Microwave extraction and digestion in water/sediment analysis

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ETHOS 1


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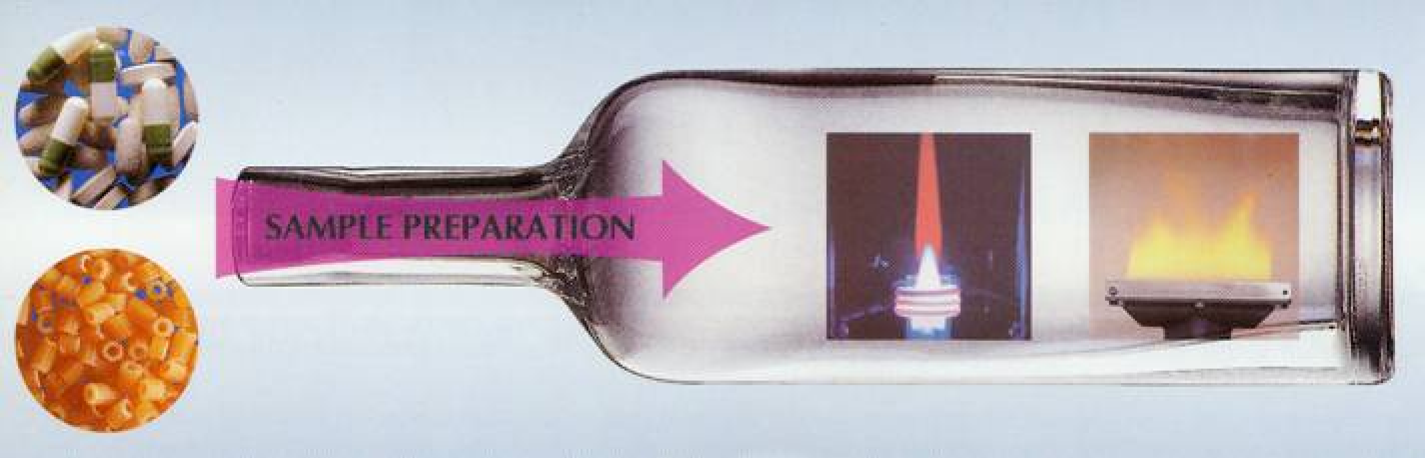
Why Microwaves?

The “Analysis Factory”

- The modern laboratory is a factory for analysis
  - Analytical tools of the 21st century (AAS, ICP-AES, ICP-MS)
  - Sample preparation tools of the 18th century (heating block, sand bath, bunsen burner)

The Bottleneck



- Sample preparation has become the bottle neck to higher productivity in the modern analytical laboratory
- Microwave eliminates the bottle neck in sample preparation for AA and ICP

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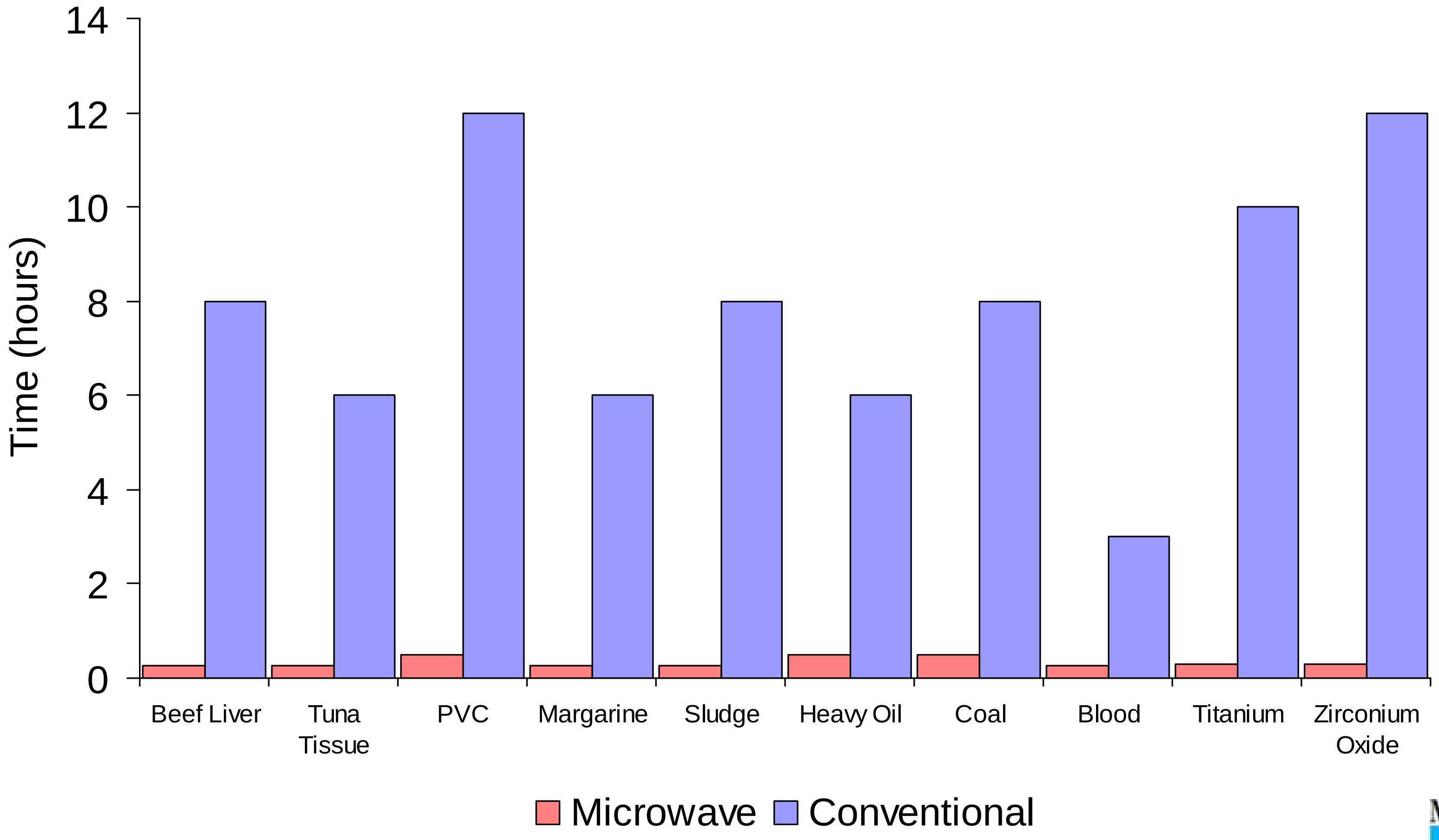
Sample Preparation Time



