METHODOLOGICAL ADVANCES IN SEDIMENTS ACID DIGESTION FOR GEOLOGICAL ACCURATE ANALYSIS

Microwave-assisted acid digestion of geological samples for elemental quantification on ICP-MS: Sediments with high organic content and resistant minerals.

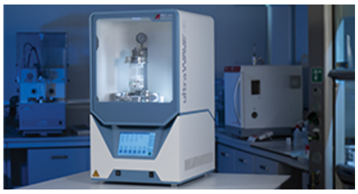
SUMMARY

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 five-step protocol specifically designed for the complete dissolution of sediments with high



organic content and resistant minerals (Clastic sediments, black shales, oil shales), ensuring complete digestion of up to 20 samples within 24 hours, thus significantly reducing the time required for elemental analysis sample preparation.

EXPERIMENTAL

INSTRUMENTATION

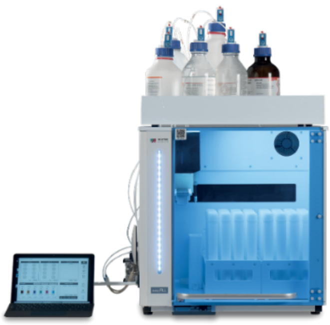
- UW3 system
- 20-position rack
- PTFE 15 mL vials with caps
- Chiller 1 kW
- Nitrogen gas line (40 bar / or min. 10 bar using gas booster)
- Hotblock with fumehood connection
- ICP-MS

REAGENTS

- HF 48%
- HCl 37%
- 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 2: Milestone's easyFILL*

SINGLE REACTION CHAMBER (SRC) TECHNOLOGY: UW3 OVERVIEW

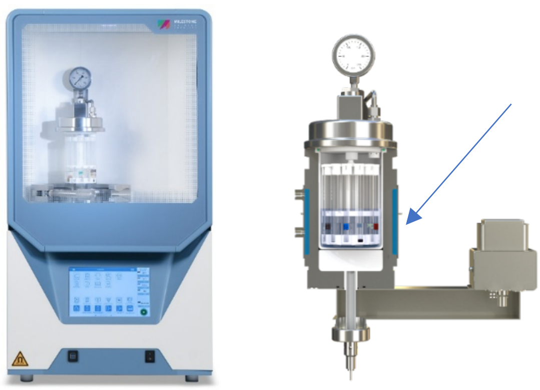
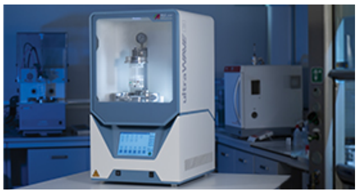


Figure 1 UW3 microwave digestion system with focus on the SRC chamber

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, specifically, sediments containing refractory minerals – zircon, monazite, allanite, garnet, etc.- comprises five essential and sequential steps, each designed to ensure complete dissolution and compatibility with subsequent elemental or isotopic analysis and avoiding the use of $HClO_4$.

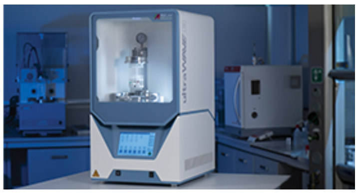
The **first stage** involves a matrix pretreatment, that consist on a hotblock digestion of carbonate and organics thanks to an acid mixture of 2 mL of distilled water, 1.5 mL of hydrochloric acid and 1.5 mL of nitric acid.

Then the **second step** is 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 **third 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 **fourth 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 dissolving fluoride species residues that may have formed during earlier steps.

Lastly, the **fifth step** involves the addition of 2 mL of nitric acid (50%) to each sample, followed by gentle heating on the hotblock for a general drydown. 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.

If samples contain more than 5% of carbonate, a reduction in step 4 temperature to 200°C may be necessary to avoid unwanted TiO_2 formation.

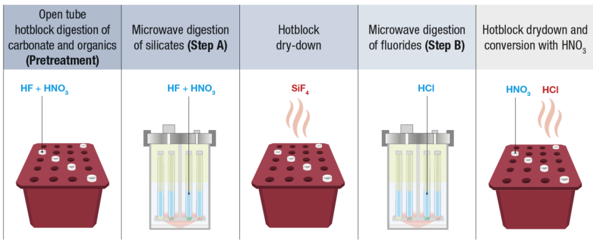


Figure 3: Schematic workflow for sediments digestion and conversion to weak HNO3 solution.

