R.C. Richter - J.A. Nóbrega - C. Pirola

THINK BLANK

Clean Chemistry Tools for Atomic Spectroscopy

Milestone Press

To Franco and Werner with gratitude

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INORGANIC TRACE ANALYSIS: WHAT DO YOU MEAN?

Inorganic Trace Analysis: What do you mean?

"...minute precautions, maniacal cleanliness purity with eight zeroes, are things which make me suffer. I know very well that in some cases it is a matter of necessary measures, but I also know that, more than often mania prevails over common sense..."

Primo Levi, The Periodic Table

The role of the analytical chemist has not changed since the inception of the discipline. However, the questions for which society wants answers have become more challenging, demanding and the range of materials requiring analysis has changed dramatically. In a recent paper de Galan discussed this trend by pointing out that in the 1960´s we worked with mg/L range and a typical analytical challenge was the determination of lead in gasoline, in the 1970´s we moved to µg/L range and the determination of polycyclic aromatics represented a typical analytical task of this period, and in the 1980´s we reached ng/L when determining by dioxine in milk.[1] Another clear demonstration of the current demands on analytical chemists is the downward trend in the maximum allowed concentration of sulfur in diesel fuel correlated with the evolution and ability of inductively coupled plasma mass spectrometers (ICP-MS) to measure ppb levels on a routine basis.[2] Recently, the United States Pharmacopeia Convention (USP) and the

U.S. Food and Drug Administration (FDA) have initiated steps to replace the 100 year old colorimetric method (USP 231) for determination of heavy metal impurities with a new inductively coupled plasma-atomic (optical) emission and mass spectroscopy based methods (USP 232 and 233) by January 1, 2018.[3]

Based on these considerations, it seems more effective to look for a definition of trace analysis not directly correlated with a certain concentration range as was done in the past but one based on the limitations of obtaining reliable results. In this sense, Prichard et al. pointed out that trace analysis "would be defined more generally as applying to an analysis where the concentration of the analyte is low enough to cause difficulty in obtaining reliable results".[4] This definition was graphically illustrated by Horwitz et al. by showing the decreasing reliability of chemical analyses at lower concentration levels.[5] This graph became known as "Horwitz trumpet" (*Figure 1*).

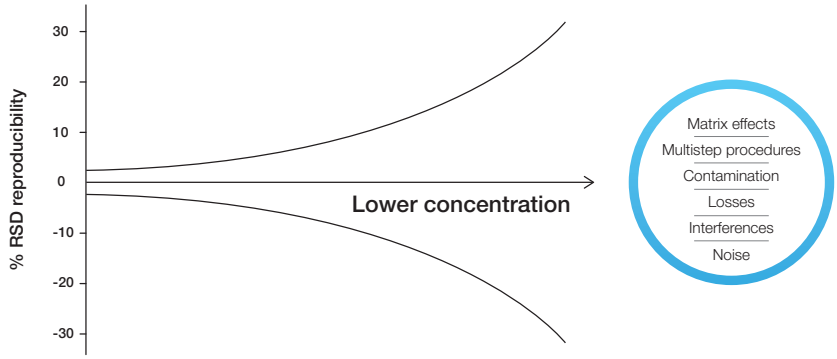


Figure 1. *Horwitz Trumpet*

These authors clearly show how coefficients of variation changes from 2 % for major nutrients to as large as 30-50 % for chemical species present in µg/kg range. This difficulty for reaching accurate and precise results was also highlighted by Howard and Stathan by

expressing that trace analysis is “an analytical procedure requiring special steps to be taken because of the low concentration of analyte which is present”.[6]

In this sense it is important to have a clear knowledge about sensitivity, limits of detection and limits of quantification. A reading of IUPAC definitions is strongly recommended and it becomes clear that sensitivity is directly the variation of the analytical signal with analyte concentration, i.e. in mathematical language the slope of the analytical calibration curve; on the other hand, limits of detection and quantification also involve the standard deviation for measurements of the blank and the method blank must be considered.[6] According to Howard and Stathan “the method blank assesses contamination which is introduced during the sample preparation and analysis. It is normally carried out by performing these operations on either no sample or a dummy sample which is known to be free of the analyte.” The method blank is more critical than both the instrument blank and the calibration blank. The former allows evaluating either memory effects or instrument fluctuations caused by different sources. The latter is related to impurities present in the reagents used for preparing analytical calibration solutions. Howard and Stathan also pointed out that the analytical blank is a cumulative factor and all efforts should be done for minimizing the number of handling steps in an analytical procedure.[6]

The level of contamination control that analysts have applied to their measurements in the past is often insufficient to meet the needs of these new measurement challenges. The analysis can be no better than the analyst performing the measurement. The decisions, judgments, and performance of the analyst all impact the quality and validity of the reported results. The critical point in inorganic trace analysis is to strive for a better understanding of the analytical task we

are dealing with, but where do the analytical difficulties come from? The major contributors are:

- contaminations caused by reagents, apparatus, analysts and laboratory environment;
- interferences caused by complex matrices;
- losses during sample preparation step.

A better understanding about these difficulties will lead to better control, better control implies better analytical blanks. Better blanks make it realistically feasible to reach low concentrations achievable by modern analytical instrumentation. This book focuses on helping today's analytical chemist understand and overcome these difficulties by learning how to THINK BLANK.

CHAPTER **1**

THE ANALYTICAL BLANK: HOW BAD COULD IT BE?

The Analytical Blank: How bad could it be?

"...sensitivity and trouble are proportional".

Primo Levi, The Periodic Table.

This analytical blank is a measure of all external sources of elemental contamination and is used to make a correction to the measured sample concentration. "The analytical blank may be considered the "Achilles' heel" of trace analysis. Modern methods of analysis have lowered the threshold of determining trace elements to the low parts per billion for many elements but the inability to control the analytical blank has seriously affected the accuracy of these methods."[7] The variability of the analytical blank and not the absolute value is what determines the accuracy of trace metals analysis.

The overall uncertainty for an analytical measurement is calculated using the following formula:[8]

$$\sigma_{Total} = \sqrt{\sigma^2_{Sample} + \sigma^2_{Blank}}$$

The variability of the analytical blank has little or no effect on the accuracy of the result when the analyte concentration of the sample is several orders of magnitude higher the blank result. For example a sample with a measured mercury concentration of 500 ± 25 ng/g and a analytical blank concentration of 10 ± 5 ng/g the total uncertainty would be:

$$\sigma_{Total} = \sqrt{25^2 + 5^2}$$

$$\sigma_{Total} = 25$$

The reported mercury concentration for this sample would be 490 ± 25 ng/g. The analytical blank had no effect on the reported result.

As the analyte concentration approaches the blank level the accuracy of the result could be obscured by the uncertainty of the analytical blank measurement. For example a sample with a measured mercury concentration of 50 ± 2 ng/g and a blank concentration of 10 ± 5 ng/g the total uncertainty would be:

$$\sigma_{Total} = \sqrt{2^2 + 5^2}$$

$$\sigma_{Total} = 5$$

The reported mercury concentration for this sample would be 40 ± 5. All of the uncertainty in the analysis is due the analytical blank which critically impacts the reliability and accuracy of this measurement.

In order to improve the precision and accuracy of an inorganic metals analysis steps must be taken to control the analytical blank.

CHAPTER **2**

CONTAMINATION: HOW DO I CONTROL MY BLANK?

Contamination: How do I control my blank?

"In trace analysis the effects of contamination from laboratory air or furnishings, apparatus, containers, and reagents have become increasingly important, as the sensitivity of analytical methods has lowered detectable limits to the nanogram and picogram level".

M. Zief, J. W. Mitchell.[9]

Laboratory Atmosphere

Airborne contamination has the most significant effect on the determination of elements which occur in naturally high concentrations in the earth's crust (Na, Ca, K, Mn, Si, Al, Fe, Mg and Ti) and are prevalent anthropological sources (Fe, Ni, Pb, Zn, Cu, As).[6,9-11] In Dortmund Germany analysts discovered that their high iron blanks were caused because nearby plants had dispersed 20 tons of ferric oxide which contaminated their ventilation system.[12]

These elemental contaminates are always present in the laboratory, primarily as dust particles. If left isolated and undisturbed dust particles will have little effect on the analytical result. Unfortunately, the daily operation of an analytical laboratory often results in the dust particles become airborne. Once airborne the heavier particles quickly settle out, while the lighter particles are suspended and carried by the air currents throughout the laboratory. Airborne particulate

concentrations have been shown to fluctuate from a low of 0.2 x 10^6 per ft^3 in the morning to a high of 1.5 x 10^6 per ft^3 by noon.[13]

Charge transfer by friction is the most common mechanism leading to transport of atmospheric particles into a sample. Friction created between two dissimilar materials, one of which is a nonconductor or a poor conductor of electricity creates a charge imbalance in the materials. The charge imbalance, either positive or negative continues to build up until it finds a means of release. Teflon has a tendency to generate a negative charge, while the components of airborne contamination tend to become positively charged (*Figure 2*). The opening of a Teflon bottle becomes negatively charged as the cap is unscrewed. Any positively charged airborne contamination in the vicinity, will be immediately attached to the cap or neck of the bottle. In extreme cases analysts can even observe the movement of particles from their clothing or gloves to charged sample containers.[14]

Figure 2. *Materials tendency to generate a static charge.*

Think Blank: How do I control airborne contamination?

The first step in controlling airborne contamination is to minimize the generation, transportation, and deposition of atmospheric particles. The major source for metal containing particulates in the laboratory is the degradation of metals objects by acid vapors, paints, cements, plastics, and other construction materials. Unnecessary shelving,

partitions and furniture should be removed from the laboratory, because they can accumulate dust and debris. Metal furniture should be replaced with wood. Stainless steel door handles, hinges, and plumbing should be replaced with plastic equivalents or coated with pigment free epoxy paint. Bench tops should be coated with epoxy paint and for added protection covered with Teflon, or polyethylene sheeting (contact paper). Ceiling panels should be replaced with ones that have a plastic laminate on each side to prevent particle formation. Low fiber emitting tissues should be used for wiping operations. Floors, benches, and apparatus should be wiped down with deionized water regularly. Bottles, containers, samples, reagents, and small equipment should be kept isolated from laboratory air when not in use by storing in plastic snap-top boxes, or polyethylene bags.[6,7,9,14-18]

Particulate contamination is minimized by filtering the laboratory air with a high efficiency particulate air filter (HEPA). This filter was developed for the Manhattan project to remove fissionable particles from the air.[19] HEPA filters have an efficiency of 99.97% for particles 0.3 μm and larger particles. They effectively remove bacteria, pollen, fly ash, and dust. Some common contaminants like tobacco smoke are not removed since their particles are less than 0.3 μm.[10] HEPA filters are incorporated into clean benches and used in conjunction with laminar/directional air flow. These clean hoods, they are commonly called, create particle-free working environments by projecting air through the HEPA filter and exhausting it across a work surface in a laminar air stream. Directional air flow provides an air curtain preventing airborne contamination from entering the workspace. Standard clean hoods are good for drying containers and apparatus after cleaning, protecting samples in the autosampler trays during analysis, and for preparation of calibration and quality control standards. The standard clean hoods should not be used to handle or store toxic or hazardous

materials, because all the fumes that are generated within the hood are carried by the laminar flow toward the analyst. Exhausted clean hoods are available for the handling of hazardous and corrosive substances. These units are constructed from nonmetallic components. The HEPA filtered air flows vertically and is drawn though a perforated work area into the laboratory exhaust system.

The best approach to controlling airborne contamination for trace metal analysis to construct a clean laboratory or clean room. This approach is expensive and is used in the production of computer, pharmaceutical, and aerospace products as well as the production of standard reference materials. Clean rooms minimize metal-containing dust by filtering the air that enters the room through HEPA filters, using specialized construction materials, and operating under positive pressure so that the flow of air is always out of the room (*Table 1*). Clean rooms also utilize antechambers to isolate the cleanroom from the general laboratory. These antechambers are for changing into specialized clean room attire and passing items into the clean environment. In a properly maintained and operated clean room sub pg/g measurements can be routinely made.

Table 1. *Particulate concentrations (ng/m^3) of metals in laboratory environments.*[20]

Environment	Fe	Cu	Pb	Cd
Ordinary Laboratory	200	20	400	2
Clean Hood	0.9	7	0.3	0.2
Clean Room	1	2	0.2	-

Even the best clean rooms can not completely remove all airborne particulate material so steps must be taken to minimize electrostatic charge build-up on surfaces and sample containers. In dry air, the imbalanced charges have nowhere to go, so they build

up until they come into contact with another conductive object that can release the excess charges. However, in humid air (greater than 45% humidity), static electricity has a natural means of release due to water's ability to conduct electricity. The moisture in humid air serves as a natural conductor that allows charges to leave objects. Tiny particles of water touch the object and absorb the charge. In turn, those particles of water come into contact with other particles of water, causing the excess charges to spread away from the original object. The authors have found that ethanol is an even more effective and efficient means of removing electrostatic charge build-up on surfaces and containers than water due to its lower vapor pressure allowing it evaporate faster.

Laboratory Apparatus, Sample and Reagent Containers

Before a sample is analyzed for trace metals, it has been collected, stored, processed, and prepared. During this process, the sample comes in contact with many different laboratory tools, containers and apparatus, which can deposit trace metal contamination into the sample. Standard laboratory motors are made of alumina or glass will contaminate the sample with Al, Si, and Fe. Mills and blenders are made of stainless steel and have tungsten carbide blades which will contaminate the sample with W, Ni, Cr, Co and Fe. Sieves are usually made of stainless steel with copper wire mesh, which will contribute Cu, Fe, Co, Cr, and Ni contamination. Ashless filter paper, used to filtering, samples contains trace metal contamination on the order of 1 mg/kg. In addition the filtration assemblies can also impart contamination to the sample. Prolonged storage of sample and reagent solutions prior to analysis is dangerous step from a contamination viewpoint. Prolonged contact with container materials will most likely impart contamination from the container into the sample.

Borosilicate Glass

The most common material used for laboratory containers and apparatus is borosilicate glass. It is resistant to most acids, but should not be used with HF or boiling H_3PO_4. Alkaline solutions should not be heated or stored in borosilicate glass because they will gradually solubilize the glass according to the following equation.

$$2\ NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

Borosilicate glass is not a good material for trace analysis, because it contains high levels of trace metals (*Table 2*) and has the potential to absorb analytes from the sample according to the following equation.[6]

$$SiOH_{glass} + M^+ \longrightarrow SiOM_{glass} + H^+$$

Quartz

An alternative to borosilicate glass is quartz. Like borosilicate glass it is resistant to most acids, but should not be used with HF, boiling H_3PO_4, or alkaline solutions. Quartz composed almost entirely of SiO_2 and the trace metal concentration depends on the type and method of production. Naturally occurring quartz laboratory components are made by electric (Type I) or flame melting (Type II). Type II quartz has a lower trace metal concentration because some of the metals are volatilized in the flame. Synthetic quartz laboratory components are produced by the vapor phase hydrolysis (Type III) or oxidation and electrical fusion (Type IV) of $SiCl_4$. Both of these methods produce quartz with low trace metal contamination.[6,7,21] The typical trace metal impurity levels for the various types of quartz are shown in *Table 2*.

Synthetic Polymers

The low levels of trace metal contamination make quartz an ideal material for trace metal analysis, but the cost and availability of common laboratory containers and apparatus limit its use in trace metal analysis. Synthetic polymeric materials are now being employed as alternative materials for containers and apparatus for trace metal analysis. The trace metal impurities of these materials are comparable to quartz, but will vary based on the manufacturing environment, type of molding, molding components and polymerization process. A dirty manufacturing environment may lead to the incorporation of airborne particulate contamination (Ni, Al, Mn, Cu, Fe) into the final product. In addition the metal molds used in the injection molding may impart contamination as well.[14,23] The most common materials used for trace metal analysis are polyethylene, polypropylene, and fluorinated polymers.

Polyethylene

There are two types of polyethylene used in trace metal analysis, conventional (low density) and linear (high density). Low density polyethylene (LDPE) is produced by high pressure polymerization of ethylene. High density polyethylene is produced at low pressures catalyzed by transition metal oxides ($[Al]R_3$, $TiCl_4$, $ZrCl_3$, VCl_3, $CrCl_3$). Polyethylene is resistant toward concentrated HCl and HF, but is oxidized by aqua regia and nitric acid. Prolonged storage of dilute solutions of HNO_3 causes the material to brown or yellow. The maximum service temperature for LDPE is 80°C and 110°C for HDPE. The use of LDPE is preferable to HDPE because it has lower levels of trace metal contamination (*Table 3*).

Polypropylene

Polypropylene is produced catalytically (Al, Ti) from propylene and like HDPE has elevated levels of some trace metal contaminates (*Table 3*). Polypropylene is less resistant to concentrated HCl and becomes yellow or brown by prolonged exposure. Its resistance to dilute HNO_3 and aqua regia is similar to polypropylene. Polypropylene is harder and more rigid that polypropylene and is stable up to 135°C. Polypropylene is well suited for open vessel digestion containers and applications that require sterilization.

Polystyrene

Polystyrene is a rigid, transparent thermoplastic, produced from the polymerization of styrene. Polystyrene has excellent chemical resistance to acids at concentrations of 5% or less. Polystyrene is stable at temperatures up to 60°C. Polystyrene is well suited for centrifuge and autosampler tubes.