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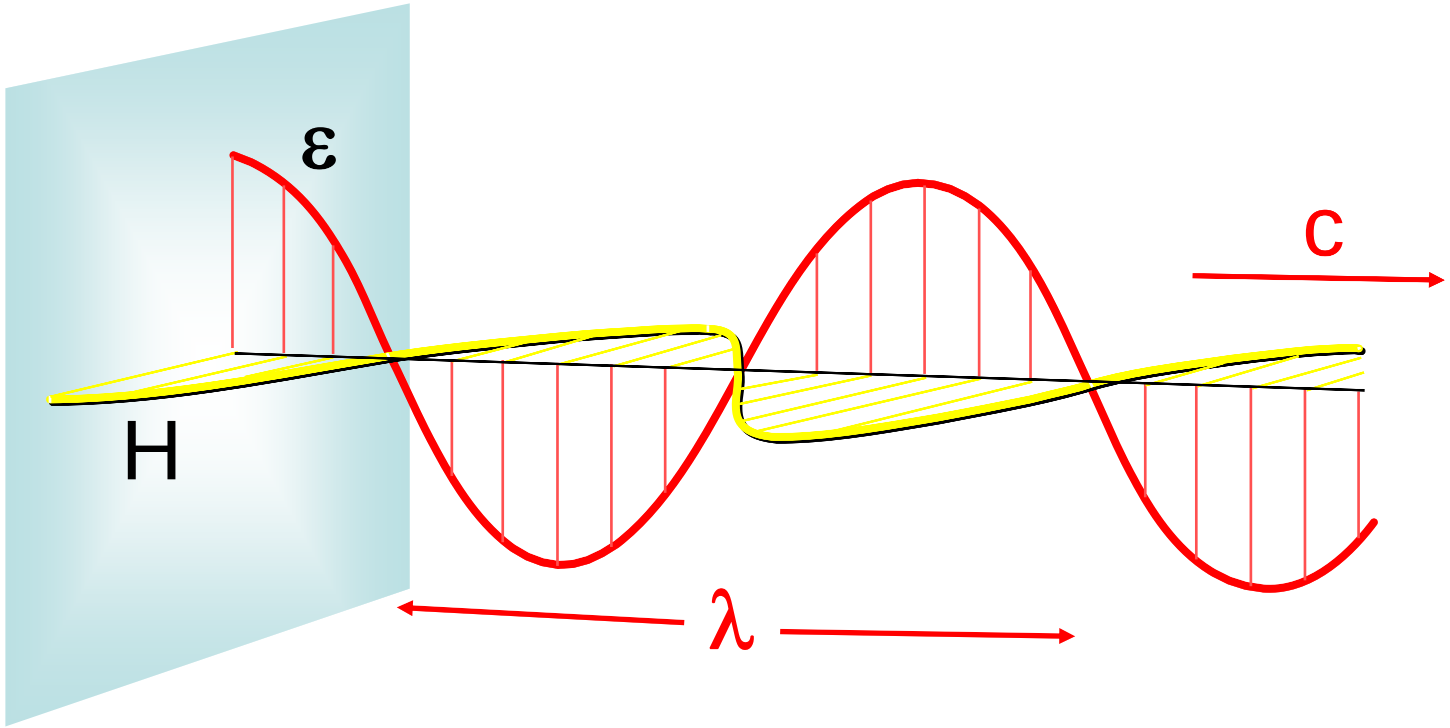
Sample Preparation Quality

- No losses of volatile elements, complete recovery of Hg, Se, As etc.
- Low blanks, minimum quantities of acids are used
- No sample contamination from the environment or from other samples
- Reproducible and fully documented sample preparation procedure
- No acid fumes for improved laboratory personnel and working conditions

Microwave Heating

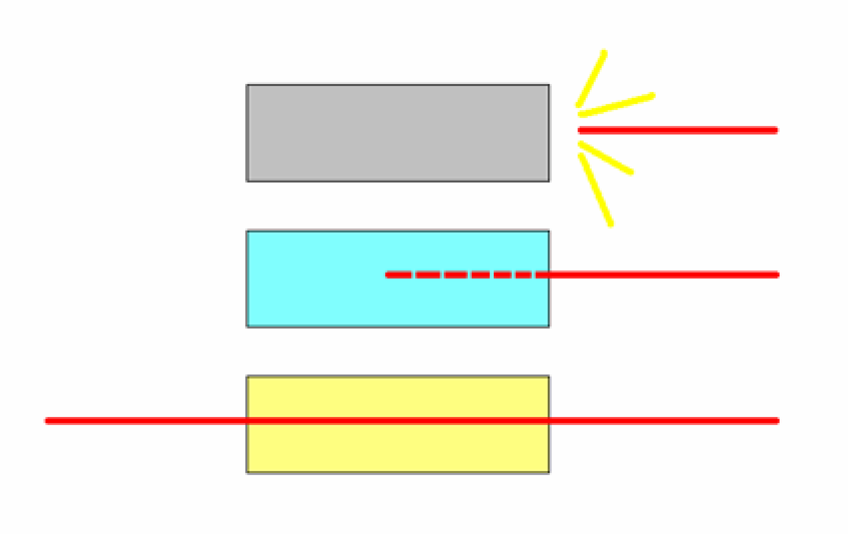
Microwaves



Microwaves

- Microwaves are electromagnetic energy
- Microwaves frequency ranges from 300 to 300.000 MHz
- Microwaves wavelength ranges from 1 m to 1 mm
- Frequencies for industrial, medical and scientific uses are 915 MHz, 2.450 MHz (12,25 cm wavelength), 5.800 MHz and 22.125 MHz

Materials Interaction



- Materials can be
  - – Reflective (metals)
  - – Absorptive (water)
  - – Transparent (PTFE)

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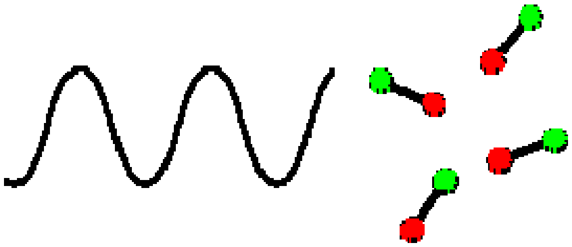
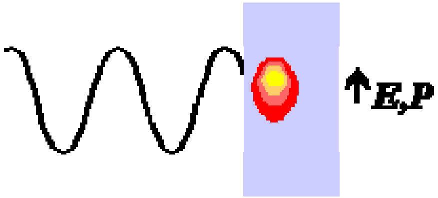
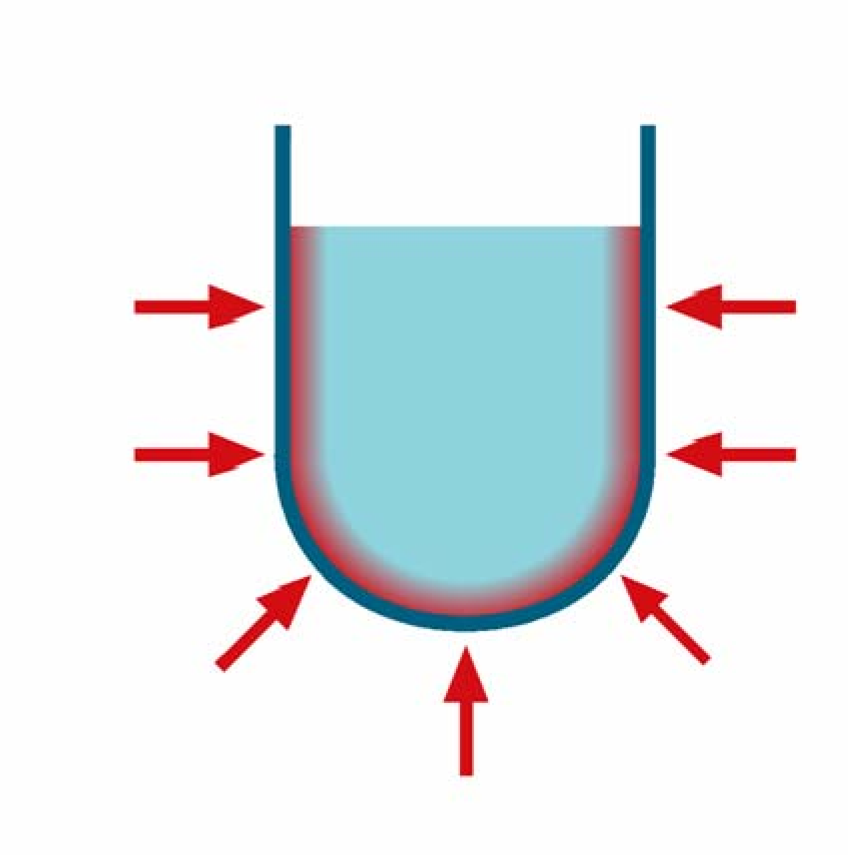
Microwave Heating Mechanism