OPERATING CONDITIONS ON UW3

For the first digestion on UltraWAVE technology, 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 involves the addition of 4.5 mL of HCl with the following program:

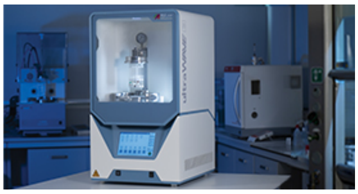
Last digestion step, operating conditions:

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: Dulski (2007), Magaldi et al. (2019), Govindaraju (1994), Khan et al. (2015), Korotev (1996).

Element	Reference value (µg/g)	Uncertainty (µg/g)	Silicate method digestion (n=4) (µg/g)	RSD (µg/g)	Accuracy *(fraction)*
Li	140.200	0.432	141.00	3.53	1.006
Ti	1565.822	15.967	1580.00	79.00	1.009
V	122.850	0.645	122.00	2.93	0.993
Cr	31.079	0.312	30.80	0.92	0.991
Sr	379.638	3.208	381.00	4.95	1.004
Ni	30.572	1.496	29.20	0.41	0.955



Zn	121.224	0.333	117.50	1.18	0.969
Cu	62.534	0.785	60.00	1.92	0.959
Zr	42.876	0.355	42.00	1.30	0.980
Y	9.302	0.105	9.60	0.28	1.032
Ba	276.911	2.311	265.00	10.07	0.957
As	68.015	2.289	66.20	3.31	0.973
Eu	0.466	0.003	0.47	0.01	1.010
Pb	38.064	0.371	38.00	1.05	0.998

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 95%, with an average of 99%.

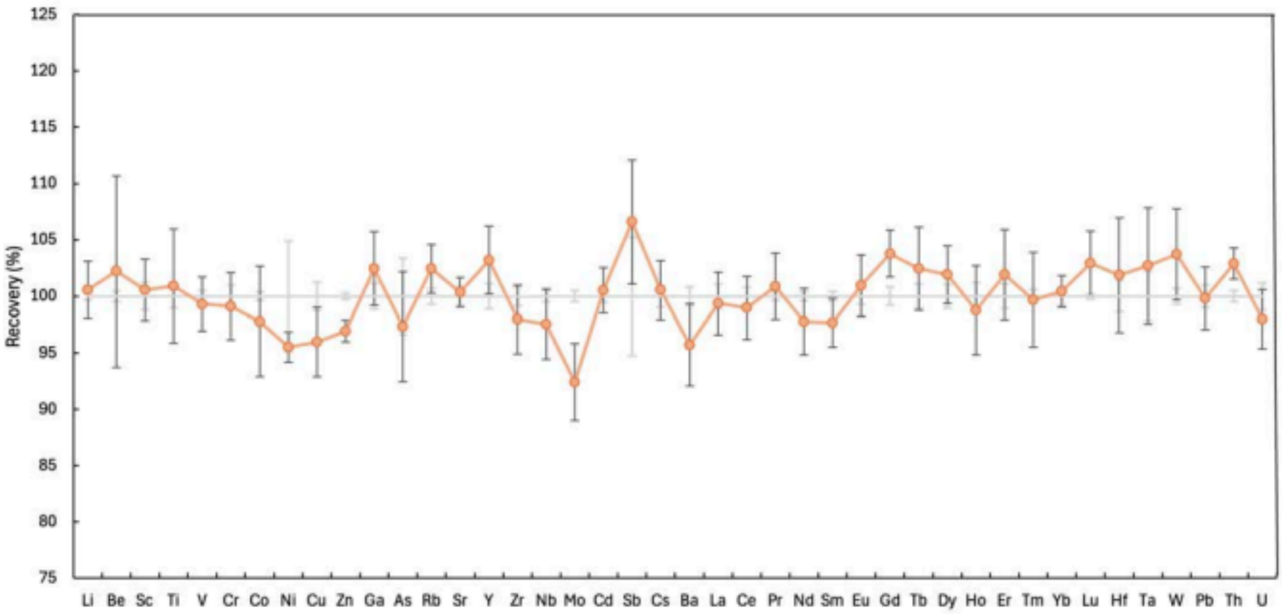
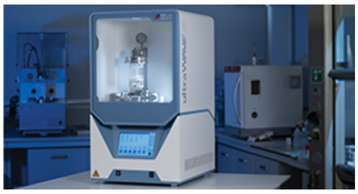


Figure 4: elements sorted by atomic number and relative recovery.

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



CONCLUSION

SRC technology successfully achieved complete digestion of sediments with high organic content 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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