MICROWAVE DIGESTION
MOVES INTO THE 21ST CENTURY

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For optimum sample analysis, it’s not just the chemistry, it’s the preparation.

As with any new technology, microwave digestion systems have evolved into complex and advanced instruments. However, the principles of chemistry that underlie the efficacy of the process of pressurized digestion have remained the same for more than 25 years.

History of Microwave Digestion
Unlike other heating mechanisms, true control of microwave heating is possible because cessation of the application of energy effectively and instantly halts the heating. The direction of heat flow is reversed from conventional heating, as microwave energy is absorbed by the contents of the container, energy is converted to heat, and the bulk temperature of the contents rises. Heat is transferred from the reagent and sample mixture to the container and dissipated through conduction to the surrounding atmosphere. To take advantage of this technology, pressure and temperature feedback control mechanisms were soon added to early commercial microwave digestion systems to fully utilize the instantaneous on/off application of energy.

Vessel and Container Developments
Over the past 20 years, microwave digestion vessels have developed from simple containers capable of withstanding small pressures above atmospheric pressure to today’s high-pressure temperature systems. Manufactured from advanced microwave transparent or inert composite materials and engineered to be light and incredibly strong, these materials allow microwave energy to be concentrated on the reagent mixture and provide better control over the reaction. Pressure and temperature capabilities have increased from commercial limitations of 160 °C and 120 psi to today’s advanced vessels capable of controlled digestions at 240 °C and 800 psi. Although higher temperatures can be used, lower pressure limits apply. These limitations are necessary because of the nature of the fluoropolymer materials used for the internal liner and wetted surfaces of the pressure vessels. Materials such as Teflon, which are extremely chemically inert, possess very limited mechanical strength, and care must be taken when using these materials at elevated temperatures approaching the flow point of the polymer. Use of light yet strong advanced composite plastic technology allows the inert wetted materials to be reinforced for strength with other components.

Development of Methodology
Initial equipment focused on simple oxidative dissolutions of organic materials and leaching procedures for soils and sediments. Improvements in temperature and pressure capabilities enhanced the quality of the dissolution within samples containing high amounts of carbon, such as plant materials and tissue samples. During the digestion process of samples containing organic compounds, largely insoluble gases such as CO₂ are formed. These gases combine with the vapor pressure from the reagents, at any temperature, to produce the total pressure inside the vessel. Since the heat flow from a microwave digestion vessel is reversed from that of resistive devices, the total pressures generated for microwave digestions are significantly lower at the same temperature than other comparably heated devices or systems. This means larger samples
can be digested at higher temperatures and lower pressures than would normally be expected from such pressurized vessels. However, the pressure limitations of the vessel still restrict both the sample size that can be used to reach a required dissolution temperature and the maximum temperature that can be achieved due to the vapor pressure resulting from the reagents.

Advancements in the technology lead to the development of systems where 200 °C could be achieved with 0.5 g of organic material. This progression led to the development of inorganic digestion methods at higher-temperatures, where the vast majority of the total pressure is reagent vapor pressure. The application of microwave technology to such sample types has revolutionized the analysis of these matrices. Previously, these samples were commonly prepared with fusion techniques, which leave a matrix that can pose significant instrument problems. However, as the temperatures of the reactions exceed 200 °C, more suitable reagents, such as acids, can be used. The oxidizing power of common mineral acids such as nitric acid significantly improves at temperatures of 80–100 °C above its atmospheric boiling point. For organic materials, the carbon destruction with nitric acid alone is equivalent to that which previously could be achieved only by the use of high-temperature oxidants such as sulfuric or perchloric acid. Finally, after cooling, mineralized samples are prepared for analysis and are diluted to volume in a reagent matrix of lower viscosity, well-solvated elements, and lower matrix effects.

High-Temperature Inorganic Digestions

Historically, hafnium oxide and chromite ores were commonly prepared for elemental analysis by fusion methodology, where sample is heated with a caustic solid material, often an alkaline hydroxide, in a platinum crucible with a heat source to an extreme temperature to fuse the materials together and form a flux, which is amenable to subsequent dissolution (Figure 1). With the development of high-temperature microwave digestion vessels and sensors capable of control feedback at elevated temperatures, mixed mineral samples and ores can be digested with mineral acids in 20–45 min under reproducible temperature conditions. However, to obtain full dissolution of these samples, stoichiometric considerations may apply as well as the order in which the oxidative and solvation reagents are added. Although using this procedure can successfully break down a matrix with a reagent, care should be taken since analytically important elements can be precipitated out in other forms and remain as a solid after the procedure.

Large Organic Samples

One limitation of microwave-pressurized digestion techniques has been the limited practical volume of the vessels. Manufacturers make vessels an optimum size that enables the strength components to work effectively and withstand high pressures, yet not make the vessels unwieldy, so that a reasonable number of them fit inside the cavity. However, if the vessel is too heavy you can only run one at a time, reducing throughput. Because most high-pressure vessels have an internal volume of approximately 100 mL, the sample size in a difficult organic matrix, such as heavy fuel oil or a polymeric material like polypropylene, is limited due to the fact that it will generate around 600–800 psi of gaseous digestion products and reagent vapor pressure at the temperatures required for adequate digestion (200–220 °C). Adding more sample increases the pressure level to the limit of the Teflon materials used for most vessel designs, and although quartz vessels can be used, the seals are still made of Teflon. In addition, rigid materials like quartz have proved to be problematic and can fail catastrophically, unlike nonrigid polymeric materials.

