APPLICATION REPORT

ultraWAVE *technology* | EXOTIC ROCKS

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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-HNO_3 mixtures (e.g., $ZrSiO_4$, $FeCr_2O_4$, $BaSO_4$). 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.

| 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%
- HNO_3 67%
- HNO_3 50%
- Distilled water

| 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 1: Milestone's easyFILL

SINGLE REACTION CHAMBER (SRC) TECHNOLOGY: UW3 OVERVIEW

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.

Figure 2: UW3 microwave digestion system with focus on the SRC chamber

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 (SiF_4), 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 (AlF_3) 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 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
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%.

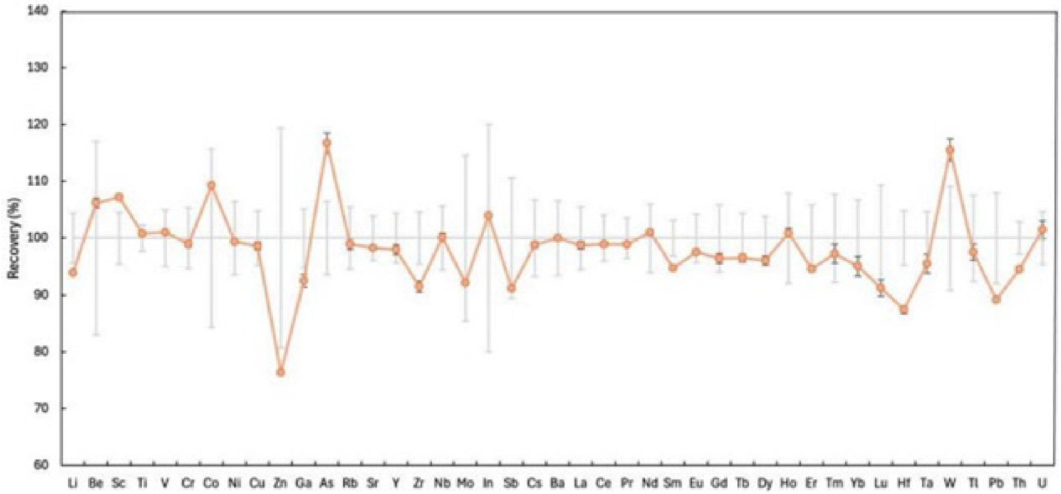

Figure 3: Graph BCR-2, elements sorted by atomic number and relative recovery.

Figure 3 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.

| 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.

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