Reprinted from *American Laboratory* November 1999

An integrated microwave digestion system for the modern laboratory

Kenneth Borowski and Amy Schmaling

The ability to directly control and rapidly change the heating process is one of the major advantages of microwave heating over traditional methods. Control of this process, however, is dependent on several variables that are not normally considered in the laboratory when working with traditional methods. The nature and number of samples, weight of the samples, and relationship between the temperature and pressure within a sample vessel become important issues. Method development for microwave sample preparation can be time consuming, and the transfer of traditional methods to the microwave environment can be difficult or impossible. Historically, process monitoring and control schemes that rely exclusively on temperature and pressure, the two parameters most commonly monitored, have not been completely reliable.

The ability to directly control and rapidly change the heating process is one of the major advantages of microwave heating over traditional methods.

The Ethos PLUS labstation (**Milestone Inc.**, Monroe, CT) (*Figure 1*) integrates three components: advanced vessel technology, a sensitive chemical sensor, and Windows® (**Microsoft**, Redmond, WA)-based software that controls and monitors the entire process. EasyWAVE software (**Milestone**) continuously integrates classic control parameters (such as the temperature and pressure of the reaction medium) with data from the sensitive QP chemical sensor (**Milestone**), while dynamically adjusting the delivered power to maintain a defined temperature or pressure profile. This combination ensures the integrity of every vessel and simultaneous control over all monitored parameters. Combined, these three components (along with an internal temperature monitoring system) completely control the heating process, prevent sample loss, and increase safety of operation. The chemist has complete quality control of the physical and chemical reactions performed within the system.

Vessel technology

The sample vessels used in the labstation incorporate a patented closure mechanism, which is both the vessels' cover and resealing pressure relief valve. Each vessel cover is fitted with a high-performance spring. When the vessels are installed in a rotor body, they are secured using a calibrated torque wrench. The predefined closing pressure provided by the torque wrench ensures that the vessels can be operated throughout the entire dynamic range of their physical design properties. The spring allows the vessels to safely vent and release excess pressure, then rapidly reseal to prevent the loss of sample components. The use of the torque wrench on the springs provides a precisely controlled pressure seal, which cannot be ensured by other types of vessels and closure mechanisms.

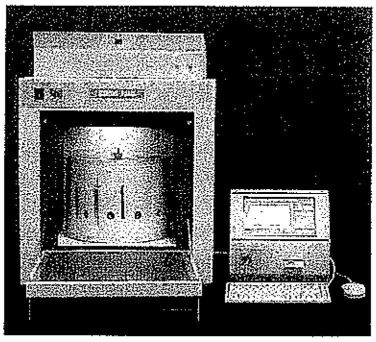

Figure 1 *Ethos PLUS microwave labstation with laboratory terminal controller.*

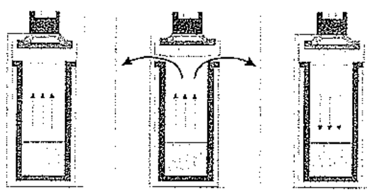

Figure 2 *Overpressurization inside the vessel presses against the cover, compresses the spring, and lifts the cover to release pressure. The spring action closes the cover, resealing the vessel.*

Microwave digestion of various sample materials is accomplished using nitric, hydrochloric, or hydrofluoric acid. In addition to acid vapors, volatile gases and reaction products such as NOx, chlorine, and carbon dioxide are often generated during the reaction process. As shown in *Figure 2*, in the event of overpressurization within the vessel, the reaction products pushing against the vessel cover compress the spring mechanism and allow the head gases to be released. The moment the pressure is relieved, the spring immediately closes the cover, resealing the vessel, thereby preventing any sample loss.

Chemical sensor

The QP sensor relies on the detection of reaction products within the microwave cavity. The sensor detects the presence of reaction products in the cavity and signals a system response when the concentration of such products rises above a defined limit.

Figure 3 is a schematic cross-section of an ETHOS microwave labstation. Air for continuous cooling of the vessels and rotor is taken in sidewise from the bottom of the cavity and flows over each vessel inside the rotor. By setting different limit values during the course of the microwave program, it is possible to tailor the system response to the sensor to distinguish the detected phenomena and thereby control the process for different samples and chemistries.