Large organic samples benefit from vent-and-resal technology, used as one of the earliest commercial vessel designs. However, the true advantages of this technique were not noted until the development of high-temperature systems with vessels that could maintain a set pressure limit and bleed off gas formed by the digestion in excess of this pressure. These vessels are designed to maintain a temperature at which a “good” digestion will result and vent after the oxidation is completed. Essentially, the vessel bleeds off the excess pressure during the rapid exother-
mic portion of the digestion and then reseals once the rapid gas evolution has ceased. However, such technology should be approached with care, because some manufacturers set the vent pressure above 500 psi. At these pressures, the force of the vent can be sufficient to aerosol the sample and eject a portion of the vessel contents, losing sample and analytes of interest. Before venting, ideally below 500 psi, the bulk of the sample and reagent digestion has to be complete, thus forming analytes of interest from solvated ionic species, which have an oxidation state that has no volatile species.

**Evaporation and Concentration**

With the detection limits on analytical equipment continuing to improve and ICP-MS technology rapidly becoming more cost effective, sample preparation is increasingly the limiting factor in analysis. Preparing the sample not only consumes significant time, but also potentially limits the achievement of detection limits quoted for the analysis. Microwave sample preparation can address both these issues with the recent development of automated concentration accessories.

Until recently, limitations on sample size have essentially restricted microwave digestion for samples that generate significant amounts of gaseous products. To prepare an excellent digestion requires a reagent volume of approximately 10 mL of concentrated acid for a sample size of ~0.5 g. Vessel technology and vent-and-resel technology has extended the sample size to ~1 g, but the reagent matrix must still be addressed. Dilution of a digest performed in a sealed system with 10 mL of acid made up to a final analytical volume of 50 mL results in an analytical matrix containing 20% by volume of the acid. This in itself can influence detection limits.

Through the introduction of evaporation accessories, such as the MicroVap (CEM Corp.), manufacturers have sought to take advantage of the unique nature of microwave heating to rapidly evaporate the matrix, pre- or post-digestion, and allow a significant reduction in reagent matrix for subsequent analysis. These accessories take the digestions without transfer, in the liners used for the dissolution, and apply microwave energy while the samples are under a partial vacuum. The control systems allow the instrument to automatically detect the boiling point of the reagent mixtures and continue heating the digest until the sample has been evaporated to a very low acid volume. The advantages of microwave heating are that the digestions are essentially evaporated automatically to almost or absolute dryness with no substance remaining in the microwave field to absorb energy, and the temperature drops immediately. Additionally, operators can program a temperature drop ending the heating cycle. Unlike hot plate evaporations, the temperature of the residue actually drops as dryness is approached. The microwave performs the digestions undertaken on a hot plate automatically without the need for operator observation or risk of elemental loss due to overheating of the residue. It is also very fast, with ~25 mL evaporated automatically in 15–20 min, and control of the atmosphere during the evaporation can be accomplished by the use of air inlet HEPA filters, if required. This technique allows both matrix and acid exchange for subsequent analysis, as well as concentration with a lower dilution volume in a more manageable acid concentration for analyses using 2 or 4% nitric.

The advances in computer and sensor technology in the last 2–3 years have enhanced throughput considerations in microwave sample preparation and dramatically altered microwave technology in the past 6 months. Computer-aided design technology has allowed vessels to be designed that maximize strength-to-weight ratios and take advantage of the disequilibrium found in microwave preparative pressure systems. The heat loss from the vessel, while the energy is coupled into the reagent and sample alone, allows the pressure generated by the sample to be well below theoretical values for the elevated temperatures of the digestions. Designing vessels specifically to maximize this concept has recently allowed the development of a vessel and control system, the MARS Xpress, which can process up to 40 pressurized digestions in a single batch at temperatures exceeding those of previous systems which could only process a maximum of 14 high-pressure vessels. This technology allows better microwave digestion in terms of the quality of the analytical solution for applications with very large throughput requirements. Innovative sensor controls allow control and continuous output of the temperature of every vessel and digest in the batch. The process is controlled by data collected on the temperature of each vessel, which is much more representative of the whole batch than previous generations of equipment that control with a single reference vessel.

**The Future of Microwave Digestion**

The near-term future of microwave digestion technology lies in further technical improvements in ease of use, throughput, and materials advancement. Combinations of improvements will allow significant advances in these areas. Enhanced flexibility improvements will enable the treatment of different sample matrices within the same run or batch to be independent of each other in terms of reagents and methodologies, allowing the operator freedom from traditional limitations of matching sample sizes and types within a batch. Thus, a customized program providing the optimum analytical solution for analysis independent of all other samples can essentially treat each sample separately. Improvements in computing power are also allowing finer control of the processes, allowing the instrument to follow the set measurement processes required for application areas such as speciation studies.

Vessel technology and improvements in materials are allowing smaller, stronger, and more effective vessels to be developed, which include or incorporate features to control processes that are currently separate and discrete from the dissolution. This process, begun recently with automated concentration, is continuing to develop and evolve to require minimal operator involvement in the analytical process. Consistency and control are becoming the premise of a new generation of equipment.

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