Fluorinated Polymers

Fluorinated polymers are more expensive than polyethylene or polypropylene, but have lower initial trace metal impurity levels (*Table 3*), and increased chemical resistance. Fluorinated polymers are only attacked by molten alkali metals and by fluorinated organic compounds at elevated temperatures. The increased resistance is due to the high energy C-F bonds and the protection of the carbon backbone by the fluorine atoms. The three most common fluorinated polymers used in trace metal analysis are polytetrafluroethylene (PTFE), perfluoroalkoxy-flurocarbon (PFA or PTFE-PFA), fluorinated ethylene propylene (FEP) and PTFE-TFM (TFM). PTFE is a linear polymer of tetrafluoroethylene with a melting point of 327°C and a maximum service temperature of 290°C. PFA and TFM are chemical modifications of PTFE using

Table 2. *Trace element concentrations (µg/g) in borosilicate glass and various types of quartz.*[7,21]

Element	Borosilicate Glass	Quartz Type I	Quartz Type II	Quartz Type III
Al	Major	74	68	< 0.25
B	Major	4	0.3	0.1
Ca	1,000	16	0.4	< 0.1
Cr		0.1	ND[b]	0.03
Cu		1	1	< 1
Fe	3,000	7	1.5	< 0.2
K	3,000	6	< 1	0.1
Li		7	1	ND
Mg	600	4	ND	ND
Mn	1,000	1	0.2	< 0.02
Na	Major	9	5	< 0.1
Sb	2.9	0.3	0.1	0.1

ND = not detected

perfluoropropylene-vinyl-ether (PPVE) as co-monomer. PFA contains 3-15% PPVE while TFM contains about 0.1% PPVE. Both materials retain the basic properties PTFE, but PFA is more flexible and has a lower melting point (305°C) and maximum service temperature (260°C). TFM has a denser structure with fewer voids leading to lower gas permeability. Additionally, it has an extremely smooth surface which prevents contamination and makes cleaning easier. FEP is a copolymer of hexafluoropropylene and tetrafluoroethylene. It has the same chemical resistance but a lower service temperature (200°C) than the other fluorpolymers. FEP and PFA can be easily processed using conventional thermoplastic techniques, making them the preferred choice for storage containers and sample introduction systems for ICP instrumentation. PTFE and TFM are used in applications where better mechanical and temperature stability are needed, such as microwave vessels.

Table 3. *Trace element concentrations (µg/g) in polymers materials used for sample containers.*[23]

Element	LDPE	HDPE	PP	PFA	FEP	PTFE
Al	0.5	30	55			
Ca		800				
K	> 5000	> 600			0.2	0.23
Na	1.3	15	4.8	0.1	0.4	0.16
Sb	0.005	0.2	0.6			
Ti		5	60			
Mn		0.01	0.2		0.6	
Zn		520				

Think Blank: How to I control contamination from containers?

Picking a material with low trace metal impurities does not guarantee low blank levels. Metal impurities can be leached from the container by the sample over time. One must take the additional precautions to limit the influence of this contamination.

1. The surface area/volume of the container should be as small as possible.
2. The duration of contact between the solution and the surface of the container should be as short as possible.
3. Containers should be preconditioned by acid leaching, ideally with acid vapors.

Precautions one and two are heavily influenced by the type of analysis being performed. Homogeneity might require large samples to be collected or sample volume might require samples to be stored for several days before the analysis can be complete. These situations limit what can be done to limit the surface area and duration of contact. When preparing samples one should use the smallest container which you to accurately complete the task i.e. do not use a 250 mL container to process 10 mL of sample. When preparing calibration standards do not prepare 100 mL of a standard in a 100 mL volumetric if you are only going to use 25 mL for calibrating your instrument. Prepare 25 mL in a 25 mL volumetric flask and cut the surface exposure by 4 times.

Preconditioning containers is the most effective method for controlling contamination imparted from container walls. Preconditioning will dissolve and remove the metal impurities that were incorporated into the material during the process. Once these are removed there is no longer a threat for significant contamination in the future from within the container. This effect is clearly shown from the data in *Tables 4-8*.

Table 4. *Element concentrations (µg/L) in leaching solution after 59 h at 60°C.*[24]

Element	LDPE	HDPE	PP	FEP	PFA
Na	0.33	0.56	0.34	0.72	0.76
K				0.13	
Ca		0.22		0.29	0.14
Fe		1.18		0.55	1.66
Mg		0.09	4.6	0.14	0.09
Cr	0.026	0.029		0.05	0.24
Mn					0.009
Cu	0.114				
Ni				0.11	0.097
Al			0.7		
Total	0.47	2.079	5.64	1.99	2.996

Table 5. *Impurities (ng/cm^2 of surface) leached from plastic containers in one week with 1:1 HNO_3/Water. HDPE and LDPE were leached at room temperature while FEP was heated to 80°C.*[23]

Element	LDPE	HDPE	FEP
Pb	0.7	2	2
Tl	1	< 1	< 1
Ba	2	< 0.2	4
Te	< 0.5	0.2	0.6
Sn	< 0.8	1	1
Cd	0.2	0.2	0.4
Ag	ND	0.2	< 8
Sr	0.2	1	0.2
Se	3	0.4	0.2
Zn	2	8	4
Cu	2	0.4	2
Ni	0.5	1.6	2
Fe	3	3	20
Cr	0.8	0.2	0.8
Ca	10	0.6	80
K	2	2	2
Mg	0.7	0.6	8
Al	1	1	6
Na	8	10	6
Total	38	50	148

ND = not detected

Table 6. *Impurities (ng/cm^2 of surface) leached from plastic containers in one week with 1:1 HCl/Water. HDPE and LDPE were leached at room temperature while FEP was heated to 80°C.*[23]

Element	LDPE	HDPE	FEP
Pb	18	0.6	2
Tl	3	< 0.6	< 1
Ba	0.3	1	2
Te	0.7	ND	2
Sn	< 0.8	< 1	1
Cd	0.2	0.2	0.6
Ag	ND	ND	< 6
Sr	0.2	0.2	< 1
Se	< 0.3	0.4	0.8
Zn	1	9	4
Cu	0.7	1	6
Ni	0.3	0.8	0.8
Fe	1.0	1	16
Cr	0.3	0.8	4
Ca	0.8	60	2
K	0.7	1	1.6
Mg	0.7	0.4	1.0
Al	10	4	4
Na	42	6	2
Total	81	89	58

ND = not detected

Table 7. *Metal concentrations (ng/L) measured in ultrapure water stored for 21 days.*[25]

Element	LDPE		HDPE		PFA		FEP	
	Received	Leached	Received	Leached	Received	Leached	Received	Leached
Ca	160 ± 10	<20	600 ± 600	30 ± 20	440 ± 150	< 20	70 ± 60	< 20
Fe	110 ± 60	4 ± 3	110 ± 140	< 3	45 ± 13	< 3	22 ± 8	< 3
Zn	8 ± 3	< 3	9 ± 6	< 3	< 3	< 3	< 3	< 3
Na	< 5	< 5	86 ± 24	< 5	8 ± 6	< 5	< 5	< 5
Mg	15 ± 5	4 ± 4	27 ± 25	2 ± 1	26 ± 8	< 1	12 ± 15	< 1
Al	70 ± 30	9 ± 8	120 ± 130	40 ± 40	9 ± 2	< 3	5 ± 2	< 3
K	< 7	< 7	9 ± 10	< 7	< 7	< 7	< 7	< 7
Mn	4 ± 1	< 0.2	3 ± 2	< 0.2	0.8 ± 0.3	< 0.2	0.5 ± 0.4	< 0.2
Cu	36 ± 30	1.0 ± 0.8	21 ± 2	< 0.9	10 ± 2	< 0.9	5 ± 3	< 0.9

Error expressed as standard deviation n=3

Table 8. *Trace metals concentrations (ng/L) in 15 mL polystyrene autosampler tubes after a 12 h leach with 1% HNO_3.*[26]

Element	Leached As Supplied	Acid Washed then leached
Ca	2.7 ± 0.6	0.030 ± 0.029
Na	0.65 ± 0.37	0.041 ± 0.034
Zn	0.66 ± 0.07	0.004 ± 0.003
K	0.41 ± 0.22	0.018 ± 0.019
P	0.49 ± 0.04	0.005 ± 0.002
Al	0.45 ± 0.21	0.005 ± 0.005
Fe	0.19 ± 0.14	0.016 ± 0.009
Mg	0.14 ± 0.04	0.007 ± 0.010
Ti	75 ± 5	0.7 ± 0.5
Cu	41 ± 32	2 ± 1
Pb	14 ± 12	0.1 ± 0.1
Cd	4.1 ± 1.9	0.01 ± 0.01

Error expressed as standard deviation n=12

There have been a variety of preconditioning methods reported in the literature. The best method for a particular application will vary with the chemical behavior of the element of interest. A good general procedure for cleaning all types of containers is sequential leaching with 10% v/v hydrochloric acid for 12 h then 10% v/v nitric acid for 12 h. For polyethylene a 48 hours soaking with 10% v/v nitric acid is effective for initial and routine cleaning.[23,27]

Steam cleaning with nitric or hydrochloric acid vapors is also a very effective cleaning method for preconditioning and routine cleaning of containers and apparatus (*Table 9*).[28-30] In this method, the container 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 (*Figure 3*). This method of cleaning is a preferred alternative to the soaking preconditioning methods for the following reasons:

1. The trace metal contamination found in the reagent grade acid remains in the lower reservoir and does not come in contact with the component to be cleaned.
2. The clean component does not remain in contact with the cleaning acid after the surface contamination is removed.
3. The critical surfaces of the clean component are dry when the cleaning process is complete. This eliminates the need for rinsing and air drying.
4. The cleaning process takes place in a sealed container which minimizes airborne contamination and provides a clean environment for the components to be stored until they are needed.

See page 121 for detailed information on the available instrumentation: Milestone traceCLEAN.

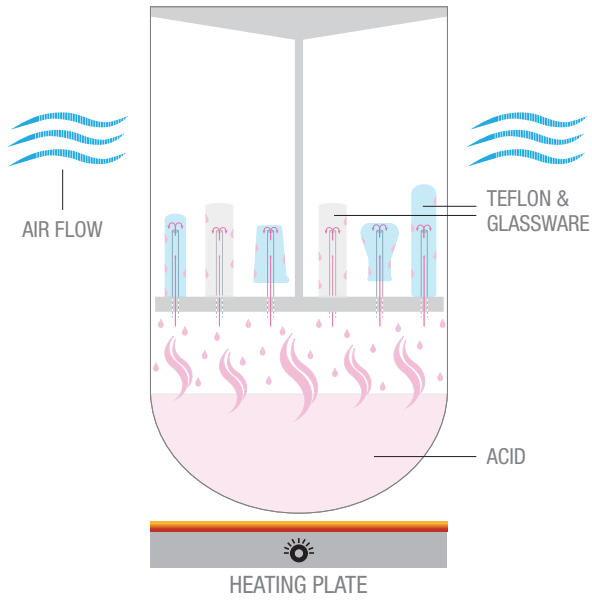


Figure 3. *Automated acid steam cleaning apparatus*

Table 9. *Comparison of high-temperature acid leaching cleaning vs acid steam cleaning. Trace metal contamination (ng/L) in 5% HNO_3 blanks prepared after cleaning are listed below. The acid leaching was performed at 180°C with mixture of HCl and HNO_3.The steam cleaning performed with HNO_3 only.*[29]

Element	TFM Teflon Vessel		Quartz Vessel	
	Acid Leaching	Steam Cleaning	Acid Leaching	Steam Cleaning
Al	287 ± 46	258 ± 24	398 ± 28	327 ± 18
Mg	289 ± 22	232 ± 15	441 ± 56	347 ± 26
Na	< 121	< 121	1190 ± 350	608 ± 67
Fe	< 474	< 474	< 474	< 474
Ni	< 55	< 55	< 55	< 55
Co	< 56	< 56	< 56	< 56
Cu	144 ± 39	117 ± 12	170 ± 15	109 ± 9
Cr	< 85	< 85	176 ± 57	< 85
Cd	< 72	< 72	< 72	< 72
Tl	< 261	< 261	< 261	< 261
Pb	< 57	< 57	< 57	< 57
Zn	995 ± 80	< 876	1640 ± 1000	1005 ± 124

Error expressed as one standard deviation (n =3)

Trace Analysis Reagents

The instrumentation used for trace analysis usually requires homogenous solutions. Instrumental calibration solutions are prepared by diluting a concentrated stock with water. Samples requiring analysis are treated with mineral acids to liberate the analytes. The purity of the reagents used for these operations is of vital importance because the amount of reagent used is usually several orders of magnitude greater than the original sample size. This means that metal contamination in the reagents must be low enoμgh to accurately measure the analyte concentration in the sample. For example if you wanted to measure a sample with a total of 10 ng of analyte prepared with 25 mL of reagents. The analyte contamination in the reagents must be less than 0.2 ng in order to measure a reliable analyte signal above the blank contribution.

Think Blank: How do I obtain reagents with minimal contamination?

No single purification method is capable of removing all contamination from reagents used for inorganic metals analysis. For liquid reagents distillation has been used for over a century to improve their quality. When this method applied to the purification of water and mineral acids "significant contamination of the distillate occurs from the creeping of unrectified liquid and entrainment of particles in the vapor steam formed during bubble rupture."[31] An alternative technique developed by researchers at the National Institute of Standards and Technology in the early 1970's called sub-boiling distillation eliminated the problems associated with traditional distillation (*Table 10*).

Sub-boiling distillation uses infrared heaters to vaporize the surface liquid. The vaporized liquid is collected on an inclined water-cooled condenser and drips into the collection container (*Figure 4*).

Vaporization without boiling is the key element of this purification process because it prevents the formation of aerosolized particles. Creeping is minimized through careful positioning of the condenser (*Figure 5*). This configuration is extremely efficient for separating the low vapor pressure metal ions from the higher vapor pressure acids. *Tables 11* and *12* show the quality of acids that can be obtained from commercial sub-boiling distillation systems.

See page 120 for detailed information on the available instrumentation: Milestone duoPUR.

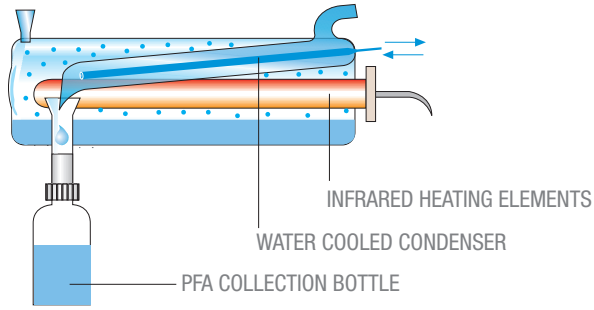


Figure 4. *Schematic of a sub-boiling distillation system.*

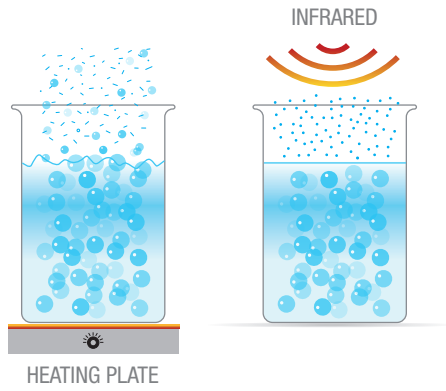


Figure 5. *Conventional vaporization vs sub-boiling.*

Table 10. *Comparison of metal contamination (µg/L) in nitric acid purified by traditional and sub-boiling distillation.*[7]

Element	Sub-Boiled Distilled	Traditional Distillation
Pb	0.02	0.2
Tl	-	0.2
Ba	0.01	8
Te	0.01	0.1
Sn	0.01	0.1
In	0.01	-
Cd	0.01	0.1
Ag	0.1	0.03
Sr	0.01	2
Se	0.09	0.2
Zn	0.04	4
Cu	0.04	20
Ni	0.05	20
Fe	0.3	24
Cr	0.05	6
Ca	0.2	30
K	0.2	10
Mg	0.1	13
Na	1	80
Total	2.3 µg/L	220 µg/L

Table 11. *Trace metal contamination (ng/L) in nitric acid produced by sub-boiling distillation in a quartz still.*

Element	Source 1[a]	Source 2[b]	Source 3[c]
Mg	42	90	< 10
Al	147	700	< 10
Ca	157	110	< 10
Ti	8	ND	< 50
V	11	ND	< 10
Cr	5	60	< 10
Mn	2	ND	12
Fe	210	350	< 10
Co	1	ND	< 10
Ni	23	80	< 10
Cu	21	50	< 10
Zn	49	60	< 10
Se	1	60	< 10
Sr	1	20	< 10
Ag	2	6	16
Cd	2	20	< 30
Sn	9	20	11
Ba	4	20	< 10
Tl	< 1	60	< 10
Pb	3	30	31
B	ND	ND	< 10

[a] Reference 32: Microwave evaporation with ICP-MS analysis
[b] Reference 33: Hot plate evaporation in Class 100 hood with ID-SSMS analysis.
[c] Reference 34: Hot plate evaporation in a Class 10 clean room with ICP-MS analysis.