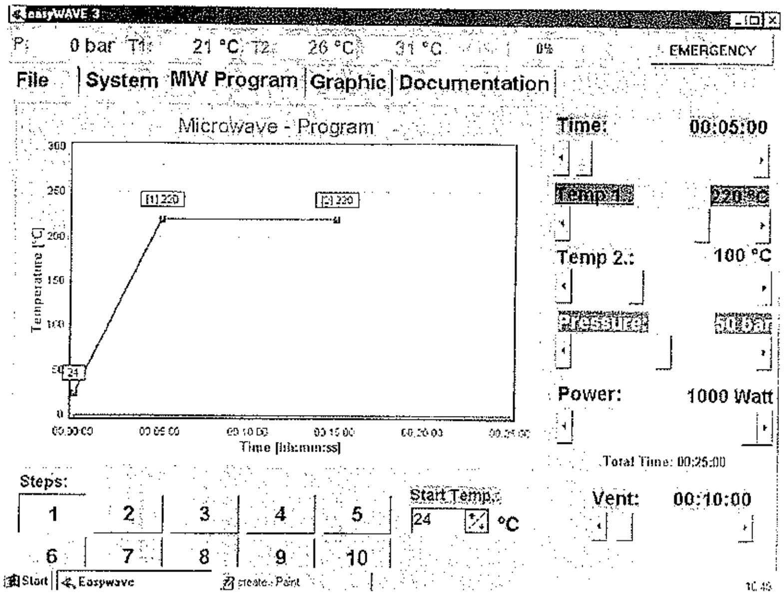

Figure 4 *EasyWAVE screen showing the program for the routine digestion of soil.*

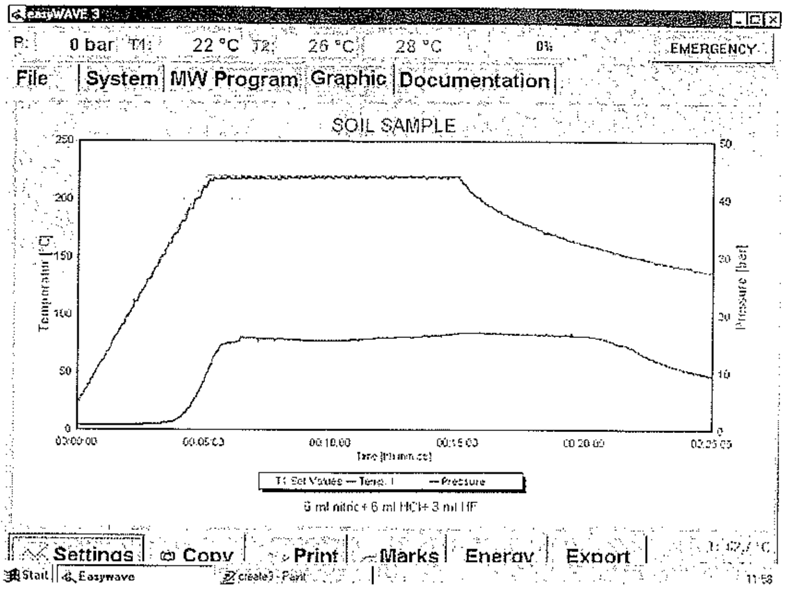

Figure 5 *EasyWAVE screen showing the dynamic temperature and pressure monitored within the sample vessel during the run.*

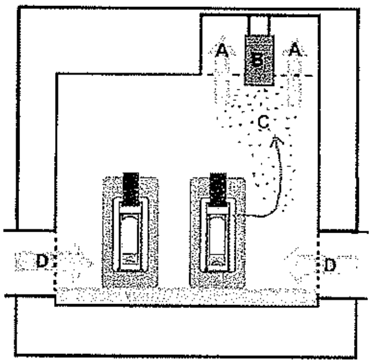

Figure 3 *Continuous ventilation of the microwave cavity allows continuous process monitoring with the QP sensor. a) Gases are removed through the exhaust to the fumehood. b) The QP sensor detects reaction gases instantaneously. Once the gas level reaches a preset limit, the sensor takes control of the power output. c) Pressure forces reaction gases to diffuse through the Teflon™* ***(DuPont,*** *Wilmington, DE) vessel. d) Outside air is brought in from both sides of the cavity.*

The vent and reseal mechanism of the sensor acts primarily as a safety device, protecting the vessel from overpressure and the sample from sudden loss. The sensor can further increase safety and process control by controlling the microwave heating process to prevent overpressure in the first place and vessel venting.

