



EFFICIENT ROCK DIGEST PREPARATION FOR GEOCHEMISTS: A REVOLUTIONARY APPROACH

Microwave-assisted acid digestion of geological samples for elemental quantification on ICP-MS: Exotic rocks with rare and resistant minerals.

| SUMMARY

Historically, the preferred analytical technique for mineral analysis was arc emission spectroscopy, but this is no longer suitable in the isotope ratios determination. This is one of the reasons why, in contemporary laboratories, more advanced techniques such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) have become standard. These techniques, particularly for trace element analysis, necessitate complete sample dissolution—a critical step that is typically achieved through strong acid digestion.

It is important to make an analytical distinction when dealing with samples containing refractory minerals that are not readily dissolved in open-vessel HF-HNO₃

mixtures (e.g., ZrSiO₄, FeCr₂O₄, BaSO₄). For such materials, closed-vessel digestion is required to reach significantly higher temperatures and pressures and effectively digest the sample. This is where Milestone's Single Reaction Chamber (SRC) technology becomes essential. The SRC system utilizes microwave-assisted digestion in a fully stainless-steel, 1-liter pressurized reactor. With the UltraWAVE 3 platform, temperatures up to 300 °C and pressures up to 199 bar can be achieved.

In collaboration with Petrology Professor Kamber Balz (*Queensland University of Technology*) and with contributions from geological laboratories, Milestone has developed a comprehensive sample preparation method applicable to a wide range of geological materials. These have



been classified into five categories based on their chemical behavior and composition. This document presents a four-step protocol designed for the complete dissolution of exotic rocks samples that contain rare and refractory minerals (Pegmatites, ores, hydrothermally altered rocks, carbonatites,), significantly reducing the time required for elemental analysis sample preparation.

I EXPERIMENTAL

INSTRUMENTATION

- UW3 system
- 20-position rack
- PTFE 15 mL vials with caps
- Chiller 1 kW
- Nitrogen gas line (40 bar / or min. 10 bar using gas booster)
- Hotblock with fumehood connection
- ICP-MS

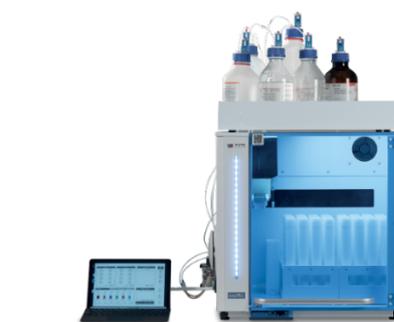
REAGENTS

- HF 48%
- HNO₃ 67%
- HNO₃ 50%
- Distilled water

I REAGENT HANDLING

Reagent addition, a common task during the sample preparation process, poses safety concerns for the operator, is time-consuming, and can lead to contamination if not performed correctly. The use of an automatic dosing station, such as Milestone easyFILL, mitigates and limits these risks, especially when the operator is exposed to

toxic acid as HF, very common on geochemical methods. Specifically designed to precisely add reagents to digestion vessels and vials, easyFILL helps chemists optimize their procedures by reducing the risk of human error in trace analysis. Capable of dispensing various types of reagents into digestion vessels and vials, easyFILL minimizes manual handling of the digestion mixture, thereby reducing the risk of contamination. EasyFILL is fully compatible with all UW3 racks, including the 20-position rack.



• *Figure 2: Milestone's easyFILL*

SINGLE REACTION CHAMBER (SRC) TECHNOLOGY: UW3 OVERVIEW



Figure 1 UW3 microwave digestion system with focus on the SRC chamber

SRC technology represents the latest revolution in microwave closed-vessel digestion. Unlike traditional microwave



ovens, SRC utilizes a pressurized one-liter stainless steel microwave reactor which is also the digestion vessel. The process is straightforward: samples and reagents are loaded into vials and placed inside the reactor cavity together with a suitable baseload that allows heat homogeneity around the samples. Once loaded, the reactor is securely closed and sealed. Automatic introduction of nitrogen gas (40 bar) follows for internal pressurization, which also serves to raise the boiling points of the solutions and not lose the volatile elements. At the end of the process, the reactor is cooled using a powerful water-cooling system.

METHOD DESCRIPTION

The acid digestion protocol developed for the preparation of geological samples, for exotic rocks containing rare and refractory minerals. Due to the wide range of potential minerals present, no generalized method can be provided. However, for pegmatite-associated silicates and oxides, this four-step method is a good starting point.

