A new technology for difficult digestions

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Alumina is a class of inorganic oxides whose major industrial uses would be difficult to overestimate. Analysis of trace metal contaminants in alumina and other refractory inorganic oxides has long been a major problem for the analytical chemist. With levels normally too low for a direct technique such as X-ray fluorescence (XRF), the methods of choice have been either fusion or closed-vessel dissolution followed by inductively coupled plasma (ICP) analysis.

The fusion technique is problematic due to contamination from the fusion salts. The closed-vessel dissolution technique uses either hydrochloric acid (HCl) or a mixture of sulfuric and phosphoric acids (H_2SO_4/H_3PO_4) and is not compromised by fusion salt contamination. This technique, using either conventional or microwave heating, is not without its own problems related to the pressure constraints for the closed vessel or temperature control for the heating process. The temperature of 240°C required for HCl dissolution corresponds to a vapor pressure of 700 psi (47 bar) within the closed vessel. The temperature of 280°C required for the H_2SO_4/H_3PO_4 dissolution is near the softening point of a Telzon® (DuPont, Wilmington, DE) vessel (a quartz or glass vessel cannot be used since the H_2PO_4 attacks these materials).

The issues of closed-vessel dissolution have been addressed with the introduction of the MARS™ (Microwave Accelerated Reaction System) and Plus™ (CEM Corp., Matthews, NC). This technology combines the speed of microwave heating with a novel pressure vessel design to allow the superheating of acids to 300°C or 800 psi (56 bar) under temperature and pressure-controlled conditions. The MARS 5 is a microwave laboratory workstation (Figure 1) designed to handle the most difficult microwave digestion methods. The workstation's temperature and pressure features provide feedback control up to 300°C using a thermoplastic insulated temperature probe or 800 psi using a pressure transducer. Both control features take a direct measurement of the conditions inside the sealed vessel.

The closed-vessel technology of the XP-1500 Plus (CEM Corp.) incorporates a dual-sealing system (see Figure 2). A rim seal around the edge of the vessel ensures complete sealing at lower pressures, while the plug seal provides added strength at higher pressures. This dual seal ensures that the digestion takes place under completely closed conditions over the full range of available pressures. Up to 12 samples can be safely processed using the XP-1500 Plus vessels in the MARS 5 for fast, complete, and reproducible digestions.

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This microwave technology has been used for the dissolution of calcined alpha alumina samples. The dissolution has been carried out using both HCl and H_2SO_4/H_3PO_4 for a 1-g sample size. The methods for the HCl and H_2SO_4/H_3PO_4 are as follows:

1. HCl: Weigh 1 g of alpha alumina into the XP-1500 Plus liner. Add 20 mL of HCI. Assemble the XP-1500 Plus vessel. Insert the vessel(s) into the turntable in the MARS 5 cavity and connect the control sensors to the control vessel. Program the MARS 5 system to reach 240°C and maintain at that temperature for 60 min.

2. H_2SO_4/H_3PO_4: Weigh 1 g of alpha alumina into the XP-1500 Plus liner. Add 6.5 mL of H_2PO_4, and 3.5 mL of H_2SO_4. Swirl to ensure the solution is well mixed. Assembly the XP-1500 Plus vessel. Insert the vessel(s) into the turntable in the MARS 5 cavity and connect the control sensors to the control vessel. Program the MARS 5 system to reach 280°C and maintain at that temperature for 30 min.

The temperature and pressure profile (Figure 3) shows the sample reached the 240°C control temperature in about 10 min and maintained that temperature for the remainder of the digestion program. The maximum pressure was 660 psi at about 15 min into the run and then slowly fell to 590 psi by the end of the program. In some cases, alumina particles will remain after the digestion program due to original particle size. In this instance, the digestion program should be rerun to ensure complete digestion.

Subsequent digestion work has been performed on zirconium oxide and alumina with a corundum modification. The approach using H_2SO_4/H_3PO_4 was modified by the addition of 4 mL of hydrofluoric acid. A 280°C microwave heating program for 30 min provided complete dissolution of both materials.

**Conclusion**

The MARS 5 with temperature and pressure feedback control in conjunction with the XP-1500 Plus vessel technology has the potential to digest difficult refractory oxide samples for subsequent elemental analysis. The robustness of the feedback control sensors and the Plus vessel technology allow these digestions to be performed under safe and reproducible conditions.