank as it is on the accuracy and precision of the instrument making the measurement."

- US EPA SW-846, Chapter 3, Update IVB

Sources of contamination: Sample prep to analysis

Considering a routine lab (non-cleanroom environment) performing microwave digestion prior to trace metal analysis, there are a number of potential sources of contamination that can be broken down generally into the following:

ITEM/STEP	SOURCE
Reagent Purity	Deionized water and digestion acid quality
Vessel Cleaning	Cleanliness of digestion vessels, sample intro components
Microwave Digestion	Vessel/vial material, acid volume

Reagent purity

Blank contribution due to impurities in the reagents used—deionized water (DIW) and digestion acid—is well known. For DIW, a modern DI water system with a reverse osmosis column should be used. The system should be well maintained and preferably fitted with a footswitch for easy operation and to avoid contamination of the tip of the water dispenser. Monitoring the boron blank is a good way to check the condition of the column because boron breakthrough occurs first as the column reaches the end of its useful life. Correct choice of digestion acid grade (and the acid used to prepare standards and rinse solution) is a more challenging issue. Traditionally, trace metal (TM) grade acid, which typically contains impurities of 1ppb or less, has been used for acid digestion and also generally for preparing dilute stock solution for sample dilution and standards prep in ICP-OES. ICP-MS users typically use high-purity-grade acid (typically 10-50 ppt impurities) for sample dilution and standards prep. At around $500 for 500mL, however, high-purity-grade acid is expensive. TM grade, at $50 for 500mL, is reasonably priced, but not quite clean enough for acid digestion when ICP-MS is used to measure the digests. Part of the problem is the packaging used for TM grade, which is polypropylene-lined glass. TM grade acid is specified at 1ppb for most elements *at the point of bottling*—it can be significantly higher after bottling. An alternative to buying high-purity acid is to apply Clean Chemistry principles and purify TM grade acid using a sub-boiling still such as the proprietary SubPUR or DuoPUR.

DuoPUR and SubPUR

Sub-boiling distillation is recognized as the best method to obtain high-purity reagents and the lowest blank values for ultra trace analysis. Sub-boiling distillation vaporizes a liquid by gentle infrared heating of its surface, avoiding boiling. This prevents the formation of aerosol or droplets. In conventional distillation, violent boiling action generates aerosolized droplets, resulting in contamination of the distillate. Surface evaporation by sub-boiling distillation prevents this, yielding a much higher purity distillate. The DuoPUR consists of two high-purity quartz distillation units (Figure 1), each comprising a heating element, water cooled condensers and a PFA collection bottle. The SubPUR is the same system, but with only one sub-boiling distillation unit. Distillation time and power level is selected. Infrared heating gently vaporizes the surface liquid, which condenses on an inclined cold finger and is collected in a PFA bottle.

Starting with low-cost reagent-grade acid, the DuoPUR can produce 1 liter of high-purity acid in approximately six hours, and the total cost of producing 5 liters of high-purity acid is around $90 —a significant savings. Thus the lab has an on-demand supply of high-purity acid, at a price that makes it viable for use in microwave digestion for ICP-MS *and* ICP-OES use, and even for cleaning components. When ICP-MS is used to measure microwave digested samples, the use of high-purity digestion acid will significantly reduce the analytical blank.

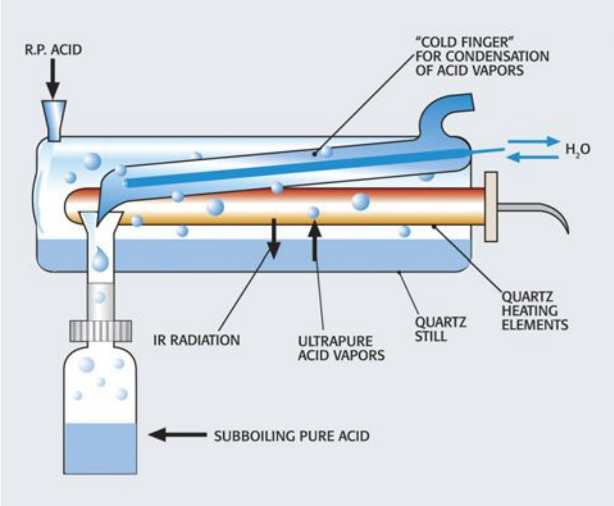

Figure 1. Schematic diagram of Milestone SubPUR/DuoPUR.