- Liquids rapidly absorb microwave energy by two mechanisms which take place simultaneously
  - Dipole rotation
  - Ionic conduction

Conductive Heating



- Heat passes through the vessel walls prior reaching the reactants
- Slow and inefficient method dependent from vessel material thermal conductivity
- Vessel temperature in excess of reaction mixture temperature

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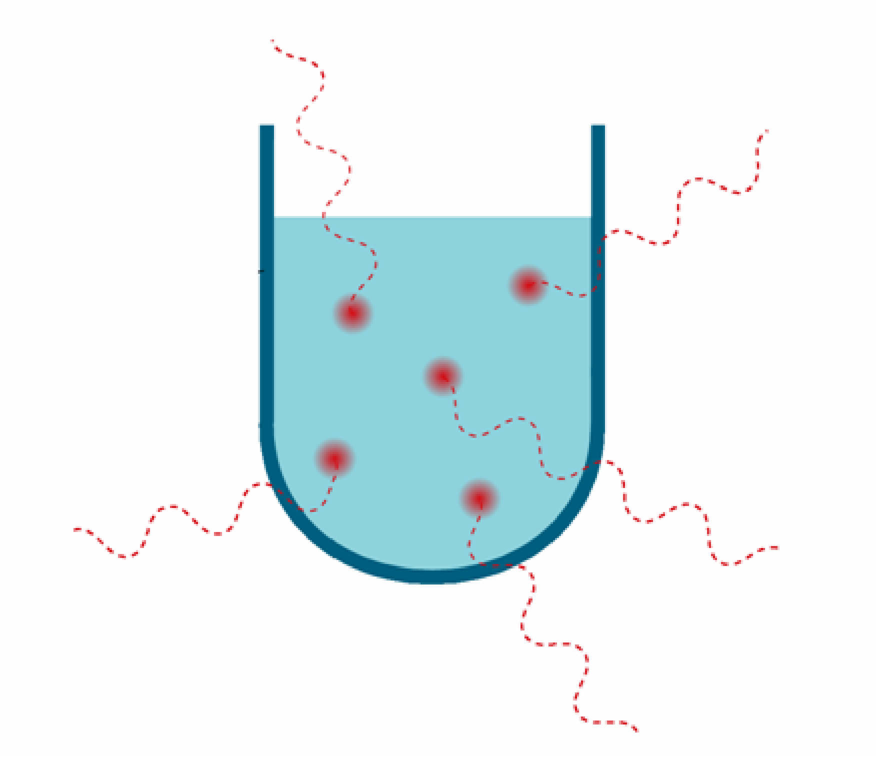
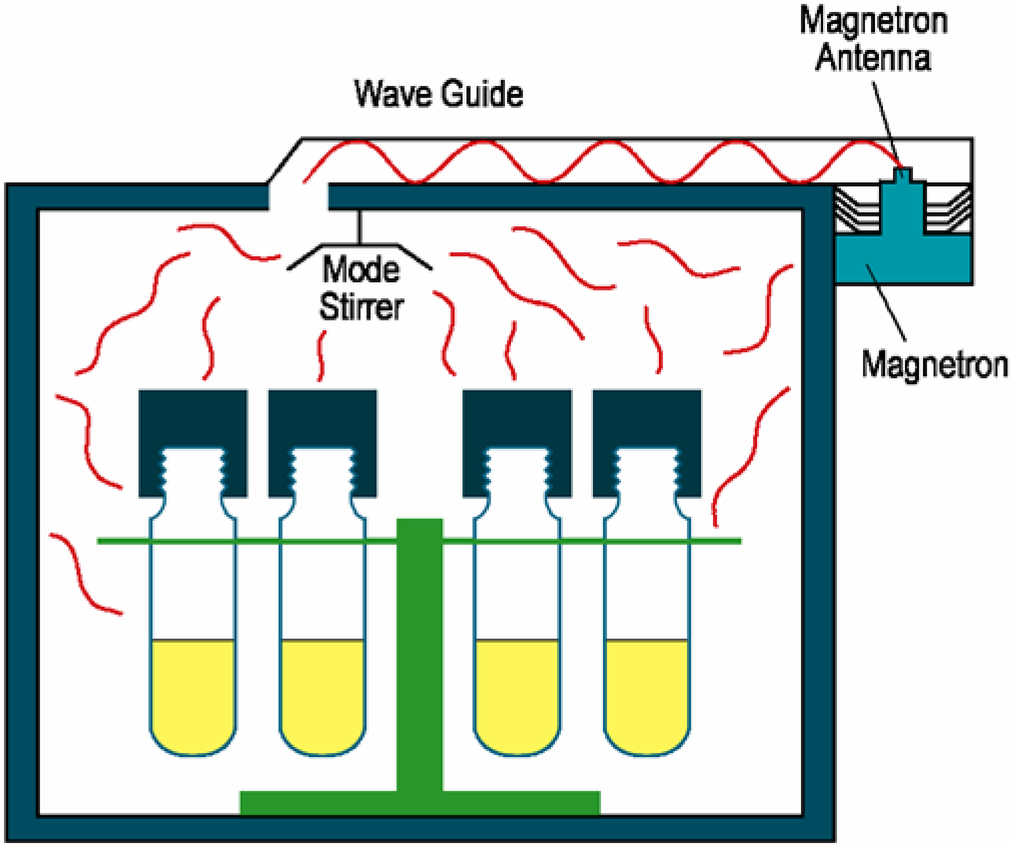
Microwave Heating



- Microwaves couple with reaction mixture molecules
- Rapid temperature increase
- Independent from vessel material thermal conductivity
- Instantaneous localized super-heating by ionic conduction and dipole rotation
- No inertia (instant on-off)
- Dependant from ionic conduction and dipolar polarization

Multi-mode Microwave System



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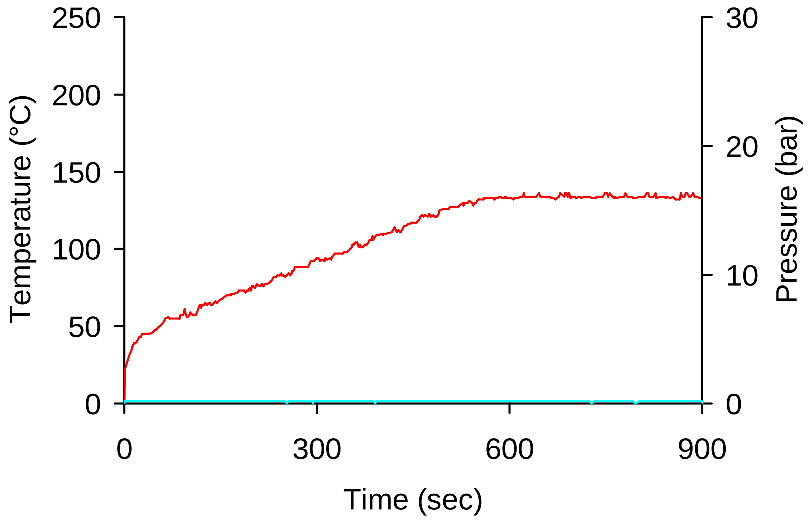
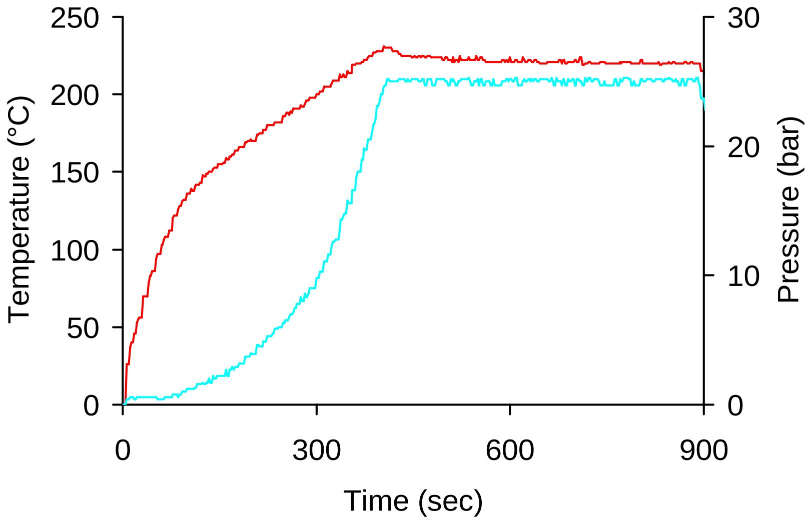
Open Vessel Microwave Heating