ND = not detected

Table 12. *Trace metal contamination (ng/L) in nitric and hydrochloric acids produced by sub-boiling distillation in a Teflon still.*[35]

Element	Acid	
	HNO_3	HCl
Ag	28	107
Ba	76	160
Be	5	41
Bi	2	14
Cd	ND	51
Co	27	135
Cr	30	131
Cs	0.6	8
Cu	ND	540
Mn	81	245
Pb	68	145
Sr	59	149
Rb	7	31
V	20	68
Zn	ND	724

ND = Less than LOD

A good water supply is also essential for trace metal analysis. The most common methods are sub-boiling distillation (previously discussed), reverse osmosis, and ion-exchange. Reverse osmosis separates dissolved material from the water by forcing contaminated water through a membrane against osmotic pressure. The membrane preferentially allows water to pass rejecting 90-99% of dissolved ions and particulates. The reverse osmosis system is generally used to pre-treatment technique for water before it is further purified by either sub-boiled distillation (previously described) or ion-exchange. In the ion-exchange method the contaminated water passes through a column of resin. The resin is composed by styrene-divinylbenzene copolymers

engineered to have an affinity for either cations or anions. The resins exchange the charged metal contaminates for hydrogen and hydroxyl ions. This results in an exchange of the trace metal contamination for clean water. Sub-boiling distillation and ion exchange both produce water with low levels of trace metal contamination (*Table 13*).

Table 13. *Contamination levels (µg/L) of laboratory water produced by various methods.*[26]

Element	Ion Exchange	Double Distilled	Commercial Ultra-Pure
Na	9 ± 2	18 ± 2	21 ± 2
Al	11 ± 1	3.5 ± 0.7	4.4 ± 0.9
Mg	2.0 ± 0.2	1.3 ± 0.3	0.52 ± 0.03
Fe	3.6 ± 0.7	1.2 ± 0.1	1.5 ± 0.2
Ba	1.2 ± 0.2	0.025 ± 0.003	0.031 ± 0.005
Cu	3.8 ± 0.3	1.7 ± 0.2	1.7 ± 0.2
Mo	0.65 ± 0.03	0.11 ± 0.03	0.64 ± 0.04
W	0.072 ± 0.012	0.023 ± 0.002	0.260 ± 0.020
Pb	0.110 ± 0.010	0.031 ± 0.015	0.068 ± 0.008
Sb	0.028 ± 0.003	0.010 ± 0.001	0.150 ± 0.010

Error expressed as standard deviation n = 12

The Analyst as a Source of Contamination

Nearly all inorganic trace analysis procedures require some intervention by the analyst. Serious sample contamination can occur from who is just doing his job or careless manipulation of the sample or reagents. An adult will generate 100,000 particles per minute when motionless, and will generate 1,000,000 particles per minute when walking (*Table 14a*). In addition simple routine activities produce a variety of particulate matter which can be carried by into samples (*Table 14b*).

Table 14a. *Particulate generation from human movements.*[36]

Activity	Particle / min. (> 0.5 µm)
Sitting without moving	100,000
Moving hands, arms, head	500,000
Active hand/arm movement	1,000,000
Standing up from a sitting position	2,500,000
Rapid movement, climbing stairs, etc.	110,000,000

Table 14b. *Particulate generation from laboratory activities.*[37]

Activity	Size of Particle
Rubbing a painted surface	90 µm
Crumpling paper	60 µm
Metal sliding on metal	50 to 100 µm
Writing with a ball point pen	15 to 30 µm
Rubbing skin	15 to 300 µm

The most significant sources of contamination produced by humans are skin and hair flakes. The dead cells flake off when skin is gently abraded and will be carried off by the convection currents surrounding the body. A typical lab worker will lose about 6-14 g of dead skin material every day, which is equivalent to 10,000,000 particles per day. Dried skin contains 6 µg/g of Zn and 0.7 µg/g of copper, while sweat and hair contain Zn, Cd, Pb, Fe, Cu, Ni, Mn, and Na (*Tables 15* and *16*).

Hand lotions and creams contain Al, Zn, Ti, Mg and other trace metal contaminates. Traces of Ag, Au, Cr, Cu, Fe, and Pt can be deposited from watches, rings, and bracelets. The use of cosmetics by the analyst can be also a significant source of contamination, because of the metal oxides and other materials which were added for color and texture (*Table 17*). Some hair dyes and shampoos contain Pb and Se.

Table 15. *Concentrations of Metals in Human Hair.*[38]

Element	Concentration µg/g
Mg	49.7 ± 8.6
Zn	167 ± 5
Cu	16.1 ± 1.2
Co	0.17 ± 0.03
Cd	2.76 ± 0.48
Pb	17.8 ± 2.17
Ni	0.97 ± 0.15
Cr	0.69 ± 0.63

Error expressed as standard deviation n=117

Table 16. *Concentrations of metals in human sweat.*[39]

Element	Concentration in µg/L
Zn	960 ± 425
Cd	24 ± 16
Pb	62 ± 40
Fe	630 ± 587
Cu	1427 ± 505
Ni	57 ± 26
Mn	23 ± 14
Na	264500 ± 36800

Error expressed as standard deviation n=6

Table 17. *Particulate contamination from cosmetics.*[9]

Cosmetic	Number of Particles < 0.5 µm Per Application	Elements Present
Lipstick	1.1×10^9	Bi, Zn,Fe,Mg, Ti, Mn
Blusher	6.0×10^8	Bi, Si, Fe,Mn, Ti, Al, Cr, Mg
Powder	2.7×10^8	Ti, Si, Bi, Fe, Zn, Mg, Ca
Eye Shadow	8.2×10^9	Bi, Si, Fe, Mn, Ti, Al, Cr, Mg
Mascara	3.0×10^9	Na, Fe, Mg, Ti, Cr, Al

The cumulative effects of the analyst on the blank are best illustrated by following a bottle of ultrapure water through a typical 8 h work day. The total metal contamination for 10 common contaminate elements was 74 ng/L in freshly prepared ultrapure water. Through human interaction with the water became gradually contaminated and by the end of the shift the total contamination ranged from 368 – 2,627 ng/L in the four bottles tested (*Table 18*).

Table 18. *Influence of analyst on ultrapure water contamination.*[26]

Element	Reference Bottle Freshly Prepared	Range of four bottles used for routine preparation operations over 8 hr day
Al	11	40 - 120
Ca	20	100 - 700
Cr	0.3	0.4 - 2
Cu	2	2 - 12
Fe	4	5 - 60
K	20	100 - 300
Mg	2	9 - 70
Na	10	100 - 1300
Ti	0.2	0.3 - 13
Zn	4	11 - 50

Think Blank: How can I protect my samples from myself?

In order to control analyst contamination the analyst must first be isolated from the samples. The most fundamental precaution is to wear gloves when performing procedures that require manipulation of the sample. The gloves must be impervious to skin oils and perspiration, in addition to being power free. Clear polyvinyl chloride or polyethylene gloves are the best for routine handling of the samples. When working with concentrated acids nitrile gloves are a good compromise between chemical resistance and cleanliness and are often worn in conjunction with long cuff vinyl gloves. One should remember that gloves are only as clean as the last thing touched and must be changed on a routine basis to avoid the glove becoming a contamination source. The best results are achieved when gloves are worn in conjunction with a head cover, shoe covers and a laboratory coat.

Protective garments (lab coats, head and shoe covers) worn during trace metal analysis should not be cotton or linen. These materials should be avoided because the product a considerable amount of lint which can contaminate the sample. The best materials for laboratory garments are nylon, Dacron® polyester, and Tyvek®. Garments made from these materials do not shed fibers, are lightweight, and resistant to acids and reagents. Garments used in trace metal analysis should also have all cut edges enclosed and be made without components that corrode i.e. metal buttons and zippers.

The analyst can also be responsible for cross contamination from other samples or work being performed in the laboratory. If the analyst is not aware of the history of the laboratory containers and apparatus used for the analysis contamination can occur from using a vessel or container that was exposed to high concentrations of the analytes. The use of paper towels in another part of the laboratory can introduce large quantities of airborne contamination into the

atmosphere. Careless handling of the reagents can led to contamination of the sample as well as calibration standards. Contamination from these sources is very unpredictable. The analyst must be constantly aware and think about how his/her actions will affect the blank. Most importantly the analyst must avoid those actions which tend to increase the blank, or whose effect on the blank is unknown.

CHAPTER **3**

LOOKING FOR AN IDEAL ANALYTICAL PROCEDURE

Looking for an ideal analytical procedure

"The ICP source has been a very bright "star" of 20th century analytical chemistry, and the ICP will continue to fulfill this role in the foreseeable decades as the need for ultrasensitive, matrix-free, and ultramicro analyses intensifies".

R. M. Barnes[40]

According to Laitinen "New or improved methods are sought because of limitations ranging from lack of sensitivity, specificity, precision, accuracy, universal applicability, speed, or simplicity, to cost of reagents, equipment, or personnel. In addition, existing methods may not yield sufficiently detailed information about the oxidation states, compounds, or species involved".[41] Interestingly, Laitinen also stated that "an analytical method is a means to an end, and not an end in itself" and "the ideal method is the one which most conveniently and efficiently handles the problem to be solved". Twelve years later, Fassel listed the ideal requirements for elemental analysis methods as the following:[42]

- applicable to all elements
- simultaneous or rapid sequential multielement determination capability at the major, minor, trace and ultratrace concentrations

levels without change of operating conditions;
- no interelement interference effects;
- applicable to the analysis of microliter- or microgram-sized samples;
- applicable to the analysis of solids, liquids, and gases with minimal preliminary sample preparation or manipulation;
- capable of providing rapid analysis; amenable to process control;
- acceptable precision and accuracy.

Based on further development of analytical chemistry, we may add that in addition to these attributes emphasized by Laitinen and Fassel nowadays we are also looking for low cost for implementation, reduced impact to the environment and most importantly the ability to control the analytical blank.

It is also useful to think about an ideal procedure for sample preparation. Recently, Nóbrega and Donati had listed the following attributes for an ideal sample preparation procedure:[43]

- able to digest large masses of samples;
- compatible with multielement analysis;
- safe to both environment and analyst;
- compatible with green chemistry requirements;
- capability for high sample throughput;
- avoidance of losses
- the ability to control the analytical blank

We must always remember the analytical procedure is a sequence of steps beginning with the definition of the analytical task and finishing with the analytical results (*Figure 6*). This means that sample preparation step must be performed considering that solutions generated must be fully compatible with instrumental requirements for successful measurements.

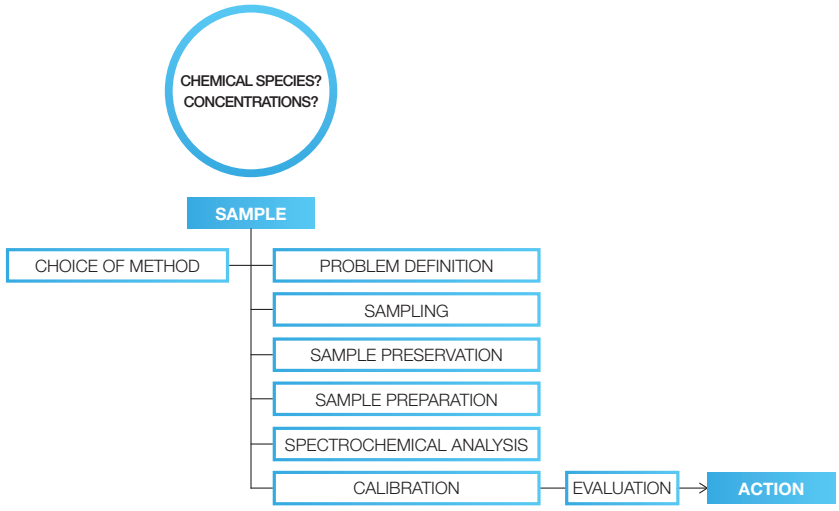


Figure 6. *Analytical procedure steps*

Think Blank: What is the best combination of sample preparation and elemental analysis techniques for controlling the analytical blank?

"Individually or collectively, these methodologies (ICP OES, ICP-MS and ICP AFS) either have had a major impact on the way elemental analyses are being performed, or are destined to be performed."

Fassel[42]

Surely Fassel's statement may be seen as too optimistic, but we believe that nowadays our limitations are related to adopting analytical procedures that do not deteriorate the power of detection offered by ICPs. Consequently, extremely low limits of detection and quantification may be reached.

An essential aspect for any instrumental method is to establish proper operational parameters and to be aware of the most critical ones. An ICP OES is composed of a device for sample introduction, a radiofrequency electric power supply, a quartz torch, a polychromator, a detector(s), and a computer with proper software for controlling the equipment, data acquisition and data treatment. A pneumatic nebulizer and an aerosol chamber are typically combined for inserting solutions into the argon plasma. The argon plasma is initiated using a Tesla coil and it is kept by the radiofrequency power supply. A high-resolution polychromator must have enough resolution for separating several emission lines and for transferring resolved wavelengths for each analyte to the detector(s). Radiation signals either in ultraviolet or in visible region are converted to electric signals and their intensities are correlated to their concentrations using proper multielement analytical solutions for calibrations.[44] Taking into account transport and matrix interferences, analytical solutions must be physically and chemically similar to the sample solutions to be analyzed. This is a critical aspect when deciding about sample preparation.[45]

Among argon characteristics that make it attractive we may cite:[45,46] (1) suitable electrical resistivity for effective coupling and power dissipation; (2) suitable thermal conductivity to transfer heat from the outer region of the plasma to the central channel; (3) high gas temperature (4500 – 8000 K) and electron temperature (8000 – 10,000 K); (4) high electron number density (1-3 x 10^{15} e-/cm^3); (5) vaporization-atomization-ionization-excitation in a nearly chemically inert environment; (6) 2-3 ms residence time of the sample aerosol inside of the plasma; (7) molecular species present at low levels; (8) robustness of the plasma; (9) acceptable cost.

In the 1980´s ICP OES has evolved from radial view to axial view to improve sensitivity[47] (*Figure 7*). The possibility of transferring

a higher amount of emitted radiation from the plasma to the polychromator entrance was attractive for increasing sensitivity, but as usual together with higher analytical signals we had an increment of background signals and it was necessary to develop shear gas and end on gas interfaces to minimize background and self-absorption effects.[47] Based on performance of each plasma view, analysts and companies assumed that axial view could be applied for trace analysis when samples did not present complex matrices. On the other hand, radial view measurements would be used for applications where sensitivities were less required, but matrices contained a higher amount of dissolved solids and more complex emission spectra. Of course, we demand both, i.e. high sensitivity and capability to work with complex matrices at the same time. Arrangements with dual view capacity became rapidly available; however these plasmas may be seen as presenting typically either an axial or a radial behavior depending on the position of the quartz torch. Nowadays new arrangements are being proposed with capability for simultaneous measurement of axial and radial view special arrangements and devices.

As proposed by Mermet and Poussel, different instrument compartments can be diagnosed based on simple experiments.[48] Resolution at ultraviolet range, which is related to selectivity, can be evaluated by measuring the line profile for Ba(II) at 230 nm. The repeatability and performance of the sample introduction system can be established by measuring the relative standard deviation for successive measurements of Mg(I) 285 nm line. The warm-up time of the instrument can be determined by measuring the stability along the time for Ar(I) 404 nm, Ba(II) 450 nm and Zn(ii) 206 nm emission lines. These same lines can be used for measuring the long term stability. Robustness, which is a parameter for evaluating the capacity of the argon plasma to cope with matrix effects, can be measured by the

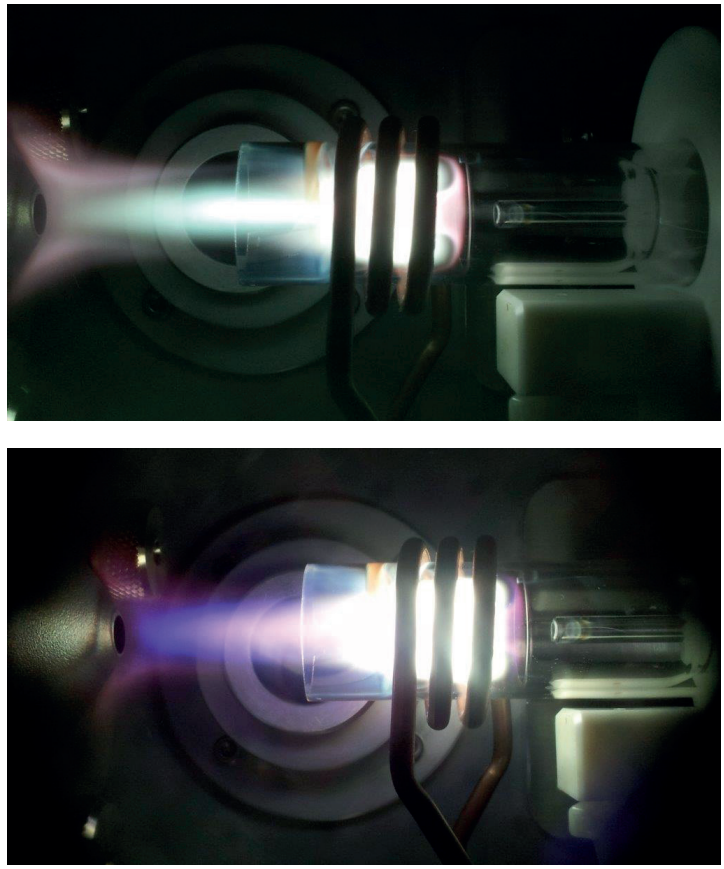


Figure 7. *Argon plasma with transition metals solutions being aspirated. Courtesy: Ross Ashdown, Agilent Technologies*

net line intensity ratio for Mg(II) 280 nm / Mg(I) 285 nm. Remember that (I) and (II) represents atomic and ionic lines, respectively. A further reading of reference 48 is strongly recommended and demonstration of practical application of this diagnosis approach can be seen in reference 49.