Perhaps the most important phenomenon that the QP chemical sensor can respond to is the diffusion of reaction components through the PTFE walls of the sample vessels. The rate of diffusion is related to the internal temperature and pressure, and the diffusion rate can be correlated precisely with the maximum working pressure of the vessels and the onset of controlled venting.

When the sensor detects diffused reaction components, it immediately moderates the delivered microwave power, reducing the internal pressure in every vessel, thereby preventing overpressurization and venting. This monitor and control function applies equally to every vessel in the microwave cavity. The sensor can effectively set a limit or cap on the

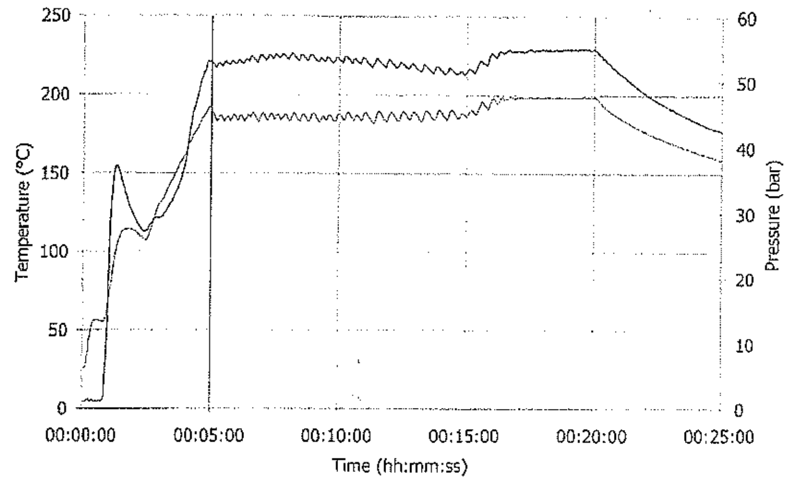

Figure 6 *Temperature and pressure monitored during the heating process of BCR 150 Milk Powder.*

internal pressure in every vessel. Computer-controlled, variable-sensitivity settings allow chemists to control the internal pressure of vessels during the entire digestion process. The extremely rapid response time of the sensor, coupled with highly efficient microwave power control, results in an optimized, user-friendly process.

The vessel monitoring and process control technology cannot be used with vessel designs based on the burst disk or rupture membrane techniques for limiting the maximum pressure within a vessel. With that design, even in the best case, only a total loss of sample can be detected (as the sample is expelled when the burst disk ruptures).

System software

With EasyWAVE software, the operator draws the desired temperature/time or pressure/time profile on the graphic display of the laboratory terminal and starts the program. The software follows the curve by continuously comparing the defined profile and the monitored sensors, and dynamically adjusting the applied power. Only the minimum of microwave power needed to maintain the defined profile is applied. The software incorporates sophisticated pulse ionization discharge (PID) algorithms to precisely compare all data from the temperature or pressure sensors, and dynamically throttles the delivered microwave power. Any deviation from the curve is immediately recognized and the power is adjusted accordingly. The software continuously integrates all monitoring sensors and responds accordingly. With this technique, it is possible to monitor spontaneous reactions from the very start and therefore be able to compensate for them.

All control data and procedures are permanently stored, and the operator automatically receives a complete laboratory report for quality assurance.

Creating a software program

It is very easy to create a comprehensive microwave process control program with EasyWAVE software. The user simply sets a temperature profile over a given period of time, and the desired run is shown graphically on the screen.

Figure 4 shows the digestion of a routine soil sample. To start, a HNO_3/H_2O_2 mixture was added to the sample, which was then heated from room temperature to 220 °C over a 5-min period, and was then held at 220 °C for another 10 min. The defined temperature profile can be seen on the screen. As many as 10 separate ramps or plateaus can be defined, each specified by a time and sample temperature; if desired, limits can be set on the internal pressure or external temperature. In *Figure 5*, the dynamic temperature and pressure monitored within the sample vessel during the course of the entire run is graphically displayed. The software follows the defined profile. At the end of 15 min, power is shut off and the reaction mixture begins to cool. Once an EasyWAVE program is created, it can be saved and recalled from memory to be used when needed.