The method was successfully deployed to analyze REE-rich samples that also contain Ti-Nb-Ta minerals.

The **first stage** involves a high-temperature digestion aimed at the decomposition of silicate structures. This is achieved through the addition of concentrated hydrofluoric acid to the samples placed within a 20-position rack. Digestion is performed using the SRC technology, which maintains a stable temperature of 250 °C for an extended duration. Under these conditions,

silicon is effectively complexed with fluoride ions, as hydrofluoric acid is capable of cleaving strong metal-Si-O bonds.

The **second step** consists of an evaporation phase carried out on a hotblock, in which the samples are brought to dryness; This step does not affect the recovery of elements, not even volatile ones. This step promotes only the volatilization and removal of silicon in the form of silicon tetrafluoride (SiF₄), effectively reducing the sample matrix and facilitating the digestion of the remaining elements.

The **third step** involves the addition of 4.5 mL of hydrochloric acid to each sample, followed by a second high-temperature digestion (280°C) on the Ultrawave 3 system. This advanced SRC-based microwave digestion unit is capable of fully dissolve compounds such as aluminum fluoride (AlF₃) and other fluoride species residues that may have formed during earlier steps.

The **fourth and final step** consists of an evaporation phase carried out on a hotblock for the drydown of all samples. Then, it involves the addition of 2 mL of nitric acid (50%) to each sample, followed by gentle heating on the hotblock. This step serves to reconvert any residual fluoride species into soluble complexes and ensures the breakdown of intermediate

APPLICATION REPORT

ultraWAVE *technology* | EXOTIC ROCKS



fluoride salts, thereby preparing the sample for the final digestion.

OPERATING CONDITIONS ON UW3

For the first digestion, a mixture of 3.2 mL of hydrofluoric acid and 1.3 mL of nitric acid is added to 0.100 g of sample in each 15mL test tube. The digestion program followed by the instrument is as follows:

First digestion step, operating conditions:

| Step | Time | Power (W) | Temp T1 (°C) | Temp T2 (°C) | Pressure (bar) |
|------|----------|-----------|--------------|--------------|----------------|
| 1 | 00:35:00 | 1500 | 250 | 70 | 120 |
| 2 | 00:20:00 | 1500 | 250 | 70 | 140 |

The second digestion step, performed using SRC technology, involves the addition of 4.5 mL of hydrochloric acid, setting the following program:

Last digestion step, operating conditions:

| Step | Time | Power (W) | Temp T1 (°C) | Temp T2 (°C) | Pressure (bar) |
|------|----------|-----------|--------------|--------------|----------------|
| 1 | 00:40:00 | 1500 | 280 | 70 | 160 |
| 2 | 00:20:00 | 1500 | 280 | 70 | 160 |

RESULTS AND DISCUSSION

Table 1: Borate/peroxide fusion ICP-MS data from supplier datapack original, supplemented with 4-acid digest data.

| Element | Reference value (µg/g) | Uncertainty (µg/g) | Silicate method digestion (n=2) (µg/g) | RSD (µg/g) | Accuracy (fraction) |
|---------|------------------------|--------------------|--|------------|---------------------|
| Li | 19562 | 852 | 18379 | 54 | 0.939 |
| Sc | 27883 | 1260 | 29888 | 5 | 1.072 |
| Ti | 12003118 | 277788 | 12097595 | 30053 | 1.008 |
| Cr | 393185 | 20848 | 389028 | 2250 | 0.989 |
| Ni | 61699 | 3952 | 61301 | 43 | 0.994 |
| Cu | 41735 | 1997 | 41138 | 301 | 0.986 |
| Zn | 120560 | 23277 | 92089 | 13 | 0.764 |
| Sr | 304797 | 11828 | 299360 | 359 | 0.982 |
| Zr | 472360 | 21450 | 432441 | 4543 | 0.915 |
| Nb | 697566 | 38980 | 698343 | 5120 | 1.001 |

APPLICATION REPORT

ultraWAVE *technology* | EXOTIC ROCKS



| | | | | | |
|----|---------|-------|---------|------|-------|
| Nd | 781295 | 46653 | 78081 | 3864 | 1.010 |
| Sb | 3708 | 391 | 3383 | 9 | 0.912 |
| Ba | 807945 | 52913 | 807493 | 2704 | 0.999 |
| La | 1369293 | 75075 | 1351814 | 9484 | 0.987 |
| Eu | 22740 | 963 | 22184 | 26 | 0.976 |
| Pb | 67209 | 5351 | 59953 | 247 | 0.892 |

Table 1 lists the main elements analyzed by ICP-MS following acid digestion according to the method presented in this document. For a complete list of analyzed elements, please refer to the eBook (*Efficient rock digest preparation for geochemists: a practical handbook*). All recoveries were accurate, exceeding 75%, with an average of 97%.