It was soon perceived that argon plasma would be a good source of ions for a mass spectrometer and four years after being proposed it became available in the instrumentation market.[44] These commercial ICP-MS systems share some components previously used in ICP OES, such as sample introduction systems, radiofrequency power supply, and quartz torch in axial position. Nowadays free running and crystal-controlled radiofrequency generators are able to work properly with complex matrices and compensate for impedance changes. Also difficulties with secondary discharge between the plasma and the sampler cone were solved by grounding the induction coil. However, instrument development was, and at certain point still is, critically dependent on the development of an interface for coupling a plasma operated at normal pressure with a mass spectrometer and detector operated under vacuum. Most proposed devices are based on combination of sampler cone, skimmer cone and electrostatic lenses for transferring cations to the mass spectrometer. Thomas discussed details about ICP-MS components in a clear and useful tutorial book and its reading is highly recommended.[50] The short orifices of both cones typically lower than 1.2 mm implies that either sample solutions should have a total concentration of dissolved solids lower than 0.1% m/m or a special device should be used for dilution and introduction of a more concentrated solution. Of course, this aspect is closely linked to the strategy adopted for sample preparation and analysts should minimize volume and concentrations of the added reagents. The analyst also must be cautious with the calibration strategies

because of matrix-induced interferences in the interface zone, usually called space charge effect. This effect is corrected by using an internal standard, matrix matched analytical calibration solutions or the standard additions method.

Since its beginning, ICP-MS has provided superb sensitivities for most elements of the periodic table, but early on it became clear that the formation of oxides[51] and molecular ions in different acid media[52] would limit its analytical capability. The critical mass region for spectral interferences in argon plasma is from 40 to 80 amu. Spectral interferences can be solved by using special calibration approaches, anayte-matrix separation, and plasma operating conditions, such as cool plasma formerly applied for specific analysis as Fe determination in semiconductor production. Instrumental strategies are also offered, such as collision-reaction cells,[53] and more recently tandem mass spectrometry.[54] All these are powerful analytical strategies to make feasible trace inorganic analysis make feasible trace inorganic analysis. These devices are based on special cells inserted between the interface cones and the quadrupole analyzer. Gases, such as He, H_2, NH_3, O_2, CH_3F, CH_4, etc., and mixtures of these can be inserted into these cells to promote reactions or collisions for destroying interferent ions and for separating analyte ions from interferent ions according to mass discrimination or kinetic energy discrimination. These cells are equipped with quadrupole, hexapole or octopole mass spectrometers for mass discrimination and focalization of analyte ions towards the quadrupole analyzer disposed in a tandem configuration. Excellent review articles may be consulted for a sound discussion of these devices considering their components and performance.[55-57]

There are several operational parameters in an ICP-MS and the analyst must know their effects for accurate and precise measurements. The main operational parameters for an ICP-MS are

the applied power for maintaining the plasma, the nebulization gas flow rate, and the sampling depth. These parameters are related to the plasma temperature, residence time of the sample aerosol being transported through the axial channel of the plasma and the species that are being sampled through the interface towards mass spectrometer and detector.

All these instrumental parameters are well established and a plethora of applications can be found in the literature. Becker presented a broad discussion about ICP-MS applications for trace, ultra-trace and surface analysis.[58] Specific sections discuss applications for materials science, environment, biology, medicine, food, geology and geochemistry, and others. A consult to specialized literature is recommended for solving specific analytical tasks.

Based on the multielement capability and fast readings of emission and ions signals typical of inductively coupled plasmas, previous digestions steps should be fast and easily applied for several samples for avoiding slow steps in the analytical procedure. Digests obtained should be stable for storage and present low residual acidity, low residual carbon content and low concentration of dissolved solids. Each one of these requirements exerts critical effects on instrumental performance. Low residual acidity, i.e. acid concentrations lower than 10% or even lower this amount for more viscous acid solutions, is important for avoiding transport interferences when introducing solutions for pneumatic nebulization with conventional nebulizers. Residual carbon content is a parameter important for evaluating the quality of the digestion process for organic samples and also for controlling charge transfer processes in the argon plasma, as typically observed for some elements such as As and Se.[59] Finally, total dissolved solids is important for avoiding clogging of concentric nebulizers typically with small tube and orifice for introduction of

solutions and also for avoiding formation of salt deposits in the quartz torch causing a decrease of lifetime. The total dissolved solids in digests are also a critical limitation for solution introduction in an ICP-MS because of clogging of interface cones, i.e. sampler and skimmer, and proper use of mass spectrometer.

Sample Preparation

The reliability of ICP based methods depends on quantitative conversion of solids to homogenous solutions. In a classical book published in 1970, Gorsuch stated: "For many years it was tacitly assumed that the removal of organic matter before determining 'non-organic' elements present introduced only insignificant errors. Consequently, little attention was paid to it. More recently it has been recognized that the severe conditions often employed for the removal of organic matter may easily introduce more error than all the other steps in the procedure combined".[60]

Conventional wet-sample preparation methods for the decomposition of solid samples are usually carried out in vessels containing the sample and a large volume of decomposition reagent(s), typically 15 to 100 mL. This mixture is then heated for several hours using hot plates, heating mantles, or ovens. Heating is terminated when the analyst decides that the decomposition of the sample is sufficiently complete. This type of open-vessel digestion has many drawbacks, which include the use of large volumes (and multiple additions) of reagents, potential for contamination of the sample by materials and laboratory environment, and the exposure of the analyst and the laboratory to corrosive fumes.

The high-pressure closed-vessel wet-ashing technique, originally described by Carius, is a more efficient way to decompose samples for analysis. The increased pressures allow temperatures

beyond the atmospheric boiling point of the reagent to be reached. While Carius' method improved the efficiency of decomposition, it also has several drawbacks. Analytes can be lost during the opening of the tube when the contents, under elevated pressure, are released suddenly. The analyst is frequently exposed to corrosive reagents, as well as glass pieces, during the opening of the tube. Steel-jacketed Teflon lined bombs are now available to perform similar high-pressure and temperature reactions in thermal ovens. While the higher pressures and temperatures inside the closed vessels increase reaction rates, digestions may still require several hours due to the inefficient, "outside-in" heating mechanism. In addition, the high pressures involved with both of these conventional closed vessel methods tend to increase the safety risk of applying these techniques. Closed-vessel microwave-assisted decomposition uses significantly different technology and fundamentally unique principles to accomplish sample decomposition.

Heating by microwave energy is a "cold" in situ process, producing heat only when there is absorption or coupling of the microwave energy to the solution or microwave absorbing objects. The two primary mechanisms for the absorption of microwave energy by a solution are dipole rotation and ionic conductance. In the dipole rotation mechanism, molecular dipoles align with the applied electric field. Oscillation of the electric field results in forced molecular movement of the dipole molecules with the resulting friction heating the solution. At 2.45 GHz, the frequency of most laboratory microwave ovens, the dipoles align, then randomize 5 billion times a second. In the ionic conduction mechanism, the ionic species present in solution migrate in one direction or the other according to the polarity of the electromagnetic field. The accelerated ions meet resistance to their flow and heating is a natural consequence.[61] These two unique heating mechanisms result in rapid heating of solutions in

comparison with conduction and convection. The heating is so fast that, in open vessels, vaporization alone cannot dissipate the excess energy. This results in solutions being able to sustain superheating above their normal boiling points by as much as 5°C for water to 26°C for acetonitrile.[62,63]

To effectively use closed-vessel microwave-assisted decomposition, one must understand the unique temperature and pressure relationships involved. Gas pressures inside microwave-closed vessels are not what would be predicted from the temperature of the liquid phase. The pressure inside a microwave vessel is dependent upon the volume of the vessel, and the temperature and composition of the gas phase. For example, when water is placed in a high-pressure steel-jacketed Teflon bomb and heated in a convection oven, an equilibrium vapor pressure is established. This vapor pressure is dependent upon the rate of evaporation and condensation of the water vapor. When the temperature is increased, there is a corresponding increase in the evaporation rate and a decrease in the condensation rate because the vessel walls heat both the solution and gas phase. The decrease in condensation rate leaves more water in the vapor phase, increasing the internal pressure. In contrast, when water is heated to the same temperature in a microwave closed-vessel, the internal pressure is significantly less than its steel-jacketed counterpart. This phenomenon is a direct result of the microwave heating mechanism and the materials for microwave vessel. The microwave-closed vessel's liner and outer casing are microwave transparent and have no insulating capacity. Thus, they remain relatively cool during the heating process. The cooler the vessel walls, the more efficient they will be at removing water molecules from the vapor phase. The increased condensation rate results in lower internal pressures at higher temperatures. This microwave reflux action is illustrated in *Figure 8*.

A more complex example of this phenomenon is the closed-vessel microwave heating of nitric acid. Nitric acid is a polar and partially ionized mixture which heats rapidly in a microwave field. When heated, nitric acid partially decomposes into NO_x gas. The gas phase inside a closed vessel becomes a mixture of NO_x gas, nitric acid and water vapor. The pressure of nitric acid during closed-vessel microwave heating is still lower than predicted, even after taking into account the partial pressure of the NO_x gas (*Figure 9*).

The decrease in internal pressure observed in the microwave vessel results from the previously described reflux action and from the loss of the ionic conductance mechanism of microwave heating in the gas

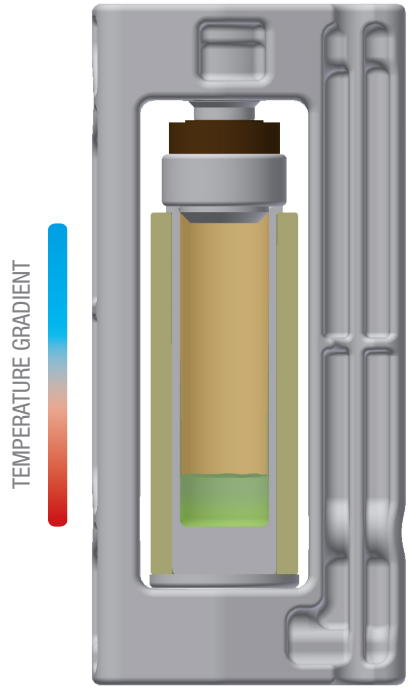


Figure 8. *Reflux conditions inside a microwave closed vessel.*[64]
Blue represents lower temperatures and red represents higher temperatures

phase. The loss of the ionic conductance mechanism in the gas phase means the NO_x gas does not convert microwave energy into heat efficiently, keeping the pressure increase associated with the heating of the gas to a minimum.

This unique temperature and pressure relationship, found only in closed-vessel microwave heating, becomes more complex and unpredictable as additional reagents and samples are added to the solution. Also, the condensation rate varies with the microwave vessel materials and geometry, the liquid volume, the duration of heating, and the system's ability to dissipate the excess energy. At the present time there is no conventional method of predicting the decrease in internal pressure associated with closed-vessel microwave heating. This phenomenon is one of the reasons that pressure control is not applicable for standardizing microwave sample preparation methods.

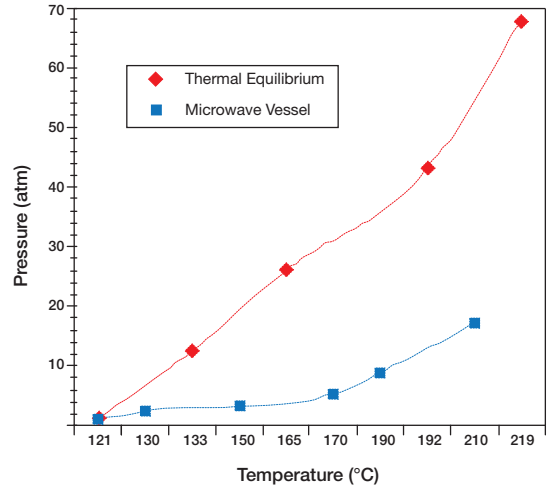


Figure 9. *Internal pressure of HNO_3 at different temperatures.*
(red) 18.9 g in a 100 ml Steel-jacketed bomb.[15]
(blue) 20.0 g in a100 mL microwave closed-vessel.[65,66]

The use of closed vessels in microwave decomposition allows the reagents to be heated above their atmospheric boiling points. The higher temperatures achieved in the closed system give microwave decomposition a kinetic advantage over hot plate digestion, as described by the Arrhenius equation.

$$\frac{d\ln k}{d\mathrm{T}} = \frac{E_a}{RT^2}$$

Integration of this equation gives:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

In this expression, k_1 and k_2 are rate constants for the reaction of interest at T_1 and T_2 respectively, E_a is the activation energy, and R is the ideal gas constant. These equations show that the reaction rate increases exponentially with increasing temperature. This translates into approximately a 100-fold decrease in the time required to carry out a digestion at 175°C when compared to 95°C digestion.[64,65,67] In addition, because the mineral acid converts the microwave energy into heat almost instantaneously, rapid heating of the sample is achieved, further decreasing the reaction times.

Closed-vessel microwave decomposition has several unique characteristics which have led analysts to reduce the sources of error and contributions to the analytical blank that were previously obscured by lengthy sample preparation procedures. Open-vessel methods cannot prevent this type of contamination because they are continuously exposed to laboratory air currents. The use of closed-vessels for microwave-assisted decomposition isolates the sample

from laboratory air currents during the decomposition process reducing airborne contamination. By preparing the samples for closed-vessel microwave digestion under clean air conditions, the sample is isolated and will not come in contact with laboratory air. Thus, the possibility for contamination by airborne particles in the laboratory air is eliminated. Similarly, by performing post sample processing, such as rinsing and dilution in clean environments, airborne contamination can be further reduced.

As previously stated in chapter 2, reagent contamination contributes to the concentration of the analytes present in the sample. The amount contamination contributed is a function of the total quantity of reagent used. For example, using 50 mL of a reagent that contains a contaminant at the 100 µg/L level will contribute 5 µg of that species as contamination. Unlike open-vessel methods that require large quantities of reagent due to evaporation losses, closed-vessel microwave methods continually reflux the reagents and do not allow the reagent vapors to escape. The reflux conditions inside a microwave-transparent vessel allow much smaller volumes of the reagent to be used, thus reducing the contamination from the decomposition reagents.

The materials used (fluorinated polymers and quartz) for microwave vessels are chemically inert to most dissolution reagents and provide a non-contaminating environment for sample preparation. TFM is preferred over PFA for the construction of microwave vessels because of its superior chemical and thermal resistance and lower blank levels (*Tables 19* and *20* plus *Figures 10* and *11*).

The skill of the analyst is perhaps the most difficult to evaluate. For open-vessel methods, the analyst must monitor the progress of the digestion in several vessels simultaneously. Compounding the problem, the vessel temperature varies with position on the hotplate.

The analyst must then subjectively decide whether dissolution is sufficiently complete and remove the sample from the heat source. In microwave methods, the efficiency of the heating coupled with the direct monitoring of the conditions inside the vessel removes the subjectivity of the analyst from the digestion process. The automation and standardization of the sample preparation method through the use of closed-vessel microwave decomposition serves to reduce the analyst's judgment from much of the sample preparation process.

The combined effect of closed-vessel microwave-assisted decomposition and clean chemistry techniques is shown in *Tables 21* and *22*. The blank results show significant reduction in the contributions of the outside environment, reagents, and materials to the analytical blank level in addition to lowering the overall measurement uncertainty. From *Table 22* we can see this combination of techniques allows trace metal analysis to be completed with increased accuracy and precision.

See page 109 for detailed information on the available instrumentation: Milestone ETHOS UP.