- 10 ml of HNO_3 are heated in Teflon open vessels at 300 W for 15’
- The highest temperature is just above the HNO_3 boiling point (125°C)
- Heating rate doubles when double power is applied

Closed Vessel Microwave Heating



- 10 ml of HNO_3 are heated in Teflon closed vessels at 300 W for 15’
- The vapor pressure generated inside the vessels increases the boiling temperature of HNO_3
- At 25 bar the temperature is of 220°C

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Pressure and Temperature

- Pressure is the mean and temperature is the goal
- Increasing the temperature by 10°C doubles the rate of a reaction
- Rapid microwave heating and the use of closed vessel allow for reducing the sample preparation time from hours to minutes

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- Advanced microwave hardware
- Advanced user interface
- Advanced reaction sensors
- Advanced vessel technology

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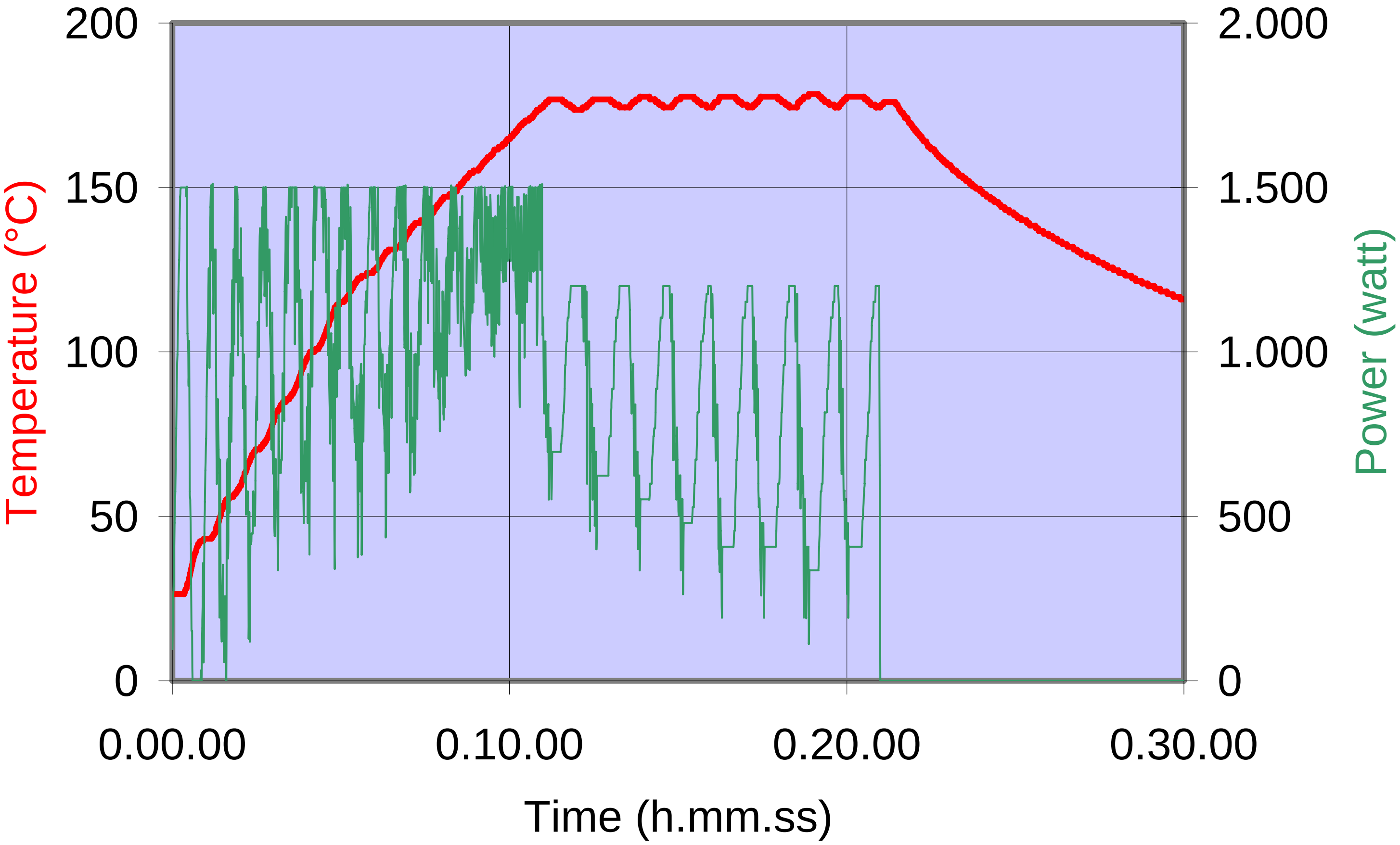
Advanced Microwave Hardware

- High microwave power
  - – Fast heating rate
- Homogeneous microwave distribution
  - – Same temperature in all vessels
- Pressure-responsive door
  - – High safety
- Rapid cooling
  - – High sample throughput

High Microwave Power
Fast Heating Rate



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500 mg Soil with 10 ml HNO3 (24 vessels)