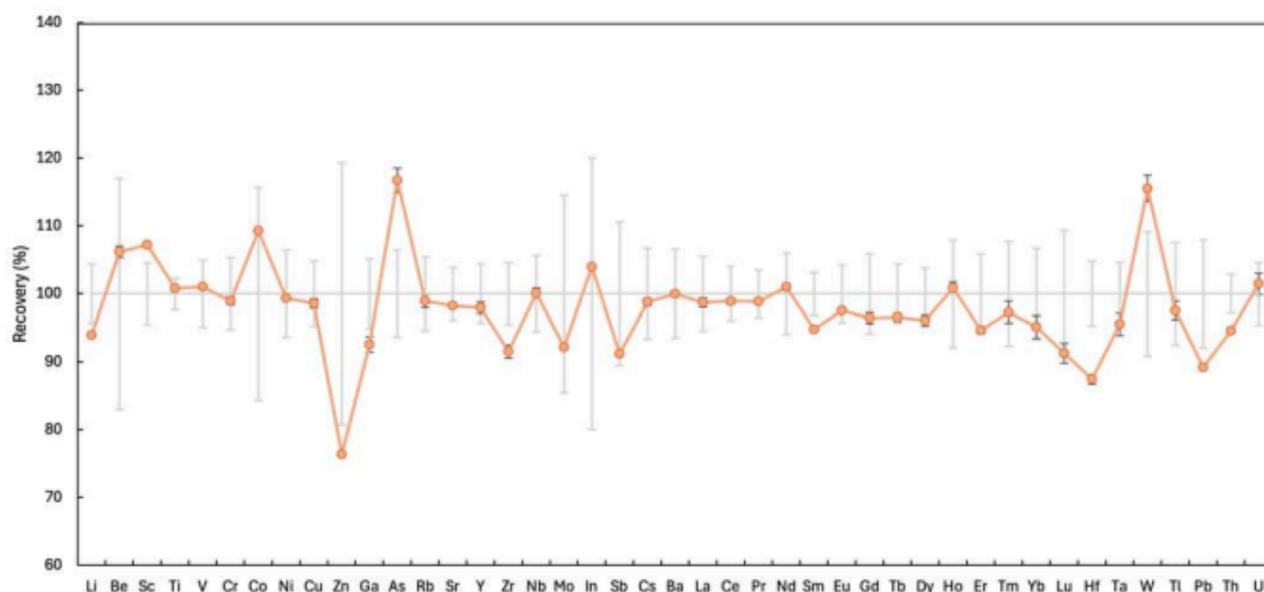


Figure 4: Graph BCR-2, elements sorted by atomic number and relative recovery.

Figure 4 graphically displays the recoveries of each element, ordered by atomic number. Notably, even for volatile elements (Cd, Pb), recovery rates fall within the optimal range, yielding reproducible results.

APPLICATION REPORT

ultraWAVE *technology* | EXOTIC ROCKS



I CONCLUSION

SRC technology successfully achieved complete digestion of exotic rock samples, obtaining excellent recoveries of all analyzed elements and optimizing sample preparation times without losing any performance quality.

Using Milestone easyFILL system, reagent handling has been improved, significantly

reducing the risk of operator exposure to hazardous acids (such as HF) and automating their addition in all 20 positions.

REFERENCES

[1] *Efficient rock digest preparation for geochemists: a practical handbook*, Milestone Helping Chemists, Balz Kamber, Diego Carnaroglio, Giulio Colnaghi, Mirco Rossetti, Gianpaolo Rota, Osama Ghidan



MILESTONE
H E L P I N G
C H E M I S T S

MILESTONE Srl - Via Fatebenefratelli, 1/5 - 24010 Sorisole (BG) - Italy
Tel: +39 035 573857 - Fax: +39 035 575498

www.milestonesrl.com - email: analytical@milestonesrl.com