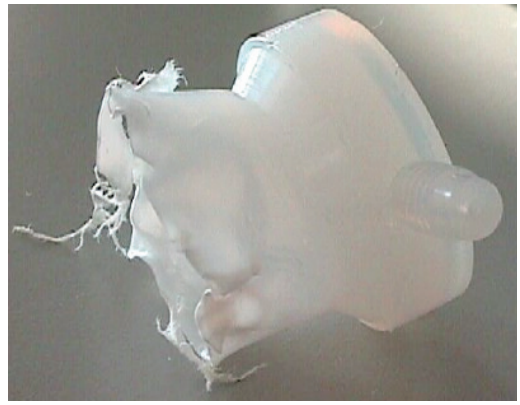


Figure 10. *Damage to PFA microwave vessel cover after venting at high temperature.*

Figure 11. *Damage to PFA microwave vessel after venting at high temperature.*

Table 19. *Trace element contamination (µg/L) of acid blanks prepared from identical reagents in PFA and TFM vessels*[68]

Element	PFA	TFM
Al	2.7	DL
B	7.5	1.8
Ba	0.9	DL
Bi	0.5	DL
Cd	4.7	0.1
Co	0.8	DL
Cr	0.8	0.1
Mo	0.6	DL
Pb	6.7	0.03
Sb	0.6	DL
W	5.4	DL
Zn	0.6	0.2
Zr	1.0	DL

DL = concentration below instrument detection limit

Table 20. *Analytical blank values for TFM microwave vessels after fifty digestions of environmental samples.*[69]

Element	µg/L	Element	µg/L
As	0.24	Li	0.09
B	0.40	Mo	0.26
Ba	0.04	Pb	0.15
Be	0.03	Sb	0.01
Cd	0.01	Sc	0.04
Ce	0.19	Se	0.01
Co	0.02	Sr	0.05
Cu	0.03	Ta	0.01
Ga	0.02	Zn	0.31

Table 21. *Comparison of analytical blank results obtained from hot plate and microwave digestion of a certified reference soil.*[70] *Concentration expressed as µg/g.*

Analyte	Hot Plate	Microwave
As	0.204 ± 0.106	0.074 ± 0.013
Cd	0.318 ± 0.122	0.029 ± 0.019
Cr	3.35 ± 2.85	0.104 ± 0.059
Cu	0.060 ± 0.020	0.030 ± 0.017
Pb	0.171 ± 0.076	0.040 ± 0.019
Hg	0.037 ± 0.004	0.017 ± 0.007
Ni	0.375 ± 0.069	0.060 ± 0.063
Se	0.548 ± 0.264	0.172 ± 0.022
Tl	0.028 ± 0.020	0.028 ± 0.020
V	2.35 ± 0.45	1.20 ± 0.51
Zn	2.92 ± 1.43	1.66 ± 0.93

Error expressed as 95% confidence interval (n=4)

Table 22. *Comparison of results obtained from hot plate and microwave digestion of a certified reference soil.*[70] *Concentration expressed as µg/g.*

Analyte	Hot Plate[a]	Microwave	Certified Value
As	12.3 ± 2.27	17.6 ± 0.9	17.7 ± 0.8
Cd	0.31 ± 0.09	0.41 ± 0.06	0.38 ± 0.01
Cr	68.8 ± 7.5	123 ± 3	130 ± 4
Cu	23.8 ± 2.7	33.5 ± 1.2	34.6 ± 0.7
Pb	10.8 ± 1.3	17.5 ± 1.1	18.9 ± 0.5
Hg	0.97 ± 0.14	1.42 ± 0.10	1.40 ± 0.08
Ni	63.4 ± 3.9	83.2 ± 3.0	88 ± 5
Se	1.61 ± 0.34	1.54 ± 0.33	1.57 ± 0.08
Tl	0.29 ± 0.05	0.63 ± 0.02	0.74 ± 0.05
V	65.6 ± 8.8	119 ± 6	112 ± 5
Zn	113 ± 13.5	102 ± 6.1	106 ± 3

Error expressed as 95% confidence interval (n=4)

CHAPTER **4**

TOOLS OF THE TRADE: MICROWAVE-ASSISTED SAMPLE PREPARATION TECHNIQUES

Tools of the Trade: Microwave-Assisted Sample Preparation Techniques

"Power is nothing without control".

Slogan of Pirelli Tyre Co.

Microwave-assisted sample preparation has evolved since its mainstream acceptance. Gone are the days when most analysts think that fast heating is the main contribution coming from microwave-assisted acid digestion. Closed vessel digestions are attractive because the confined volume containing sample and reagent mixture may be seen as a small-scale laboratory where we can reach a better control of losses of analytes and contamination using proper material for vessel construction and pure reagents. However, there is a clear limitation caused by the sample mass that can be digested without a critical increase of pressure (*Figure 12*). It is usually stated that digestion of samples rich in organic materials in closed vessels are limited to 0.5 g mass for avoiding sudden increase of pressure caused by a fast evolution of gaseous by products of the oxidation. The traditional approaches for dealing with the risk of over pressurization are (1) to limit the mass of sample, (2) to keep sample and reagent mixture

without heating during short times or even overnight for decomposition of easily oxidized compounds before closing the vessel, (3) to design vessels that can stand for high pressures, (4) to design vessels with vent-reseal mechanism for avoiding reaching levels of pressure above threshold values (*Figure 13*). All these strategies are effective for guaranteeing safety conditions for analysts, but of course some limitation may result, for instance the sample mass limitation may difficult the determination of analytes present in low concentrations when performing trace analysis.

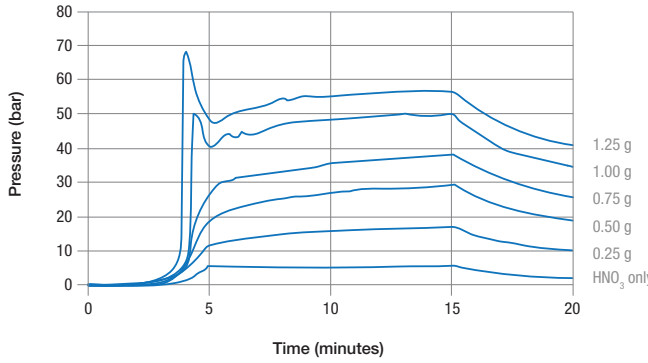


Figure 12. *Bovine Liver sample mass vs developed pressure*

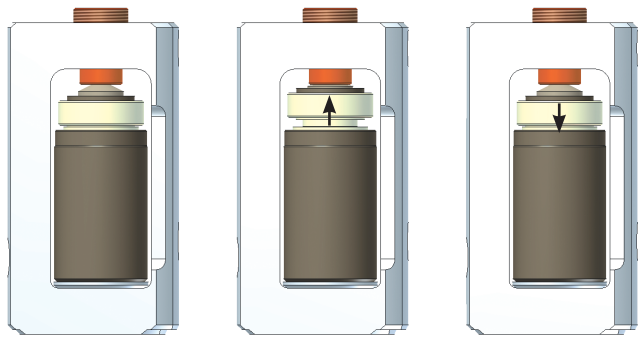


Figure 13. *Vessels with vent-reseal mechanism*

The need to improve upon microwave-assisted digestions has lead to the development of several new techniques specifically designed to minimize contamination and improve the overall accuracy and reliability of plasma based analysis.

Think Blank: How are the unique properties of microwave heating used to control the analytical blank?

Dilute Acid Digestions

It is well-known that conductive heating occurs by heat transfer from the container wall to the solution adjacent to it and proceeded by the gradual transfer to the bulk of the solution. On the other hand, microwave-assisted heating is carried out in vessels transparent to microwave and radiation interacts directly with ions and dipoles contained in the solution. Molecules in the gas phase do not absorb microwave radiation appreciably.[71] A temperature gradient is established with the absorbing solution at higher temperature and vessel walls and gas phase at lower temperatures (*Figure 14*). This reflux condition, as described in chapter 3, has been exploited by Bizzi et al. in the regeneration of nitric acid by condensation processes and reactions with oxygen when working with diluted solutions.[72]

The systematic investigation about the use of diluted solution of nitric acid started in 2002 when it was demonstrated that plant materials were efficiently digested using 2 mol/L nitric acid solution and residual carbon contents were similar for solutions containing from 2 to 14 mol/L nitric acid.[73] In more recent studies, it was demonstrated the double role of oxygen during digestion processes as an oxidizing agent as well as a reagent to promote regeneration of nitric acid under microwave-assisted heating conditions that promote condensation processes in colder upper zones of the reaction vessel.[74]

A further study, demonstrated that hydrogen peroxide acts similarly to oxygen. In other words, hydrogen peroxide is not only an auxiliary oxidant reagent to complement nitric acid action, but it also acts as a source of oxygen for promoting nitric acid regeneration.[75] These procedures allowed a pronounced reduction in the required volume and concentration of nitric acid and it means that digests require less dilution before analysis and better blanks are obtained. Both aspects are important for making feasible accurate and precise trace analysis.

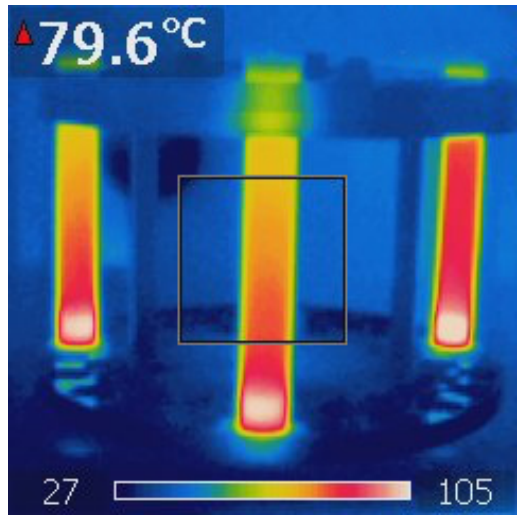


Figure 14. *Temperature gradient in the vessel*

As demonstrated by Castro et al. all these processes are more operative in a closed-vessel microwave-assisted heated comparatively to a closed-vessel conductively-heated because of the temperature gradient.[76] Based on these processes, we may propose a different procedure considering specific conditions related to the interaction between microwave radiation and solutions containing ions and dipoles. The hypothesis is that condensation promoted by temperature gradient and the temperature gradient itself may avoid losses of volatile elements. If this is true we may allow venting during digestion without critical losses of these elements. In other words, proper control of microwave-assisted heating allows control of pressure increase and we may be able to control analyte losses even in conditions with venting for avoiding over pressurization.

To test this hypothesis we carry out experiments using an Ethos UP microwave oven with a Maxi 44-vessel rotor. First experiments were performed using 2 mg/L As, Cd, Cr, Hg, Pb and Zn solution microwave-assisted heated in aqua regia and in concentrated HCl media (10 mL in both media). The following heating program was applied: 1st step – 5 min to reach 140°C, 2nd step – 5 min at 140°C, 3rd step – 10 min to reach 180°C, and 4th step – 10 min at 180°C. Recoveries of analytes were determined by measuring diluted solutions by inductively coupled plasma tandem mass spectrometry (ICP-MS/MS, Agilent, model 8800). Data are shown in *Table 23* and it may be seen that all recoveries were in the 100 ± 20% range despite losing up to 14.2% of mass. The loss of mass was measured by weighing each digestion vessel containing sample and digestion solution before and after heating.

Further experimentation was performed using a tuna fish reference material (ERM – CE 464) produced by Institute for Reference Materials and Measurements. The heating program was applied in

Table 23. *Recoveries (%) of As, Cd, Cr, Hg, Pb and Zn in spiked solutions microwave-assisted heated in different media and loss of mass in each condition.*

Medium	As	Cd	Cr	Hg	Pb	Zn	Loss of mass (%)
HCl conc.	115.8	98.2	90.2	87.5	94.8	81.6	9.3
Aqua regia	109.4	97.7	88.6	92.5	95.2	80.5	13.0
Aqua regia	109.7	98.6	85.7	88.1	96.0	80.9	14.2

Table 24. *Recoveries of Hg in tuna fish (ERM – CE 464*) using microwave-assisted acid digestion with diluted (7 mol/L) and concentrated (14 mol/L) solutions of nitric acid.*

Sample mass (g)	Medium	Recovery (%)	Loss of mass**(%)
0.5	HNO_3 conc.	91.6	10.5
1.0	HNO_3 conc.	95.0	27.3
0.5	HNO_3 dil. + H_2O_2	103.0	14.8
1.0	HNO_3 dil. + H_2O_2	103.0	10.7

*Certified concentration for total Hg: 5.24 ± 0.10 mg/kg

two steps: 1st step – 20 min to reach 200°C and 2nd step – 10 min at 200°C. Sample masses of 0.5 and 1.0 g were digested using 10 mL HNO_3 conc. or 10 mL HNO_3 conc. plus 3 mL H_2O_2 conc. Data are shown in *Table 24*. Mercury was determined by ICP OES. Recoveries varied from 91.6 to 103% despite losses of mass as high as 27.3%.

Two certified reference materials, bovine muscle and spinach leaves, produced by National Institute of Standards and Materials (Gaithersburg, MD, USA) were also digested using a heating program in two steps with a maximum temperature of 180°C applied during 20 min of ramp and 10 min of plateau. Digestions were performed using concentrated nitric acid solution, or 7 mol/L nitric acid or a mixture composed by 7 mol/L nitric acid plus hydrogen peroxide. Losses of masses in digests varied from 1.4 to 10.9 %. Arsenic and Se were

Table 25. *Estimations of residual carbon contents (RCC, %) and mass losses (%) in infant milk powder microwave-assisted acid digested.*

Sample mass (g)	RCC* (%)	Loss of mass* (%)	RCC** (%)	Loss of mass** (%)
0.5	14.0	22.8	32.7	3.8
1.0	15.7	30.9	26.1	11.8
1.5	10.5	46.1	15.1	28.7
2.0	16.0	48.3	19.9	32.5

*10 ml HNO_3 conc. **10 mL 7 mol/L HNO_3 + 3 mL H_2O_2 conc.

recovered in the 80 - 120 % range for both materials in all digestions conditions. Most data for Cd, Hg and Pb are also in this range, but some recoveries were higher than expected probably because contamination. All determinations were performed using a triple quadrupole ICP-MS (Agilent, Model 8800, Tokyo, Japan) operated either in single mode or in triple quadrupole mode with oxygen inserted into the octopole reaction system.

An estimative of efficiency of digestion was done by determining residual carbon content in samples of infant milk powder digested with concentrated HNO_3 or 7 mol/L HNO_3 plus concentrated H_2O_2 (*Table 25*). It was assumed that this sample contained 52% carbon. Residual carbon contents in digests were determined by ICP OES. As expected, higher losses of mass occurred when working at more severe conditions, i.e. higher concentration of HNO_3 and higher mass of sample. Lower RCCs were determined for digestions with concentrated HNO_3. All digests were yellowish without any solid residues indicating a sufficient efficiency for most analytes that would be determined by ICP OES.

Further experiments are in progress, but we think that the hypothesis related to quantitative recoveries of analytes, even volatile elements, is so far supported by these data. It means that condensation

mechanisms caused by temperature gradients are operative as proposed by Bizzi et al. and Richter et al.[72,77] In a comprehensive study published in 2000, Link and Kingston have demonstrated that "because the solution actually cools during microwave-assisted evaporation, volatilization due to overheating at dryness is minimized".[78]

We must carefully develop further applications of this procedure with venting because despite condensation phenomena, losses may occur for volatile species. For instance, it was demonstrated in a focused-microwave-assisted acid digestion using open vessels for samples of oyster, mussel and clam that losses can be observed for As, Cd, Pb and Se. Higher losses were observed for Cd and Pb, but no losses occurred for Zn. However, it should be emphasized that conditions in an open vessel are completely different depending on the condensing system used and the maximum temperature. In this experiment, maximum temperature of 180°C was kept for 15 min.[79] Additionally, it is well known that invertebrate samples contains large quantities of As, mainly as arsenobetaine, and Se is accumulated in soft tissues as seleniumcysteine.

Additional experimental data should test this hypothesis and if it is really confirmed we have a new strategy for digesting high masses of samples without critical safety conditions caused by too high pressure inside the closed vessel. One of the critical aspects that must be better investigated is the effect of different forms of analytes and it seems probable that more volatile species would be lost such as above mentioned for focused-microwave-assisted acid digestion. However, losses will depend on chemical forms and also probably how fast is the release of gases. It may be supposed that sudden venting without minimum control will be affected by losses and tailored heating programs should be developed taking into account the speed of pressure increase and ideally also incrementing condensation processes.

After fully developed for several different types of samples with diverse matrices, we may say that this procedure using high sample mass with controlled venting associated with diluted acid solutions will be totally compatible with requirements of trace analysis and instrumental measurements with ICPs which are affected by the total amount of dissolved solids.

Microwave Evaporation

Solutions submitted for trace elemental analysis often need to be evaporated prior to analysis. The most common reason for evaporation is to concentrate the sample, because the initial analyte levels are below the instrument detection limits. The other reason for evaporation is the sample solution contains matrix elements that will present problems for analysis. Traces of hydrofluoric acid will etch the glass components of ICP and ICP-MS systems releasing trace element contamination. Chlorine and fluorine form polyatomic ions that interfere with the ICP-MS analysis of many common elements. For example $^{40}Ar^{35}Cl^{+}$ interferes with $^{75}As^{+}$ and $^{35}Cl^{16}O^{+}$ interferes with $^{51}V^{+}$.

Obtaining the ideal solutions for trace elemental analysis is often complicated due to the formation of volatile species during the evaporation process. As the number of solvent molecules decreases, the ions begin to recombine, and at dryness the residue will consist of a mixture of recombined salts. These salts will have an associated vapor pressure and boiling point which will vary with the oxidization state and counter anion (*Table 26*). The use of traditional heating methods to perform evaporations can lead to the loss of volatile analytes, because as the evaporation precedes the temperature of the evaporation vessel approaches the temperature of the heat source. At dryness these temperatures can be in excess of 150°C.

In contrast to traditional evaporation methods, the unique

heating mechanism, exclusive to microwave-assisted heating, allows for the retention of volatile analytes during evaporation. As the

Table 26. *Potentially volatile salts from solution.*[81,82]

Element	Volatile Salts	Boiling Point (°C)
Arsenic	$AsCl_3$	130.2
	AsF_3	58
Antimony	SbF_5	150
	$SbCl_5$	79
Selenium	$SeCl_4$	170-196[a]
	SeF_4	107.8
Tin	$SnCl_4$	115
Vanadium	VCl_4	152
	VF_5	111.2
Chromium	CrF_5	117
Lead	$PbCl_4$	50
Germanium	$GeBr_4$	87
	$GeCl_4$	26

[a]$SeCl_4$ sublimes

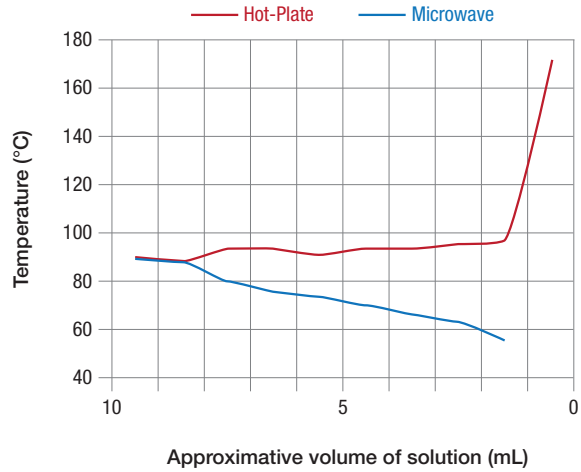
evaporation proceeds and the solvent is removed from the system the matrix volume will be reduced. As the mass of the sample solution decreases the amount of microwave energy absorbed decreased according to the following equation:

$$P_{abs} = \frac{KC_p \Delta T m}{t}$$

In this equation P is the apparent absorbed power in watts, K is the conversion factor for calorie/s to watts, Cp is the specific heat, ΔT is change in temperature, m total is mass of sample in microwave,

t is irradiation time. This unique relationship between the microwave vessels being microwave transparent and the decreased coupling or microwave energy as sample mass decreases, leads to a decrease in temperature as the sample approaches dryness (*Figure 15*). Lower temperatures at dryness decrease the potential for loss of volatile species, resulting in more complete recoveries for volatile analytes (*Figures 16* and *17*).[78,82]

See page 114 for detailed information on the available instrumentation: Milestone evaporation rotor.