Vessel cleaning

To achieve high-quality blanks when using microwave digestion, pre-cleaning the vessels is critically important. It is not sufficient to 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 blank contamination. There are two ways to thoroughly clean a microwave digestion vessel. The traditional method is to perform a cleaning run (with blank acid) in the microwave prior to each sample digestion run. The downside is that this reduces the sample processing capacity of the microwave by approximately 50 percent. The Clean Chemistry approach, which is more productive and efficient, involves placing the vessels in a closed system containing high-purity acid vapor.

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TraceCLEAN

TraceCLEAN is an automated acid reflux system that thoroughly and safely cleans microwave digestion vessel liners. The system comprises a heated acid reservoir with a metal-free cleaning chamber above it (Figure 2). TraceCLEAN, like DuoPUR, uses the principle of sub-boiling distillation: only high-purity acid vapor comes into contact with the items to be cleaned. Trace metal contaminants present in the cleaning acid remain in the reservoir and do not come in contact with the cleaned items. Built-in exhaust/cooling prevents operator exposure to acid vapors, and the system is fully safety interlocked for unattended running. A cleaning run typically takes one hour, and cleaned items are cooled inside the system, preventing airborne contamination. TraceCLEAN can be used for the unattended cleaning of all TFM, PFA, glass, and quartz digestion vessels, and also for ICP sample introduction components such as spray chambers, torches, etc.

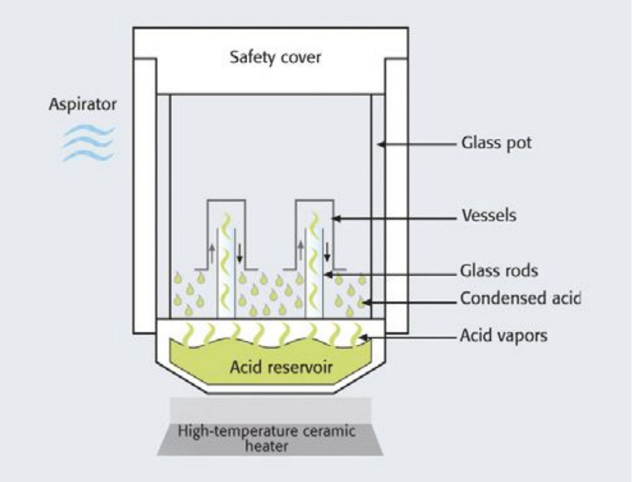


Figure 2. Schematic diagram of the TraceCLEAN.

Microwave digestion

Traditional closed vessel microwave digestion instruments, such as the Milestone ETHOS EZ and the Single Reaction Chamber microwave digestion instruments UltraWAVE and UltraCLAVE, all feature Clean Chemistry technology, but applied in different ways.