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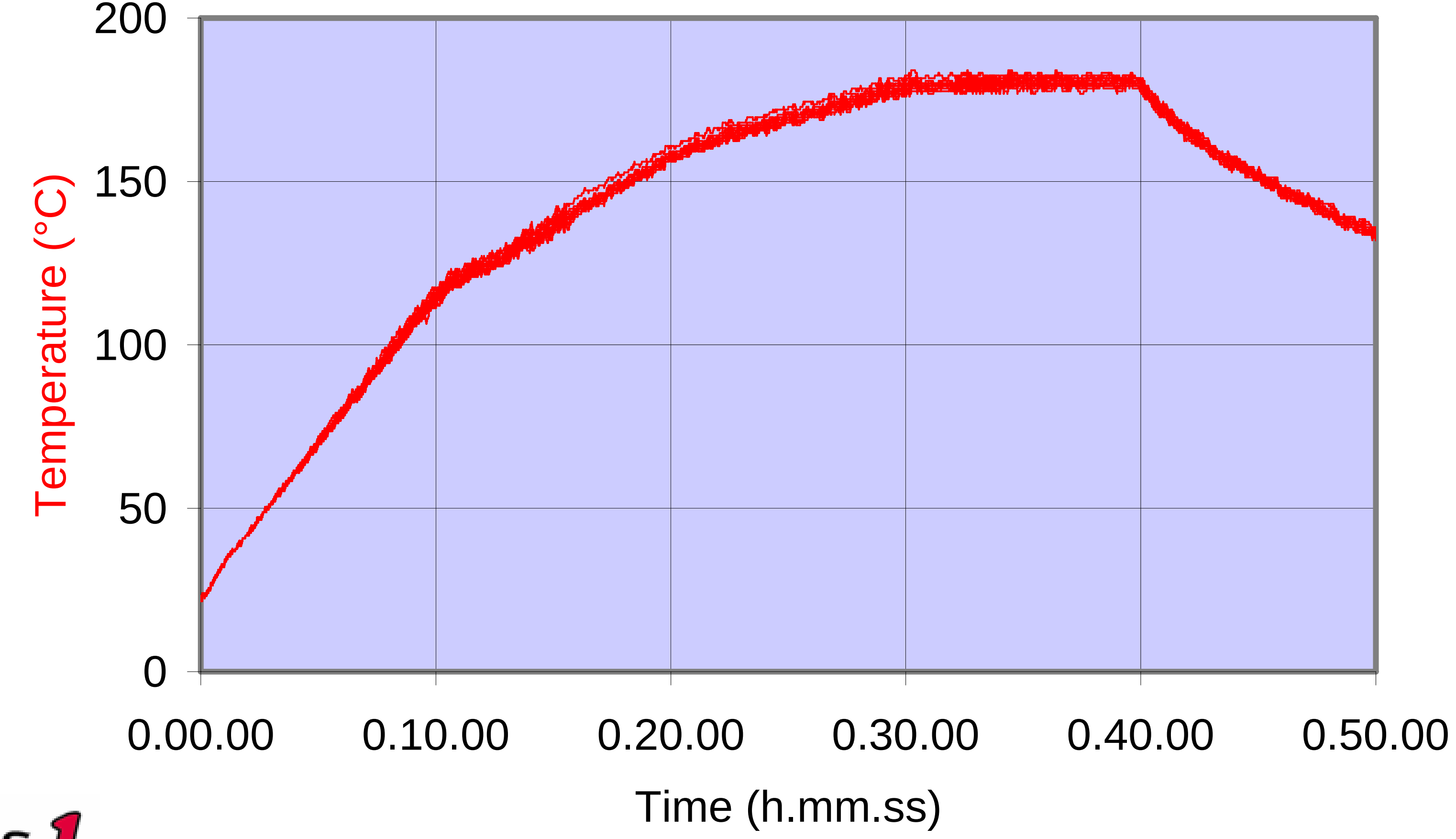
Homogeneous Microwave Distribution Same Temperature in All Vessels



20 vessels with individual temperature control

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Pressure-Responsive Door
High Safety

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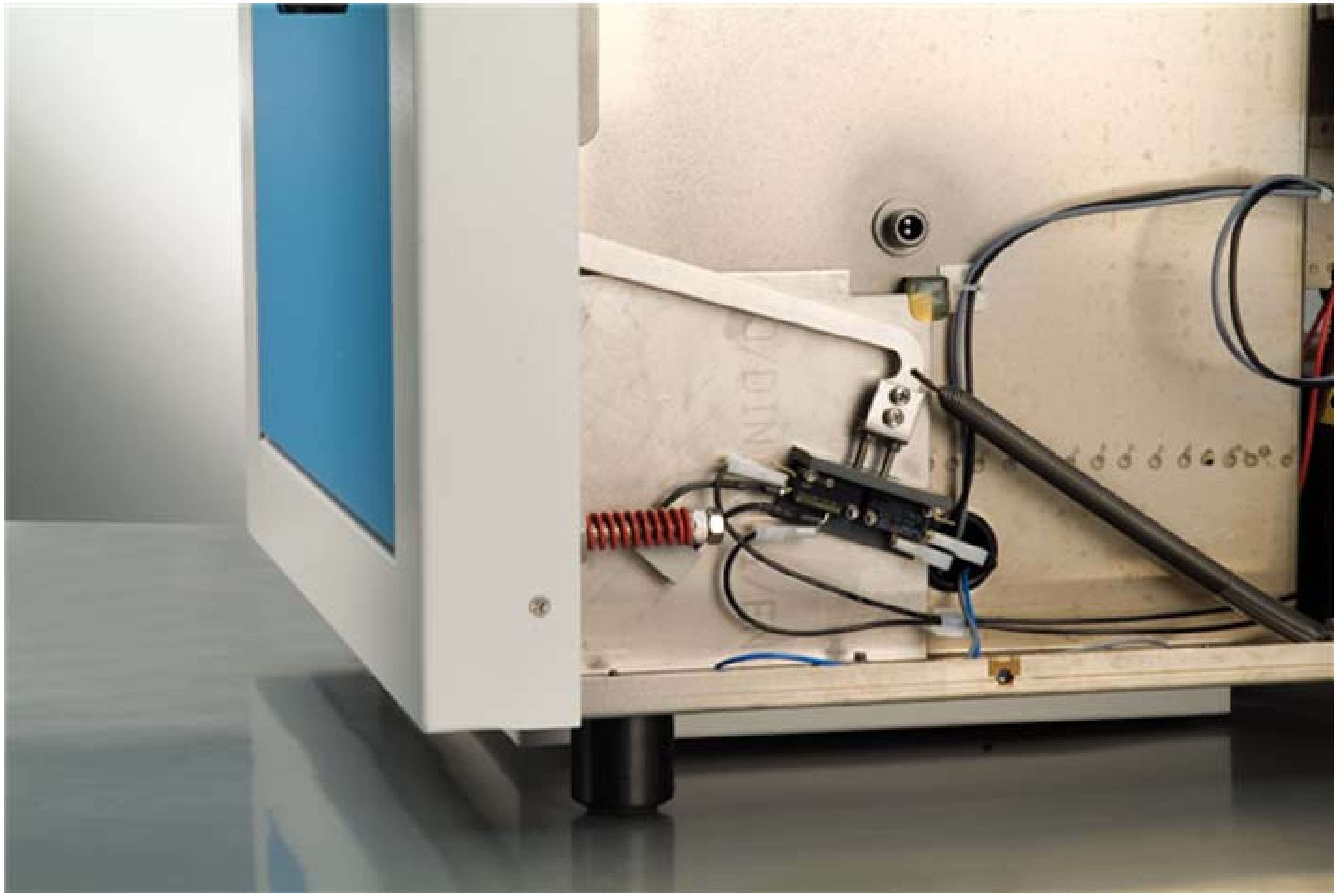
Pressure-Responsive Door
High Safety