Temperature of solution as volume decreased during microwave-assisted and hot plate evaporation. The final point in the hot plate temperature profile is that of the beaker bottom at dryness.

Figure 15. *Vessel temperature as a function of solution volume.*

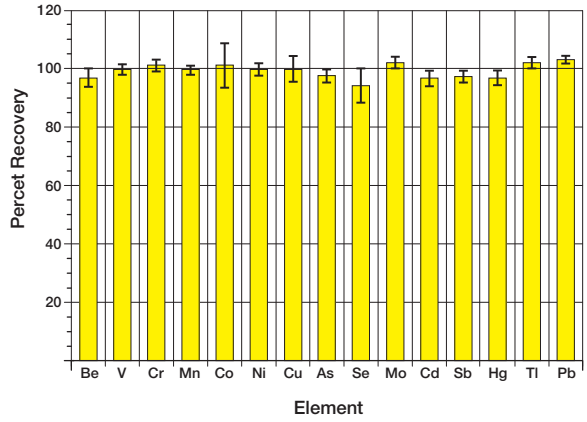


Figure 16. *Evaporation recoveries of select elements from a 9:3 solution of HNO_3/HCl. Initial solution concentration was 500 µg/L.*

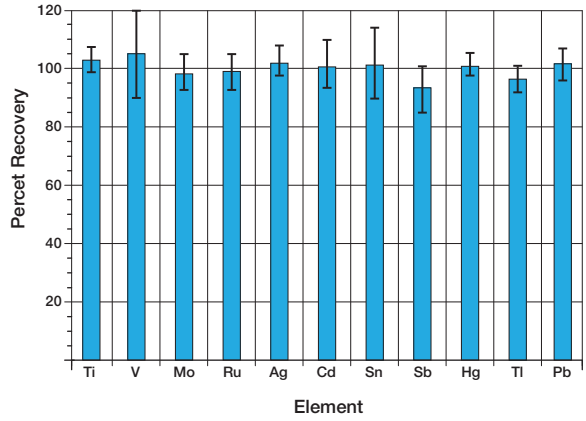


Figure 17. *Percent recovery of 2.5 ng spikes from 10 mL of HCl. Uncertainties are expressed as 95% confidence intervals with n ≥4.*[79,83]

Another factor that plays a significant role in evaporation losses is the oxidization state of the analyte of interest. It has been reported that even mild heating of a HF solution results in a 20% loss of Se(IV) and a 45% loss of As(III) and a losses of 65-100% upon dryness. Losses of antimony during evaporation are due to the formation of poorly soluble compounds and mercury is due to it being present in its elemental form. These losses can be avoided by converting these elements to higher oxidation states i.e. Se(VI), As(V), Sb(V), Hg(II). The use of traditional decomposition methods can not ensure a uniform oxidation state due to matrix interferences and reaction rate limitations.[84] This can be overcome by coupling closed-vessel microwave decomposition with microwave evaporation. The elevated temperatures and pressures decompose the matrix interferences and form stable complex ions. For example:

$$Sb_2O_{2(s)} + HCl + HNO_3 \rightarrow SbCl_{6(aq)}$$
$$AsF_{3(aq)} + HF + HNO_3 \rightarrow AsF_{6(aq)}$$

The formation of these stable complex anions leads to complete retention of these traditionally volatile elements. (*Figures 18* and *19*).

Microwave Vessel Inserts

Analytical chemists are being required to measure lower and lower levels of trace metals in samples. This frequently requires the analyst to make measurements near the method detection limit which usually result in decreased accuracy and precision. Closed-vessel microwave digestion techniques require a minimum volume of 10 mL to achieve accurate temperature monitoring of the reaction conditions. Ideally, modern spectroscopic techniques require samples submitted for analysis to have acid concentration of 1 to 5% v/v. This requires

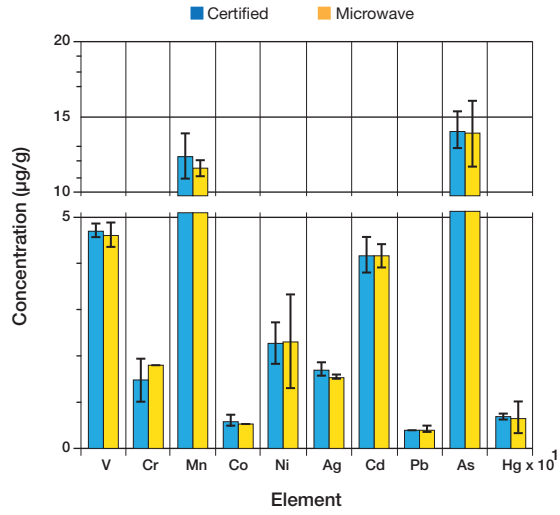


Figure 18. *Concentration of analytes in SRM 1566A (Oyster Tissue) following Microwave-Assisted Evaporation of the digestate compared with the certified total concentrations.*
Uncertainties are expressed as 95% confidence intervals with n≥3.[77,78]

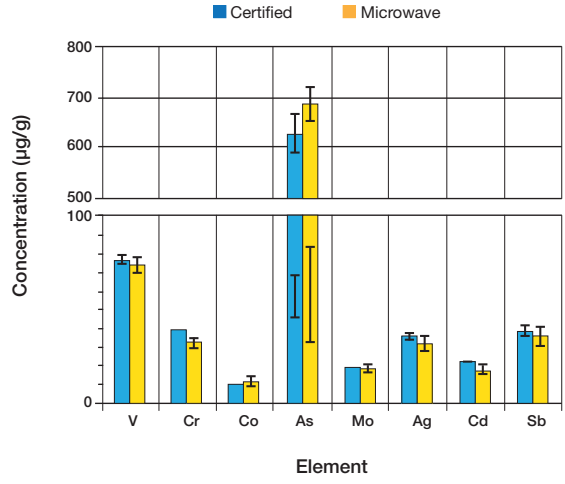


Figure 19. *Concentration of analytes in SRM 2710 (Montana Soil) following Microwave-Assisted Evaporation of the digestate compared with the certified total concentrations (* = noncertified concentration).*
Uncertainties are expressed as 95% confidence intervals with n≥3.[77,78]

samples that were digested with 10 mL of acid to be diluted by a factor of 500 to achieve the 1 to 2% acid content necessary for ICP analysis. These large dilution factors often result in some of the analytes becoming non-detectable.

These large dilutions are often overcome by maximizing the sample size relative to the amount of digestion acid. This approach works well for samples that do not contain a large amount of organic material. For samples with high organic content this is usually not an option because the reaction gases (CO_2 and NO_x) produced during the digestion can cause the microwave vessel to vent when larger sample sizes (greater than 0.5 grams) are used. Recent advances in understanding of microwave-assisted sample preparation have led to the development of vessel inside vessel technology as a means to improving method detection limits for high organic samples.

Vessel inside vessel technology uses a smaller secondary vessel inside the primary microwave vessel. The secondary vessel contains the sample and digestion reagents and the primary vessel contains the 10 mL of solution required to achieve accurate temperature monitoring (*Figure 20*). This configuration reduces the amount of acid required for any digestion to near stoichiometric quantities reducing the imparted contamination from reagents by 5 to 10 fold. In addition the smaller vessel size reduces the surface area that is in contact with the sample which will impart less contamination than a standard 100 mL microwave vessel.

This unique configuration provides better reaction control. Controlling reaction kinetics is especially important when trying to digest large quantities (0.5 to 1.0 g) of organic material because the potential for auto-catalytic decomposition increases. When the sample size is small (0.25 g) the heat released by the oxidization of the organic material does not cause a significant change in the temperature

A) Vessel-inside-vessel schematics

B) Left to right: 50 ml single quartz insert, rack with three 10 ml glass quartz and TFM inserts

Figure 20. *A) Schematic of vessel in vessel technology. B) Types of inserts available.*

of the reaction mixture. As the sample size is increased the heat released from the oxidation can cause the reaction mixture to heat faster that the programmed rate. The rise in temperature promotes further decomposition which results in the microwave vessel venting (sometimes at pressures lower than its rating) due to the sudden increase in pressure resulting from the self-sustaining auto-catalytic decomposition (runaway reaction) of the sample (*Figure 21*). The use of vessel inside vessel technology helps control these self-sustaining auto-catalytic reactions by providing a heat sink for the energy liberated during oxidization. This is accomplished by placing water in the outer microwave vessel. The water draws the heat away from the reaction mixture, slowing down the reaction kinetics and preventing a runaway reaction (*Figure 22*).

The amount of sample that can be safely digested is limited by the amount of pressure that is generated during the decomposition process. Current microwave vessel technology limits the internal pressure to 100 bar (1450 psi). For most organic samples this limits the sample size to 0.5 to 0.7 g. In order to digest organic samples larger than 0.7 g secondary reaction chemistry must be employed to lower the pressure during microwave-assisted digestion. This is accomplished with the vessel inside vessel technology by adding H_2O_2 to the outer microwave vessel to convert NO_x and CO_2 into HNO_3 and H_2CO_3 respectively.

See page 113 for detailed information on the available instrumentation: Milestone Ultratrace Inserts.

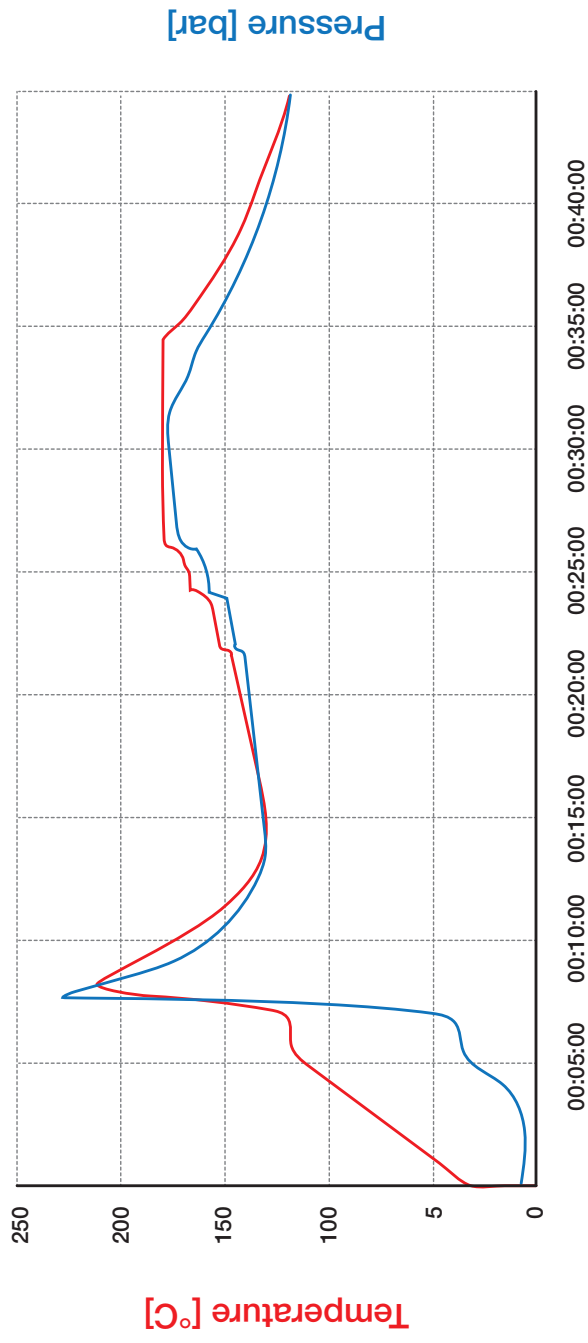


Figure 21. *Example of runaway reaction during a closed vessel microwave digestion.*

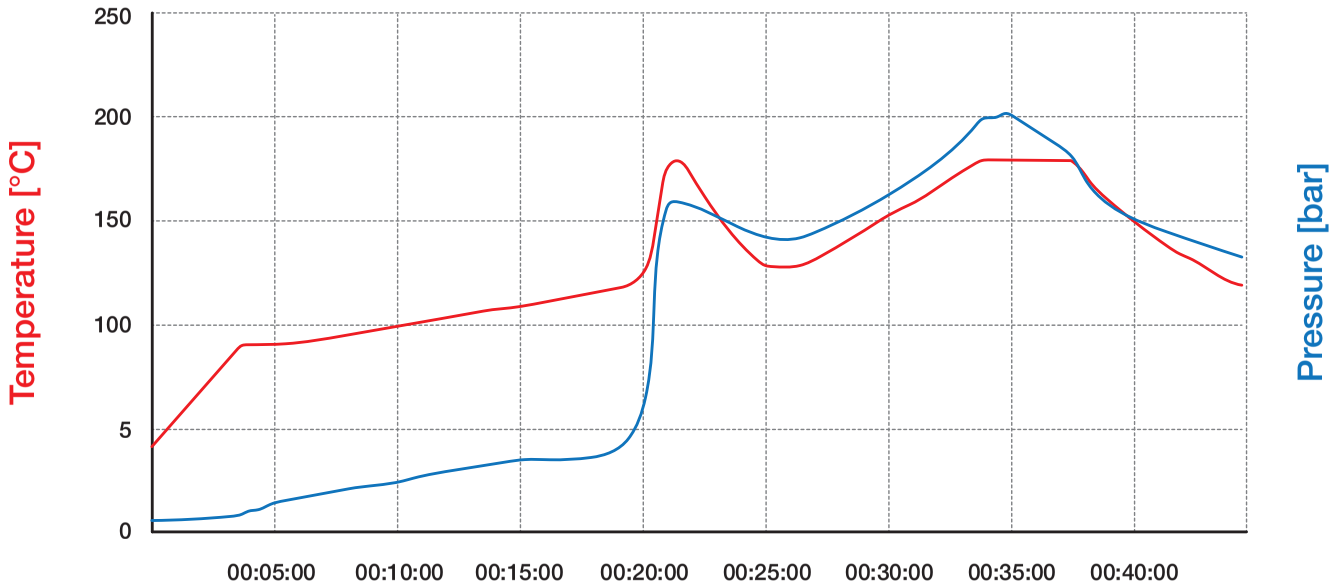


Figure 22a. *Digestion of 5 g of fresh liver using conventional microwave decomposition. Note the runaway reaction.*

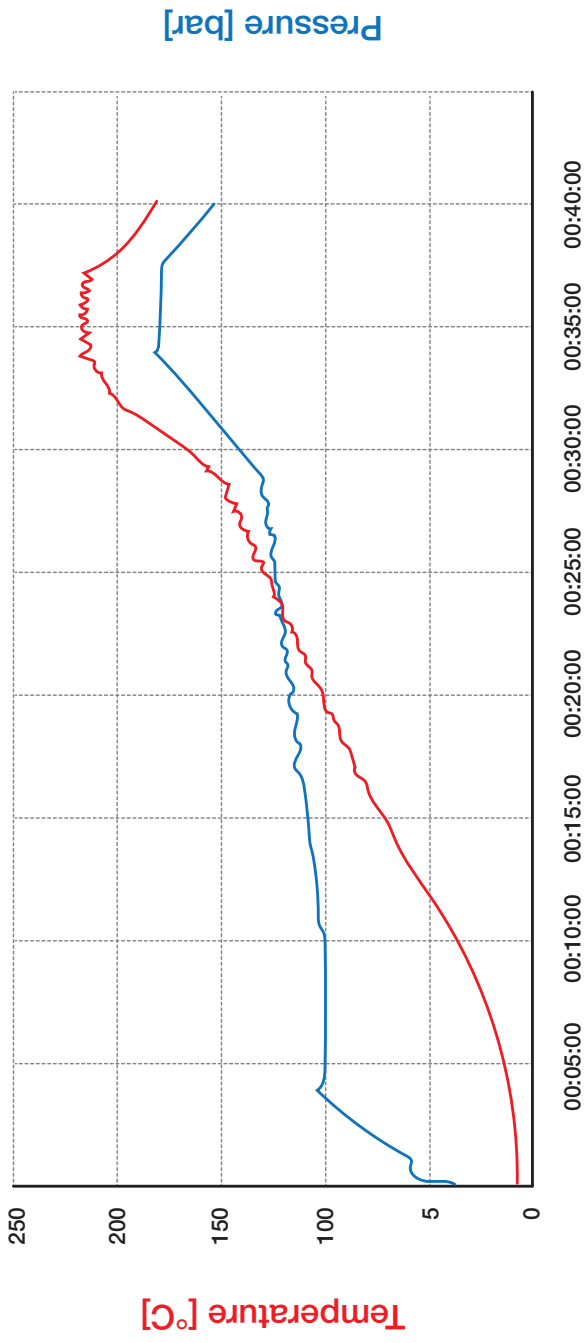


Figure 22b. *Digestion of 5 g of fresh liver using vessel inside vessel technology. There is no runaway reaction.*

Primary decomposition reaction

$$(CH_2)_x + 2x\ HNO_3 \rightarrow x\ CO_2 + 2x\ NO + 2x\ H_2O$$

Secondary reactions

$$2\ H_2O_2 \xrightarrow{\Delta} 2\ H_2O + O_2$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$3\ HNO_2 \xrightarrow{\Delta} HNO_3 + 2\ NO + H_2O$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The quantitative effect of vessel in vessel technology coupled with secondary reaction chemistry can be seen in the digestion of polyethylene. When 0.35 g of polyethylene is digested with 10 mL of nitric acid in a standard 100 mL microwave vessel the internal pressure at the end of the digestion was measured 45 bar. In contrast when 0.35 g of the same polyethylene is digested using vessel in vessel technology and the secondary reaction chemistry outlined in the above equations, the internal pressure at the end of the digestion was reduced to 22 bar. When the sample was increased to 0.70 g the internal pressure measured 38 bar. The sample size was effectively doubled and the acid volume reduced by a factor of 5 which translates into a factor of 10 decrease in the method detection limit for polypropylene analysis.