Quartz inserts for closed vessel microwave digestion

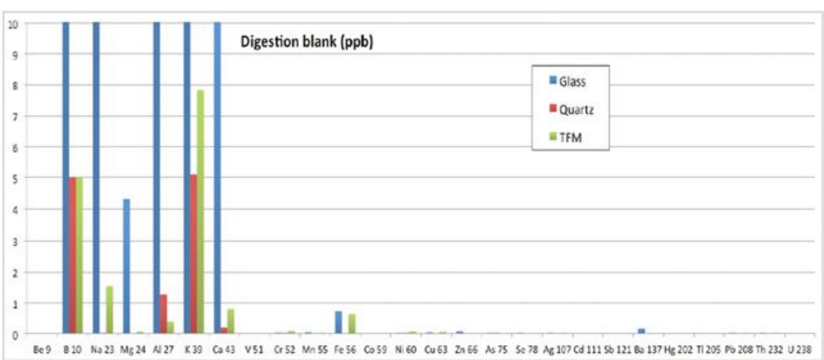
All ETHOS EZ rotors feature vessel liners manufactured from high-purity TFM, a high-density form of PTFE, which are able to withstand higher temperatures (up to 300°C). High-purity TFM is preferred to PFA for high-temperature digestions because its surface is more resistant to absorption of acid vapor and liquid. Absorption of vapor and liquid over time increases the digestion blank. However, the ultimate vessel material for producing low digestion blanks is quartz. Quartz has a very low level of metal impurities, does not absorb vapor or liquid, and is easy to clean. The high-pressure SK rotor is often used with 35mL 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 2-4mL), which reduces the digestion blank. Since the sample is digested in the quartz insert, the TFM vessel does not need to be cleaned and also lasts longer. An additional benefit of using quartz inserts is the ability to use higher weights of organic samples. The insert sits in 10mL of water/H_2O_2 mixture. During the heating cycle, the H_2O_2 reacts with the gases CO_2 and NOx produced during digestion, greatly reducing pressure buildup in the vessel. This allows higher weights of organic samples to be digested, especially with challenging samples such as oils.

Quartz vessels

An alternative to the use of quartz inserts is to manufacture the vessel liner itself in quartz. The ETHOS EZ Q-16 quartz rotor holds 16 high-purity quartz vessels and is ideally suited to ultratrace 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 Q-16 rotor. The Q-16 rotor also has an additional benefit: all vessels have indirect temperature control via IR sensor, and because quartz is transparent and has excellent heat-conduction properties, IR temperature monitoring is both very accurate and very fast. With the Q-16 rotor, direct temperature measurement is not necessary.

Single Reaction Chamber (SRC) microwave digestion vials

The UltraWAVE and UltraCLAVE are both SRC microwave digestion systems. Clean Chemistry technology has been incorporated in the SRC through the design of its sample vials. Unlike closed-vessel digestion, where samples are digested in individually pressurized vessels, with SRC the reaction chamber itself is the pressure vessel. Samples are weighed into simple autosampler-type vials and placed in a rack. The rack is lowered into the chamber, and all samples are digested together. Vials are available in glass, TFM, or quartz. The benefit of glass is that it is disposable, but for the lowest digestion blanks, TFM and quartz should be used, both of which give extremely low blanks. Digestion acid volumes of only 1-4mL further reduce digestion blank. Also, since the vials are not pressurized, absorption of vapor or liquid by the walls of the TFM vial is virtually eliminated. Vials have TFM caps to prevent airborne contamination during transfer. Figure 3 shows UltraWAVE digestion blanks (4mL high-purity HNO_3 diluted to 20mL with DIW) obtained for 26 elements in both quartz and TFM vials, measured using an Agilent 7500cx ICP-MS. Both digestion and measurement were performed in non-cleanroom conditions. The trace metal content of the digestion blank arises from impurities in the acid and water, contribution from the vial, airborne contamination, and finally, contribution from the ICP-MS sample introduction system. Only four elements were found to be greater than 1ppb. The highest levels were for B and K, which were present in both vials, suggesting the source is not the vial material.



▲ *Figure 3. SRC digestion blank data obtained from quartz and TFM vials.*

Summary

By applying the principles of Clean Chemistry, excellent analytical data can be generated from digested samples in a non-cleanroom environment using a microwave—even at ICP-MS levels, provided the necessary steps are taken. In addition to good technique and careful handling, the use of high-purity acid for digestion, correct choice of digestion vessel material, and care in vessel cleaning are all key to achieving the low analytical blanks necessary to produce good analytical data.

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