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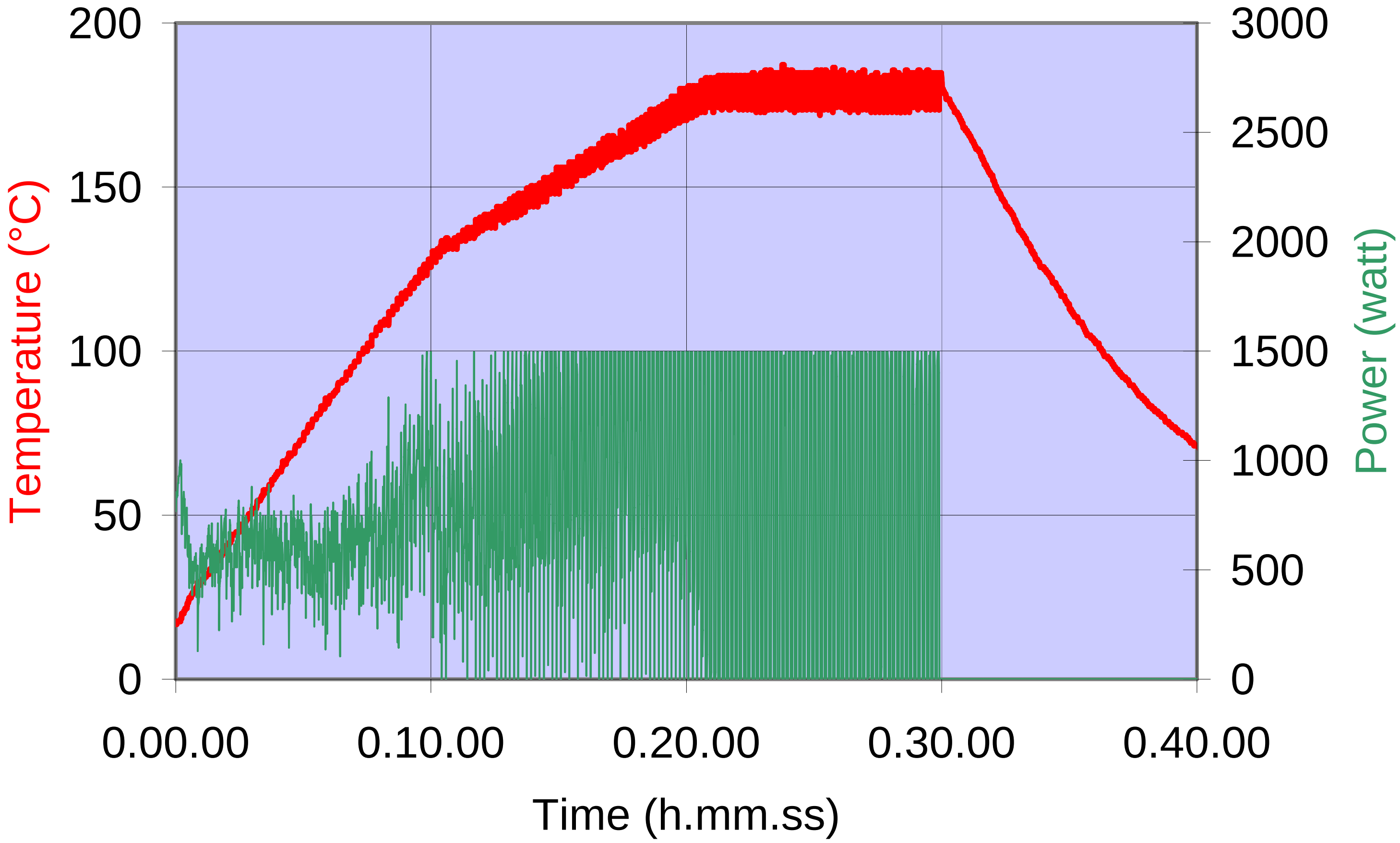
Rapid Cooling
High Sample Throughput



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Q-20 with 10 ml HNO3; air cooling time 10 minutes (20 vessels)

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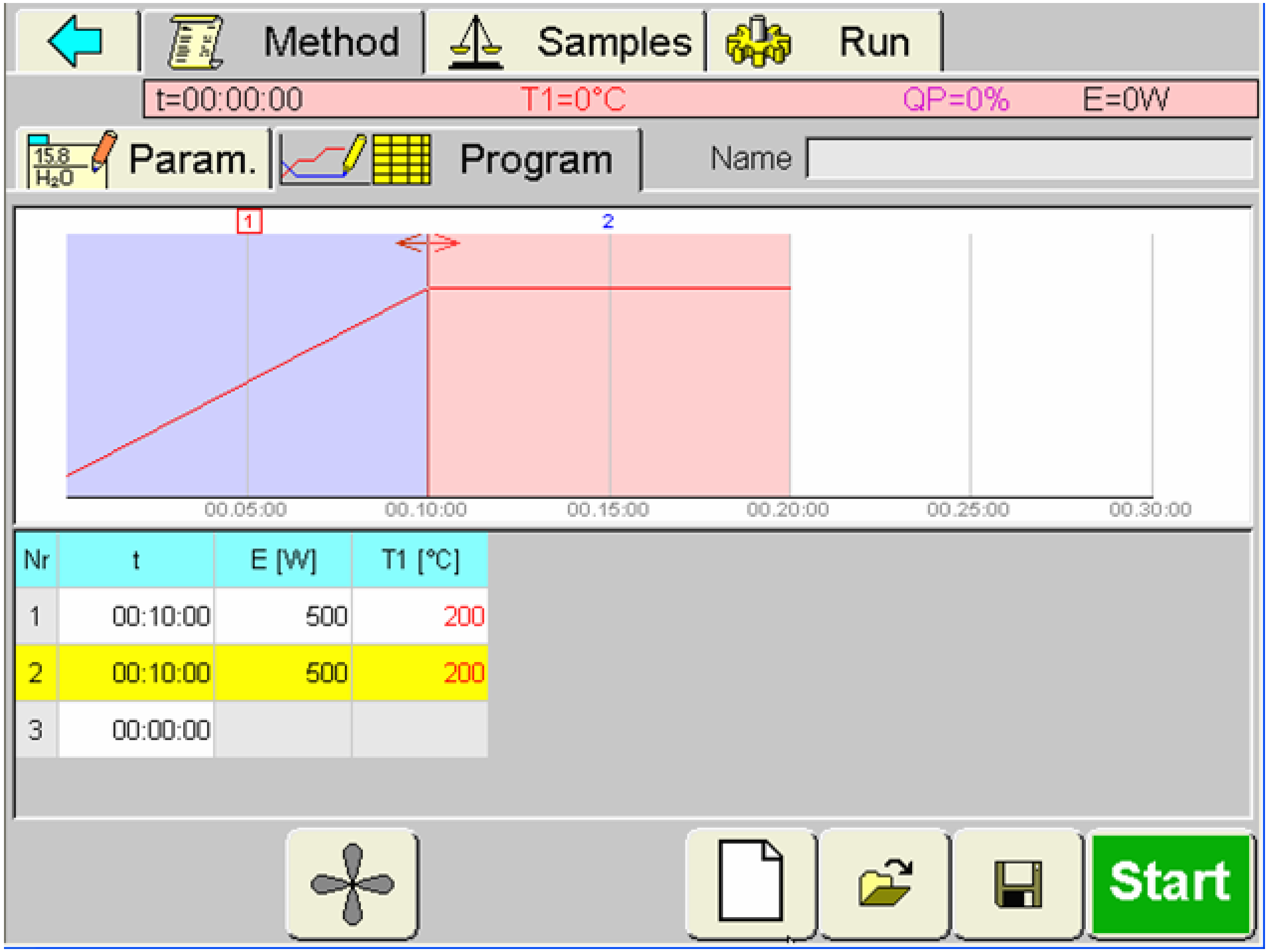
Advanced User Interface