There is also no transfer of analytes from the inner vessel to the outer vessel and complete recovery of volatile analytes is achieved. (*Tables 27-33*). Making this an ideal technique for improving inorganic metals analysis.

Table 27. *Microwave-assisted digestion of cell culture media using vessel inside vessel technology followed by ICP OES analysis. Results of six replicate samples.*

Element	Concentration (µg/g)	% RSD
Ca	454	5.04
Zn	2.22	8.24
Fe	9.44	2.52
Mo	7.03	5.49
Mg	428	4.13
K	19552	5.66
P	7527	3.69
Na	79461	2.88

Table 28. *Iron spike recoveries for microwave-assisted digestion of cell culture media using vessel inside vessel technology followed by ICP OES analysis.*

Spike Amount (µg)	% Recovery
10	95.2
25	103
50	98.8

The average spike recovery is 99.2% with a RSD of 4.3%

Table 29. *Concentrations (ng/g) of inorganic trace elements in Bovine Liver (SRM 1577A) using vessel inside vessel technology.*

Element	Measured	Certified
Cd	427 ± 50	440 ± 60
Co	208 ± 1.9	210 ± 50
Mo	3540 ± 46	3500 ± 500
Pb	135 ± 14	135 ± 15
V	104 ± 7	98.7 ± 1.6

Error expresses as 95% Confidence Interval n=6

Table 30. *Mercury analysis using vessel in vessel technology.*

Reference Material	Measured (ng/g)	Certified (ng/g)
NIST 1573a Tomato Leaves	38 ± 3	37 ± 2
NIST 1633b Coal Fly Ash	149 ± 10	141 ± 19
NIST 2711 Montana Soil	6190 ± 85	6250 ± 190
BCR CRM 061 Aquatic Plant	218 ± 10	230 ± 20
BCR CRM 062 Olive Leaf	284 ± 10	280 ± 20
BCR CRM 162 Pig Kidney	1.924 ± 82	1.970 ± 40

Error expresses as 95% Confidence Interval n=3

Table 31. *Concentrations (µg/g) of inorganic trace elements in Polyethylene (EC680) using vessel inside vessel technology.*

Element	Measured (µg/g)	Certified (µg/g)
As	29.2 ± 0.7	30.9 ± 0.7
Cd	142.4 ± 1.9	140.8 ± 2.5
Cr	117.5 ± 2.1	114.6 ± 2.6
Pb	111.4 ± 1.7	107.6 ± 2.8

Error expressed as 95% C.I. n=3

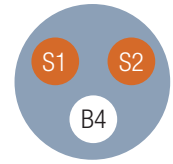
Table 32. *Concentrations (µg/g) of inorganic trace elements in Polyethylene (EC680K) using vessel inside vessel technology.*

Element	Measured (µg/g)	Certified (µg/g)
As	3.89 ± 0.15	4.1 ± 0.5
Cd	19.5 ± 0.1	19.6 ± 1.4
Pb	13.4 ± 0.4	13.6 ± 0.5
Sb	9.58 ± 0.53	10.1 ± 1.6
Zn	135.0 ± 0.9	137 ± 20

Error expressed as 95% C.I. n=3

Table 33. *Blank contamination check for a three position vessel insert during an animal blood digestion. S1 and S2: samples; B4: blank.*

Location	Cr (µg/L)	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
S1	54.79	39.56	14.38	31.61	11.00	148.5
S2	56.08	39.52	14.30	32.59	10.80	148.2
B4	< 2	< 2	< 2	< 2	< 2	< 10



Vapor Phase Microwave Digestion

As discussed previously contamination imparted to the sample from reagents and contact with the digestion containers can cause serious problems for the analyst. The advantages of dilute acids, microwave evaporation, and inserts in controlling contamination can be simultaneously exploited to provide a digestion environment that uses minimal acid for digestion, imparts little or no contamination, and leaves no residual acid accumulation in the sample.

Vapor-phase microwave digestions employs direct sample attack by high temperature acid vapors coupled with simultaneous elimination decomposition products. This is accomplished by placing the sample into an insert and the digestion acids to the outer vessel instead of directly to the sample. As the digestion acids are heated they vaporize, fill the entirety of microwave vessel, and attack the sample until the digestion is complete. This process ensures that there is minimal contact of the digestion acids with the container walls and the smallest amount of reagent use, leading to a dry digestate produced with the smallest possible contamination. In addition, the vaporization of the acids further purifies them before contact with the sample.

This methodology is most applicable to samples that are easily digested with nitric acid (biological) or a combination of nitric and hydrofluoric acids (silica based). The biological matrices take

advantage of the fact that two of the decomposition products are gases that dissipate into the vessel expanse and re-dissolve in the outer digestion acids via equations. Silica based materials use a similar reaction chemistry to eliminate the silicon matrix by trapping in as hexafluorosilicic acid (H_2SiF_6) in the outer digestion solution as well as shown in the following equations.

$$3\ Si_{(s)} + 4\ HNO_{3(aq)} + 12\ HF_{(aq)} \rightarrow 3\ SiF_{4(g)} + 4\ NO_{(g)} + 8\ H_2O_{(l)}$$

$$SiO_{2(s)} + 4\ HF_{(aq)} \rightarrow SiF_{4(g)} + 2\ H_2O_{(l)}$$

$$SiF_{4(g)} + 2\ HF_{(aq)} \rightarrow H_2SiF_{6(aq)}$$

These techniques have been successfully applied to the determination of inorganic metals in lobster hepatopancreas (*Table 34*), marine sediment (*Table 35*), and polycrystalline silicon (*Table 36*).

Single Reaction Vessel

"I believe 640 kbytes will be enough for everyone."

Bill Gates - 1981

The mainstream acceptance of microwave-assisted digestion as the preferred sample preparation methodology for inorganic metals analysis has lead to the development of numerous standard methods by organizations such as U.S. Environmental Protection Agency (EPA), American Society for Testing and Materials (ASTM), U.S Food and Drug Administration (FDA) and AOAC International. Commercial labs following these standardized methods using conventional microwave

Table 34. *Concentrations (µg/g) of inorganic trace elements in Lobster Hepatopancreas (TORT-1) using microwave vapor phase digestion.*[85]

Element	Measured	Certified
As	25.2 ± 1.5	24.6 ± 2.2
Cd	28.0 ± 1.9	26.3 ± 2.1
Co	0.40 ± 0.06	0.42 ± 0.05
Cr	2.1 ± 0.4	2.4 ± 0.6
Cu	422 ± 20	439 ± 22
Fe	190 ± 13	186 ± 11
Mn	22.5 ± 2.0	23.4 ± 1.0
Mo	1.5 ± 0.3	1.5 ± 0.3
Ni	2.1 ± 0.3	2.3 ± 2.7
Pb	11.0 ± 1.9	10.4 ± 2.0
Se	6.5 ± 0.6	6.88 ± 0.47
V	1.1 ± 0.3	1.4 ± 0.3
Zn	170 ± 12	177 ± 10

Table 35. *Concentrations (µg/g) of inorganic trace elements in marine sediment using microwave vapor phase digestion.*[85]

Element	Measured	Certified
As	10.2 ± 1.0	10.6 ± 1.2
Cd	0.69 ± 0.11	0.59 ± 0.10
Co	11.5 ± 2.0	10.8 ± 1.9
Cr	51 ± 10	71 ± 11
Cu	28.8 ± 4.5	25.1 ± 3.8
Mn	490 ± 20	513 ± 25
Ni	31.5 ± 3.5	29.5 ± 2.7
Pb	32.1 ± 5.2	29.5 ± 2.7
Sn	3.6 ± 0.5	3.98 ± 0.44
V	75 ± 15	72.4 ± 17
Zn	180 ± 14	191 ± 17

Table 36. *Concentrations (pg/g) of elemental impurities in polycrystalline silicon using microwave vapor phase digestion.*[83]

Element	Silicon	Method Blank
Cr	770 ± 35	144 ± 6
Ni	970 ± 85	120 ± 11
Cu	< 570	217 ± 20
Zn	4180 ± 700	470 ± 62

Error expressed as 95% CI n=6

technology might encounter some limitations to achieving the high throughput needed for fast turnaround times. The microwave vessels must be assembled and disassembled, which is a labor intensive process often requiring several technicians and multiple rotors for adequate throughput. In addition, the sample digestate must be transferred to another container prior to analysis, which increases handling and contamination risk. Finally, to insure full control of the digestion run, the sample weight, matrix type and acid used must be the same for every sample in the run. This means that a separate run must be performed for each sample type to ensure maximum safety.

A new technology has recently emerged to address the limitations of traditional microwave systems for high throughput laboratories. The Single Reaction Chamber (SRC) microwave-assisted digestion system utilizes a completely new and unique approach to microwave digestion. As its name suggests, the SRC is a large, pressurized stainless steel reaction chamber into which all samples are placed and digested simultaneously (*Figure 23*). With SRC, the reaction vessel in effect becomes the microwave cavity, enabling the intensity and distribution of the delivered microwave energy to be optimized to the shape of the reaction vessel providing uniform sample heating. This architecture also eliminates the need for individual

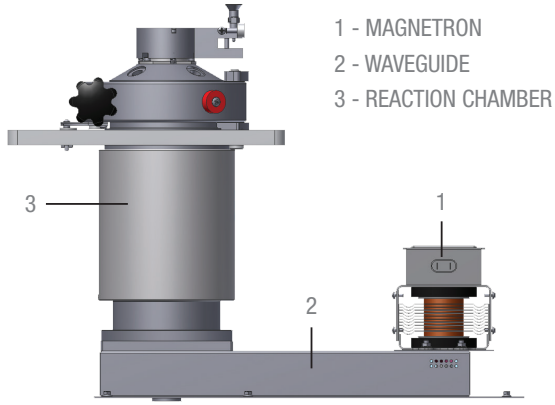


Figure 23. *SRC Technology*

pressure vessels. Samples are simply weighed into an auto sampler-type digestion vials, the appropriate digestion acid added, capped with a simple loose fitting cap to unsure pressure equalization, then placed in the sample holder. The rack is fitted to the chamber roof, the chamber is then automatically sealed, and pre-pressurized with nitrogen to 40-90 bar prior to microwave heating. Pre-pressurization raises the boiling point of the digestion mixture (water at 40 bar boils at 250°C). This prevents cross contamination or loss of volatiles analytes (*Table 37*).

All samples are processed under identical temperature and pressure conditions ensuring sample to sample and batch to batch reproducibility. In addition the SRC approach does not suffer from the shortcomings of traditional microwave technologies with respect to vessel assembly and analytical operations. SRC allows sample weighing, addition of reagents, sample digestion, dilution, and analysis to be carried out a single vessel eliminating unnecessary transfers. This significantly reduces the risk contamination and while providing the sample throughput needed to keep up with ICP analysis (*Table*

38). SCR technology has been successfully applied to the digestion of ferrochromium alloys (*Table 39*), high fat food products (*Table 40* and Ref 89), and pharmaceuticals (Ref 90).

See page 116 for detailed information on the available instrumentation: Milestone UltraWAVE.

Table 37. *40 position SCR cross contamination and mercury recovery test results.*

Sample	Measured (µg/g)	Expected (µg/g)
Blanks (n=4)	< 0.002	< 0.002
1000 µg/g Spike (n=9)	1000	1000 ± 20
NIST 1633 Coal Fly Ash (n=9)	144 ± 6	143 ± 2
BCR 145 Sewage Sludge (n=9)	1981 ± 44	2010 ± 220
NIST 2711 Montana Soil (n=9)	6198 ± 137	6250 ± 190

Error expressed as 95% CI

Table 38. *Method limits of quantitation (µg/L) for 15 position SCR operated in a normal laboratory environment with direct analysis after dilution in digestion vial.*[87]

Element	LOD	Element	LOD
Li	0.021	Zn	6.250
Be	0.009	As	0.068
B	0.561	Se	0.649
Al	3.9	Mo	0.046
V	0.114	Cd	0.016
Cr	0.317	Sn	0.499
Mn	0.092	Sb	0.068
Co	0.010	Ba	0.179
Ni	0.099	Tl	0.013
Cu	1.30	Pb	0.028

LOD = (10*SD Blank)/Slope of Calibration Line

Table 39. *Comparison of SCR and Standard Microwave Digestion results for ferro-chromium alloy.*

	Cr %		Fe %		Co %		Mn %		Ni %		V %	
	MW	SCR	MW	SCR	MW	SCR	MW	SCR	MW	SCR	MW	SCR
Sample 1	63.6	62.8	38.0	37.7	0.017	0.019	0.49	0.48	0.17	0.17	0.23	0.23
Sample 2	60.4	63.8	36.0	38.8	0.028	0.021	0.39	0.40	0.17	0.17	0.20	0.21
Sample 3	65.0	62.5	39.1	39.2	0.021	0.023	0.46	0.44	0.17	0.18	0.22	0.21
Sample 4	65.9	61.2	39.5	39.4	0.025	0.024	0.49	0.42	0.19	0.19	0.23	0.20
Sample 5	63.2	62.9	36.0	36.6	0.019	0.018	0.48	0.46	0.17	0.17	0.22	0.23
Sample 6	63.7	64.2	37.6	37.3	0.018	0.019	0.43	0.44	0.17	0.18	0.21	0.21
Sample 7	58.8	60.7	36.5	38.0	0.021	0.021	0.52	0.48	0.19	0.16	0.25	0.21
Sample 8	64.5	60.7	39.7	38.6	0.018	0.020	0.56	0.53	0.18	0.19	0.23	0.25

Table 40. *Comparison of SCR and Standard Microwave Digestion results for high fat nut samples. Concentrations expressed as µg/g.*[88]

Element	Brazil		Cashew		Walnut	
	SCR	MW	SCR	MW	SCR	MW
Al	< 0.05	< 0.145	< 0.05	< 0.145	< 0.05	< 0.145
As	< 0.79	< 2.38	< 0.79	< 2.38	< 0.79	< 2.38
Cd	< 0.03	< 0.09	< 0.03	< 0.09	< 0.03	< 0.09
Co	0.80 ± 0.06	0.81 ± 0.08	0.12 ± 0.01	0.13 ± 0.02	< 0.03	< 0.08
Cu	18.2 ± 1.10	18.7 ± 2.08	12.5 ± 1.33	12.0 ± 1.08	13.5 ± 1.28	12.4 ± 1.08
Fe	0.94 ± 0.06	0.90 ± 0.08	0.23 ± 0.02	0.25 ± 0.03	0.69 ± 0.04	0.70 ± 0.06
Mn	9.72 ± 0.51	9.63 ± 0.71	26.4 ± 2.28	24.5 ± 2.31	26.2 ± 1.98	26.3 ± 2.34
Ni	4.23 ± 0.24	4.40 ± 0.40	1.31 ± 0.10	1.30 ± 0.11	1.75 ± 0.14	1.80 ± 0.11
Pb	< 0.180	< 0.540	< 0.180	< 0.540	< 0.180	< 0.540
V	0.26 ± 0.02	0.251 ± 0.022	0.27 ± 0.03	0.26 ± 0.03	0.35 ± 0.02	0.34 ± 0.02
Zn	41.2 ± 2.11	42.4 ± 2.20	26.3 ± 1.76	28.2 ± 2.17	25.7 ± 2.41	26.0 ± 2.15

Error expressed as standard deviation, n=5

CHAPTER **5**

MILESTONE TOOLS FOR CLEAN CHEMISTRY

Milestone Tools for Clean Chemistry

"Every technology is an expression of human will".
Nicholas Carr, What the Internet is Doing to Our Brains – The Shallows. W. W. Norton & Co.

ETHOS UP

A microwave digestion system provides the first important step for a successful analysis. If there is no confidence in the initial sample preparation stage, then there can be no confidence in the results from subsequent analyses.