Control of parameters

The temperature of the previous reaction example was controlled with an automatic temperature control system (ATC-CE 400, **Milestone**), while the QP chemical sensor limited maximum pressure of all the vessels throughout the entire heating process. All reaction parameters were continuously monitored and used to control the microwave power. The monitoring sensor data were stored in memory and simultaneously shown on the screen.

Limiting internal pressure

A sample was prepared with 1.5 g BCR 150 Milk Powder and 20 mL nitric acid. Such sample generates large quantities of NOx vapors, which readily diffuse through PTFE vessels under the temperature and pressure conditions of the process. This highly organic sample is also known to undergo an exothermic reaction if heated too quickly or without adequate controls. The defined microwave program brought the sample from room temperature to 200 °C and held that temperature for 15 min. A maximum working pressure of 80 bar was imposed on the reaction. *Figure 6* presents the monitored sample temperature (red trace) and pressure (blue trace) during the course of the microwave heating process.

One can immediately note the occurrence of an exothermic event in the first few minutes of the process. Inflections in both

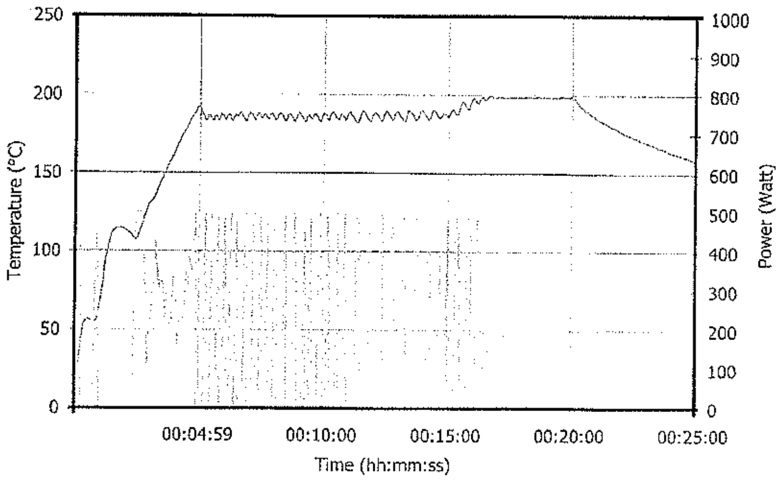

Figure 7 *EasyWAVE dynamically adjusts power throughout the course of the microwave heating process*

curves are clearly visible in the time period between 1 and 3 min into the run. EasyWAVE software immediately responds by throttling back the applied power. At the 3-min mark, the sample's temperature returns to the defined temperature profile.

Figure 7 displays the temperature and applied power (green trace) during the course of the run, demonstrating two critical features of the software's process control scheme. First, it is obvious that the power is dynamically adjusted throughout the course of the microwave heating process. Second, there are periods during the process in which no power is being applied at all.

In the time period between 1 and 3 min, when the exothermic event is occurring, EasyWAVE software detected the excursion above the defined temperature profile and turned off the power. Once the temperature returned to the defined profile, the reaction was again under control, and the software continued to dynamically adjust the microwave power to precisely follow the defined temperature profile.

At 4 min into the process, the QP sensor detects reaction vapors at a concentration above a defined limit and takes control of the process. This is evidenced by the repeated cycling of the applied power. During this period, NOx vapors continue to diffuse through the vessel walls and are exhausted from the cavity. At approx. 17 min into the process, the concentration of NOx vapors has decreased below the control limit. At this point, the software again dynamically adjusts the applied power, maintaining the defined temperature profile for the remainder of the process.

Conclusion

As demonstrated, the combination of the vessel technology described, the QP sensor, and EasyWAVE software provide optimum process control. An exothermic reaction was controlled without venting or loss of sample. The appropriate temperature was maintained to achieve the desired results. This integrated approach to microwave sample preparation gives the chemist complete and precise quality control of the physical and chemical reactions during the digestion process.

Dr. Borowski is Application Laboratory Manager, and Ms. Schmaling is Sales Manager, ***Milestone Inc.,*** *160B Shelton Rd., Monroe, CT 06468, U.S.A.; tel.: 203-261-6175; fax: 203-261-6592; e-mail: mwave@milestonesci.com.*