The ETHOS UP (*Figure 24*) fully embodies Milestone's philosophy in microwave sample preparation. Specifically designed for closed vessel acid digestion, it offers a perfect integration between microwave hardware, user interface, reaction sensors and pressure vessels. The ETHOS UP encompasses Milestone's visionary concept of "Total Microwave Sample Preparation" and, with a comprehensive choice of accessories, it offers a complete first-class solution also for microwave solvent extraction, organic and inorganic synthesis, protein hydrolysis, and vacuum evaporation.

The new Milestone ETHOS UP microwave cavity has a volume

Figure 24. *Milestone ETHOS UP*

in excess of 70 L, by far the largest currently available. Why is this important and what are the main implications of this design? Firstly, digestion rotors with more sample places can be accommodated thus improving productivity and sample preparation throughput. Secondly, the microwave unit is inherently much safer because a larger cavity better contains gases escaping from vessels, should there be a sudden over-pressurization.

The ETHOS UP is equipped with two 950 W magnetrons for a total of 1900 W. The system additionally employs a rotating diffuser that evenly distributes the microwaves throughout the cavity. High power coupled with the diffuser enables very fast and even heating of high throughput rotors.

The new Milestone ETHOS UP is equipped with the most advanced yet easy to use reaction sensors (*Figure 25a*) for complete quality control of the digestion conditions. Direct temperature and pressure control are used in a single reference vessel. Contact-

less temperature is available for all vessels. The actual temperature of each and every vessel is continuously shown on the instrument control terminal during the microwave run, allowing an instant visual check of the digestion conditions. In addition, a contact-less pressure sensor monitors and controls all vessels simultaneously, preventing any leakage or venting.

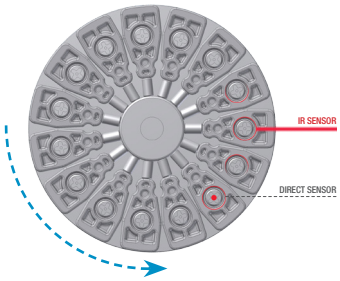


Figure 25a. *Direct and contact-less temperature control in all vessels*

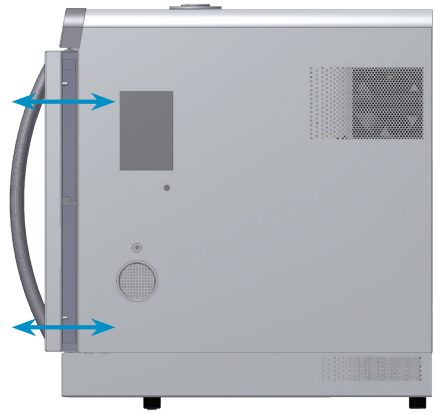


Figure 25b. *Pressure-responsive door*

The ETHOS UP features a full stainless steel door with an innovative opening and self-resealing mechanism (*Figure 25b*). Should there be a sudden over-pressurization of the cavity, the door slightly opens for rapid and safe pressure release and the microwave power is instantaneously cut off. Immediately afterward, the door is pulled back, resealing the cavity. For additional safety, an automatic door locking system does not allow the user to open the ETHOS UP door during the microwave run. At the end of the run, the door remains locked until the solutions have cooled down to a user preset temperature. This

prevents misuse of the instrument and in turn exposure of the chemist to high pressure vessels.

The ETHOS UP is controlled via a compact terminal with an easy-to-read, bright, full-color, touchscreen display. The terminal is provided with multiple USB and Ethernet ports for interfacing the instrument to external devices and to the local laboratory network. The terminal runs a user-friendly, icon-driven, multi-language software to provide easy control of the microwave run. Simply recall a previously stored method or create a new one, press 'START' and the system will automatically follow the user defined temperature utilizing a sophisticated PID algorithm. Hundreds of applications, including all US EPA methods, are preloaded in the ETHOS UP terminal. There is no need to input the number of samples or weights being digested, as the software will automatically regulate the microwave power accordingly. This assures a consistent quality of digestion and simplifies the use of the instrument.

Two completely new rotors offering both high quality digestion and high sample throughput are available. The SK-15 (*Figure 26a*) is a high-pressure rotor featuring up to 15 TFM vessels with a volume of 100 mL and suitable for all applications. The MAXI-44 (*Figure 26b*) is a high-throughput rotor featuring up to 44 TFM vessels with a volume of 100 mL and suitable for a wide range of samples including environmental and all organics. Both rotors are fully compliant with commonly used standard methods, such as the US EPA 3015, 3051, and 3052. The SK-15 and the MAXI-44 feature an enhanced 'vent-and-reseal' technology for controlling the inner pressure of all vessels with complete safety. This patented (US Patent 5,270,010) technology provides the operator with unsurpassed safety and performance capabilities: highest temperature and pressure, highest safety standards, ease of use, and very fast cooling. Only the excess

Figure 26a. *SK-15 Rotor*

Figure 26b. *MAXI-44 Rotor*

pressure is released from the vessel. This ensures that there is no stress to the door of the microwave system and no loss of sample as could happen in the case of a membrane or disk bursting. Finally, a large selection of high purity quartz and TFM inserts is available for the SK-15 and the MAXI-44 rotors for smaller sample amounts or to minimize the dilution factor of the analytical solution.

Ultratrace Inserts

Vessel-inside-vessel technology, developed by Milestone in the late 90s, uses a smaller secondary vessel inside the primary microwave vessel. The secondary vessel contains the sample and digestion reagents, and the primary vessel contains the solution required to achieve accurate temperature monitoring. This configuration reduces the amount of acid required for digestion to near stoichiometric quantities, which reduces the dilution factor. The use of vessel-inside-vessel technology is also used for the processing of larger organic sample sizes. This is accomplished by controlling the reaction kinetics and lowering the pressure inside the microwave vessel. The use of vessel-inside-vessel technology helps to control these exothermal reactions by providing a heat sink for the energy liberated during oxidization. This is achieved by placing water in the outer microwave

vessel. The water draws the heat away from the reaction mixture, slowing down the reaction kinetics and preventing a runaway reaction. A variety of inserts (*Figure 27*) are available from Milestone, in different materials (Quartz or TFM) and with different sizes and shapes, to accomplish all application requirements.

Figure 27. *Ultratrace Inserts*

Microwave evaporation rotor

The US patent 5,447,077 attested the pioneer work of Milestone in the investigation of the unique heating mechanism of microwave-assisted evaporation process.

The new MMR-15 rotor takes advantage of this technology and it is now available to chemists to improve the quality of the analytical results and to reduce the overall sample preparation time. Most US EPA microwave acid digestion methods (3015, 3051 and 3052) prescribe the use of combinations of HNO_3, HF and HCl.
HNO_3 is typically required as oxidizing acid, HF is used for silicates and HCl is recommended for soils and sediments. Solutions obtained by closed vessel digestion must often be evaporated prior analysis either

to concentrate the elements of interest or to eliminate compounds which may interfere with the analytical technique being used.

A typical setup for microwave-assisted evaporation consists of the ETHOS UP equipped with the VAC-1000 vacuum scrubber and the MMR-15 rotor. The MMR-15 can be used for vacuum-assisted sample drying prior digestion, and solution concentration at the end of the decomposition process. The MMR-15 accommodates up to 15 TFM vessels of 100 mL. They are the same vessels used in the SK-15 digestion rotor (*Figure 28*), so no transfer of the solution is required when performing drying and concentration. This minimizes the risk of contamination or loss of the analytes of interest. Each vessel fits snugly into an adapter which perfectly seals the system. An adjustable valve with in-line filter regulates vacuum and air flow. All surfaces in contact with the solution are made of high-purity TFM. Sample are therefore processed in a clean, inert environment. The VAC-1000 integrates a vacuum pump, a water cooled condenser and a neutralizing module to properly and safely handling acid vapors; it is the perfect complement to the MMR-15 rotor.

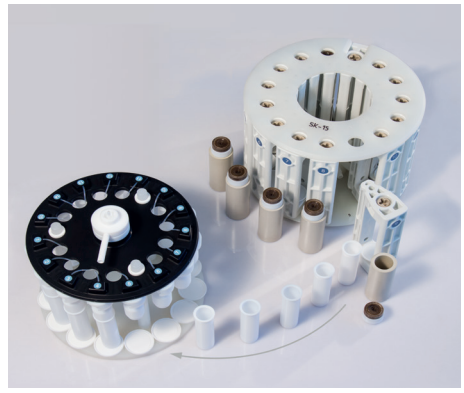


Figure 28. *Evaporation Rotor*

UltraWAVE

Milestone is committed to the constant pursuit of game changers in microwave instrumentation. The new UltraWAVE exceeds norms and breaks conventions.

The concept of the UltraWAVE was developed by Milestone years ago, and this technology is now accessible by all analytical laboratories. Milestone's unique Single Reaction Chamber (SRC) technology overcomes the limitations of all conventional microwave sample preparation systems. At the hearth of the UltraWAVE (*Figure 28*) is a Teflon-lined 1 L stainless steel reaction chamber, which serves both as a microwave cavity and a reaction vessel. Samples are weighed into vials, and suitable reagents are added. Vials are placed in a rack, which is automatically lowered into the reaction chamber. The chamber is sealed and pre-pressurized with inert gas, which physically acts as a cap for the vials, avoiding boiling of the solutions and preventing cross contamination. At the completion of the microwave run, a built-in cooling device rapidly lowers the temperature (*Figure 29*). Available rack configurations include 4, 5, 15 and 22-position (*Figure 30*). Vials are available in Teflon, quartz or disposable glass, and are fitted with Teflon caps-loose fitting to ensure pressure equalization. Unlike conventional microwave-assisted digestion systems, no vessel assembly or disassembly is required and, with disposable glass vials,

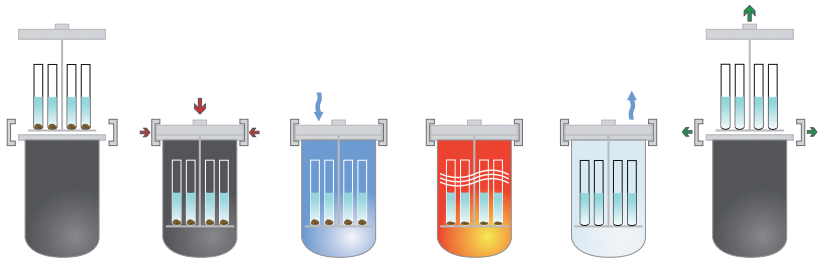


Figure 29. *Operating sequence*

no cleaning step is needed. This greatly enhances ease of use and increases your sample turn around time. The UltraWAVE vials do not require any capping tool. A reusable Teflon cap is placed on top of the vial in a fraction of a second.

The UltraWAVE (*Figure 31*) is an ultra high performance system, operating up to 199 bar pressure and 300°C. This allows the complete digestion of extremely difficult samples and of large amounts of organics. Unlike all conventional microwave-assisted digestion systems, every sample is under direct temperature and pressure and temperature control- no needs to rely on a reference vessel or to an indirect control such as infrared temperature sensors. This assures complete control of the digestion process in every sample. The UltraWAVE reaches high temperatures faster, cools faster, and is capable of higher pressure and temperature than any closed vessel system.

Figure 30. *UltraWAVE 5-places rack*

Figure 31. *Milestone UltraWAVE*

The UltraWAVE is operated via a compact control terminal with easy-to-read, bright, full-color, touch- screen display. With the Milestone UltraWAVE, any combination of sample types can be digested simultaneously; no need to batch samples into identical types. No method development is needed, as the same method can be used for almost every sample type, and no need to use different rotors for different sample types. And for the first time, blanks and reference standards of any matrix can be digested alongside samples, enabling true in-run digestion quality control. The UltraWAVE vessel has a volume of 1 L. This is far bigger than any other microwave digestion system, where the typical vessels volume is of 25-100 mL. As a result -along with an allowable pressure of 200 bar- the UltraWAVE is capable of digesting a total amount of organic sample by far greater than any other device. A total of 20 g -dry weight- organics can be digested

in a single run. This means, for instance, 4 g per sample when using the 5-place rack. Compared to all conventional microwave digestion systems, the UltraWAVE is significantly easier to use and work flow is dramatically improved. 15 samples are processed in 45 min start to finish. Furthermore, the UltraWAVE sample throughput is far better than with sequential microwave digestion systems, where each sample requires at least 15 min to be prepared. The UltraWAVE does not suffer of any cross contamination among samples. Furthermore, blanks are significantly lower than with conventional microwaves, since less acid is used and vials have a much less surface in contact with the analytical solution. The determination of the residual carbon content offers a good understanding of the digestion completeness.

Clean Chemistry Line

The Milestone Clean Chemistry Line is an innovative and complete portfolio of systems and accessories for reducing and controlling the analytical blank in ultra-trace elemental analysis. There is a growing awareness that sample preparation should evolve to the same standards of the most modern analytical techniques, such as ICP-MS, and there are a number of factors that can critically impact the quality of the data:

- The purity of the reagents
- The cleanliness of the material in contact with the sample
- The sample preparation method

Each of these factors is related to the reduction and the control of the analytical blank. To address this issue, Milestone has developed a comprehensive line of products (*Figure 32*) and accessories aimed to reduce and control the analytical blank, which perfectly complement its ETHOS UP and UltraWAVE microwave digestion systems.

duoPUR

The chemical reagents used during the analysis are an important source of the analytical blank. Sub-boiling distillation has been demonstrated to be the best method of acid purification. It uses contact-less infrared lamps to vaporize the surface liquid at a temperature typically 20°C below the boiling point. In contrast to conventional distillation, where strong boiling action generating aerosolized particles results in contamination of the original liquid with parametthe distillate, a gentle surface evaporation during sub-boiling distillation prevents the formation of spray or droplets and yields to a very high pure acid. The duoPUR consists of two quartz distillation units. Each unit contains two infrared heating elements, a water cooled condenser, a high-purity PFA collection bottle, and a fully automatic acid loading/discharge system.

The vaporized liquid is collected on the inclined water-cooled condenser and drips into the collection bottle. The distillation process is microprocessor controlled, allowing the user to set the distillation time and power level by using a compact control terminal with easy-to-read, bright, full-color, touch-screen display. The distillation rate ranges from 50 to 400 mL per hour, depending on the power setting, the temperature of the cooling water, and the acid boiling point.

subCLEAN

The Milestone subCLEAN is a compact and easy-to-use sub-boiling system, where all parts in contact with acids are made of high-purity fluoropolymers. The subCLEAN is therefore 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. All process is microprocessor controlled by using a compact control terminal with easy- to-read, bright, full-color, touch-

Figure 32. *Milestone Clean Chemistry Line*

screen display. The subCLEAN does not require cooling water or a chiller, as acid vapors rapidly condense into a collection bottle by forced air cooling.

traceCLEAN

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 changes regularly. There is also a substantial risk of exposure to hot acids and acid vapors using traditional soaking techniques. To address these issues, Milestone has developed the traceCLEAN, a fully automated, self- contained, acid steam cleaning system for trace metal analysis accessories. Place the items to be cleaned in the traceCLEAN system, program the time and temperature required, then press “Start”. Freshly distilled acid vapors will 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-MS accessories.

CHAPTER **6**

FINAL REMARKS

Final Remarks

"It can be said with certainty that most digestion will be performed in the future by means of microwave assistance".
H. Matusiewicz, Sample Decomposition Technique in Inorganic Trace Elemental Analysis, In: I. Baranowska, Ed., Handbook of Trace Analysis: Fundamentals and Applications. Springer, Heidelberg, 2015.

How heavy is a heavy metal? How low is a trace concentration? Not sure how deep down we will go, notwithstanding we have no doubts about the importance of trace inorganic analysis for a plethora of applications in life sciences, microelectronics, nanotechnology, and earth sciences. Paraphrasing Feynman, we would say that there is a lot to learn going down there in concentration scale.

The microwave-assisted digestion procedures that were discussed in the book follow two basic approaches: 1) intense reaction conditions in a single reaction chamber for promoting complete digestion; 2) use less aggressive reactions conditions for tailored digestions compatible with trace analysis and modern analytical instrumentation, such as formerly discussed ICPs. It was also show how microwave heating is applicable for evaporation without promoting losses and at the same time adjusting solutions media. These procedures give flexibility allowing the analyst to choose

the experimental conditions that fit the analytical demand considering sample matrix, analytes, concentration levels, required efficiency of digestion, sample throughput, and control of analytical blanks.

Looking ahead, the requirements for trace inorganic analysis are continuously evolving. Currently, the quest is not only to find for efficient means for the determination extremely low concentrations, but also to identify the specific chemical form of the analyte. In spectrochemical analysis, this demand implies that hyphenation of highly sensitive analysis methods with chemical separation methods is the name of the game.[91] It means that we need to integrate sample preparation, analyte preservation and separation, with detection without formation of artifacts. Of course, all these tasks must be performed for analytes at lower and lower concentrations. Microwave-assisted sample preparation will continue to evolve to meet these new challenges.

Despite all advancements in instrumentation, we will only reach this target with simultaneous evolution of all areas supporting multiple successive steps of chemical trace analysis. Last but not least, it is always important to remember that each analytical procedure answers a specific goal and we must keep our focus in “the chemical analysis of things as they are”.[92]

The critical point in inorganic trace analysis is to strive for a better understanding of the analytical task we are dealing with. Achieving a better understanding of sample preparation and measurement conditions led to better control. Achieving better control implies in better analytical blanks. Achieving better analytical blanks allows one to fully utilize the analytical capabilities modern analytical instrumentation. Achieving full utilization of modern analytical instrumentation opens the door for future scientific discovery.
THINK BLANK.

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APPENDIX **A**

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