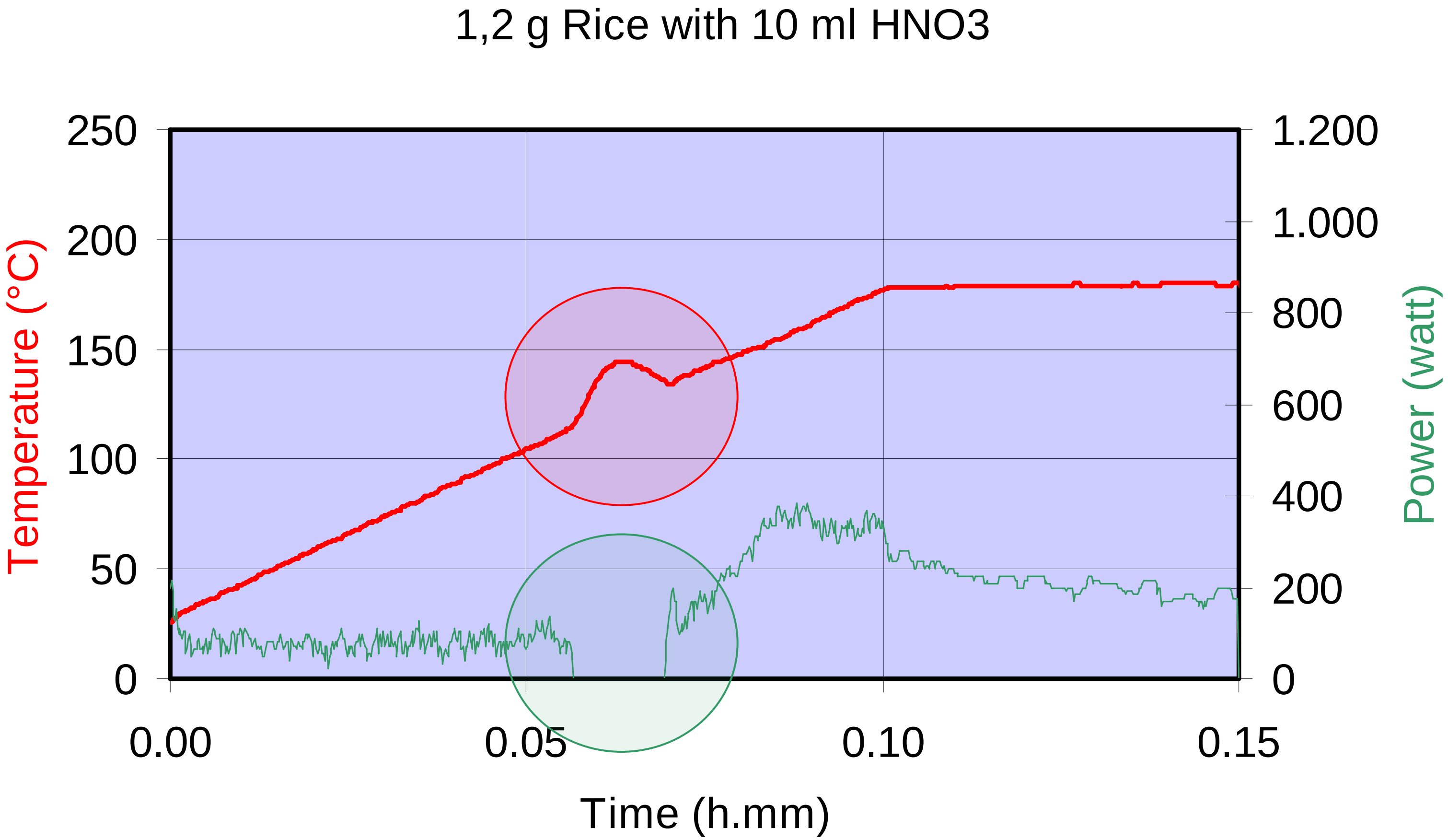
Time-to-Temperature



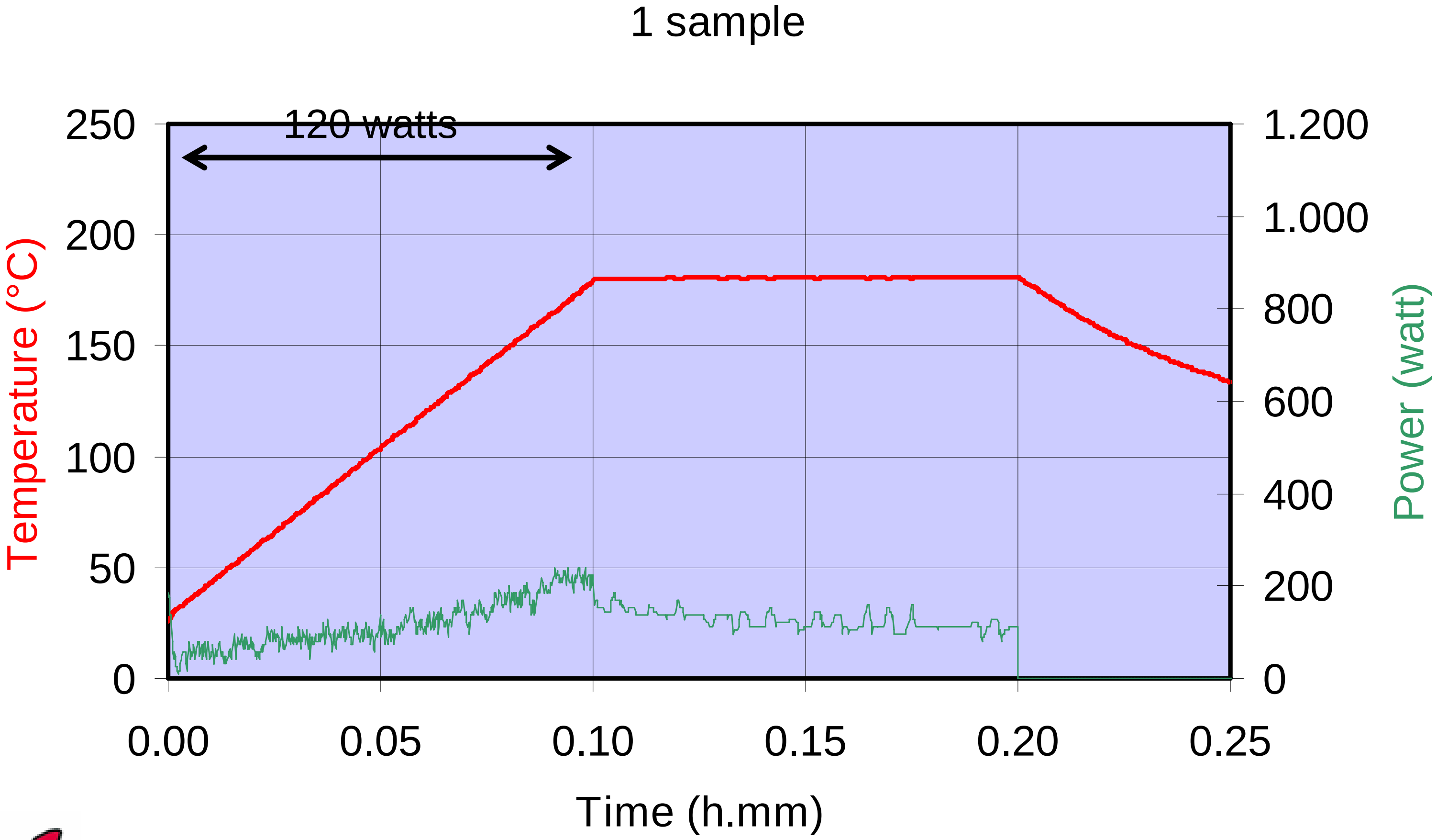
t=00:00:00 T1=0°C QP=0% E=0W

Nr	t	E [W]	T1 [°C]
1	00:10:00	500	200
2	00:10:00	500	200
3	00:00:00		

Better Control of Exothermic Reactions



Same Digestion Quality for One or Multiple Samples



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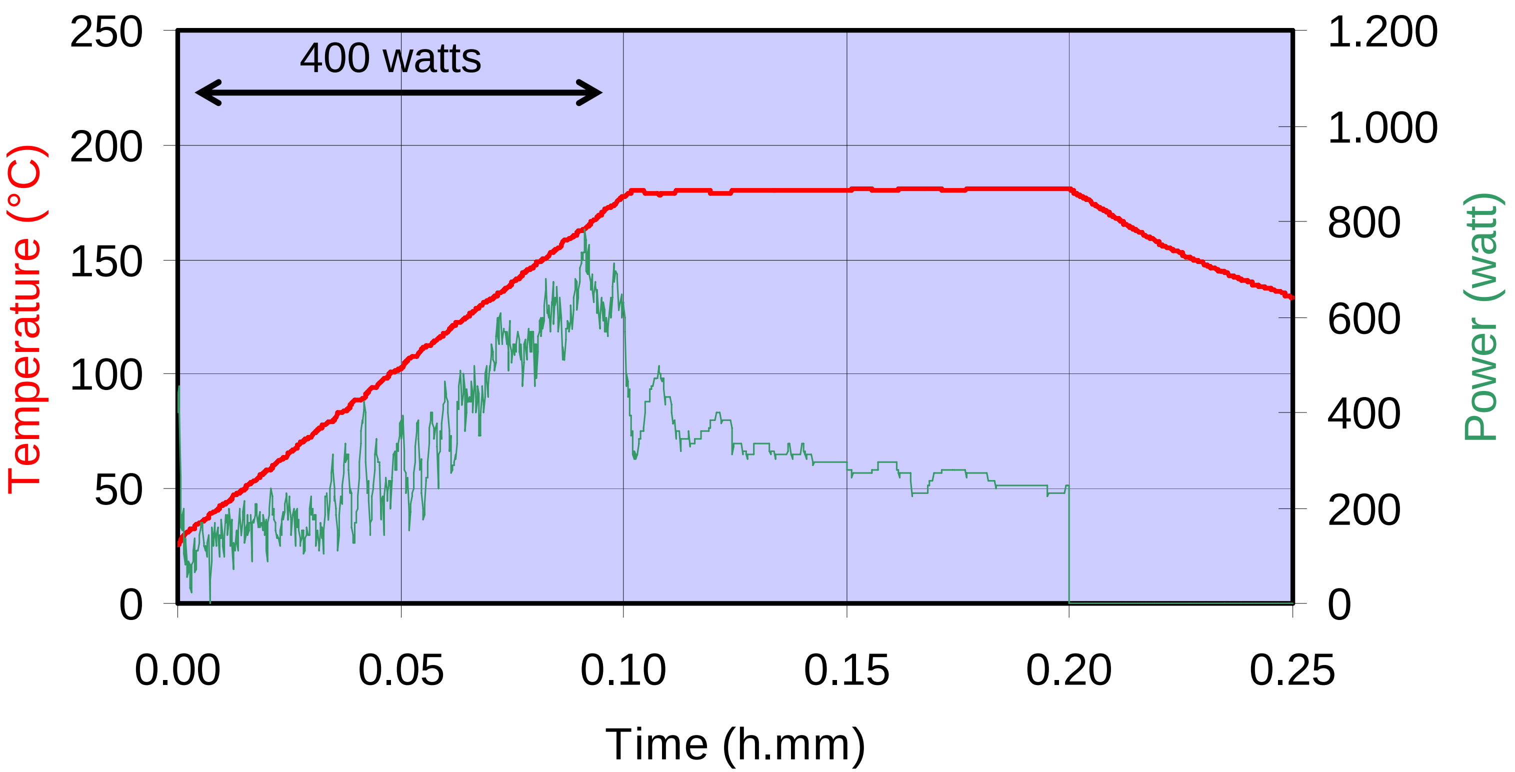
Same Digestion Quality for One or Multiple Samples



6 samples

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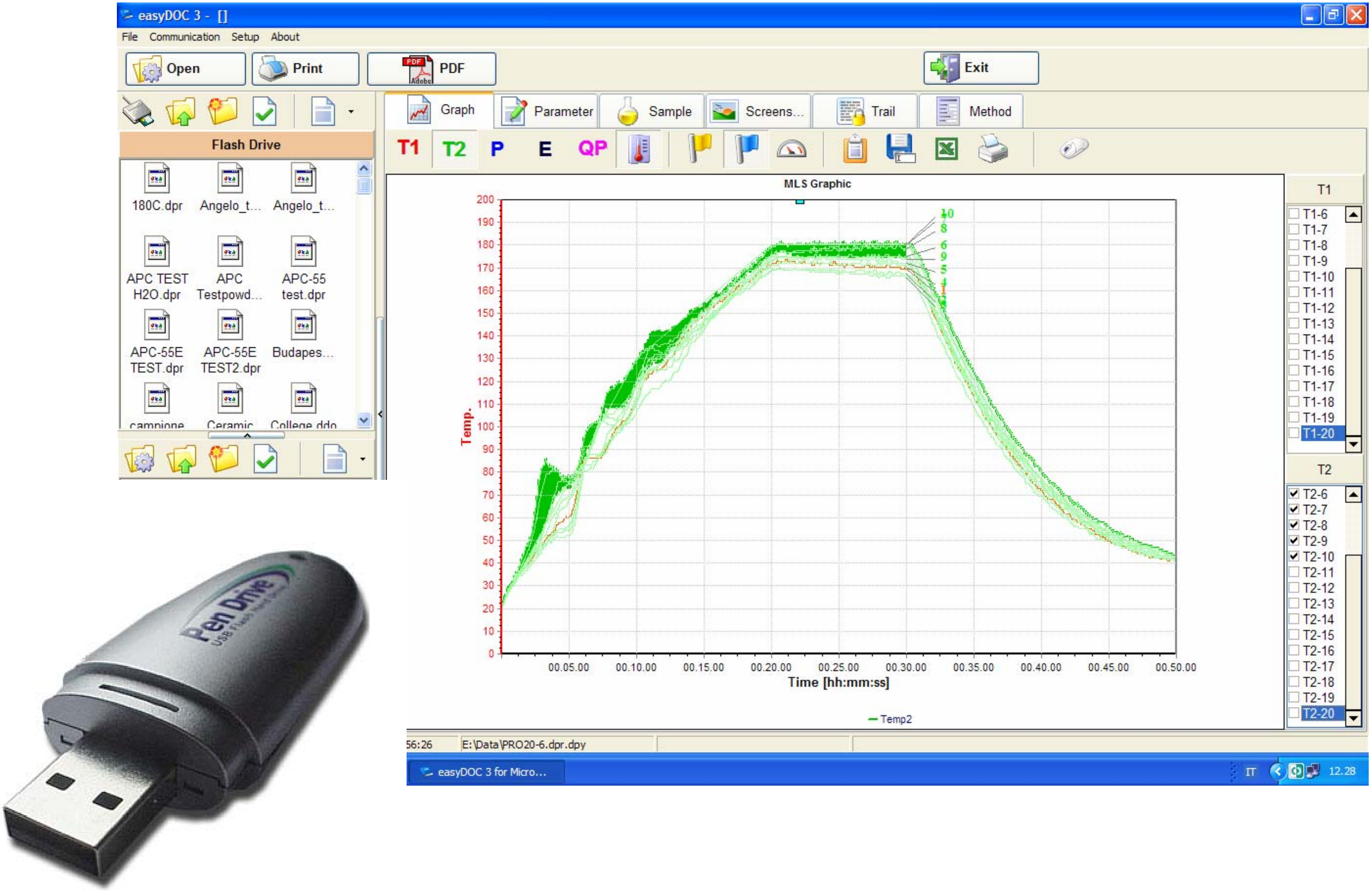
Easy Data Transfer



Advanced reaction sensors

Direct temperature control

- Direct monitoring and control of a reference vessel up to 300°C by thermocouple or fiber-optic
- Temperature is read 20 times per second
- Sensor housed in inert thermowell for trouble-free operation

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Contact-less temperature control in all vessels

- Focused, high-sensitivity infrared sensor
- Sequential contact-less temperature control in all vessels
- Individual temperature profile for each vessel

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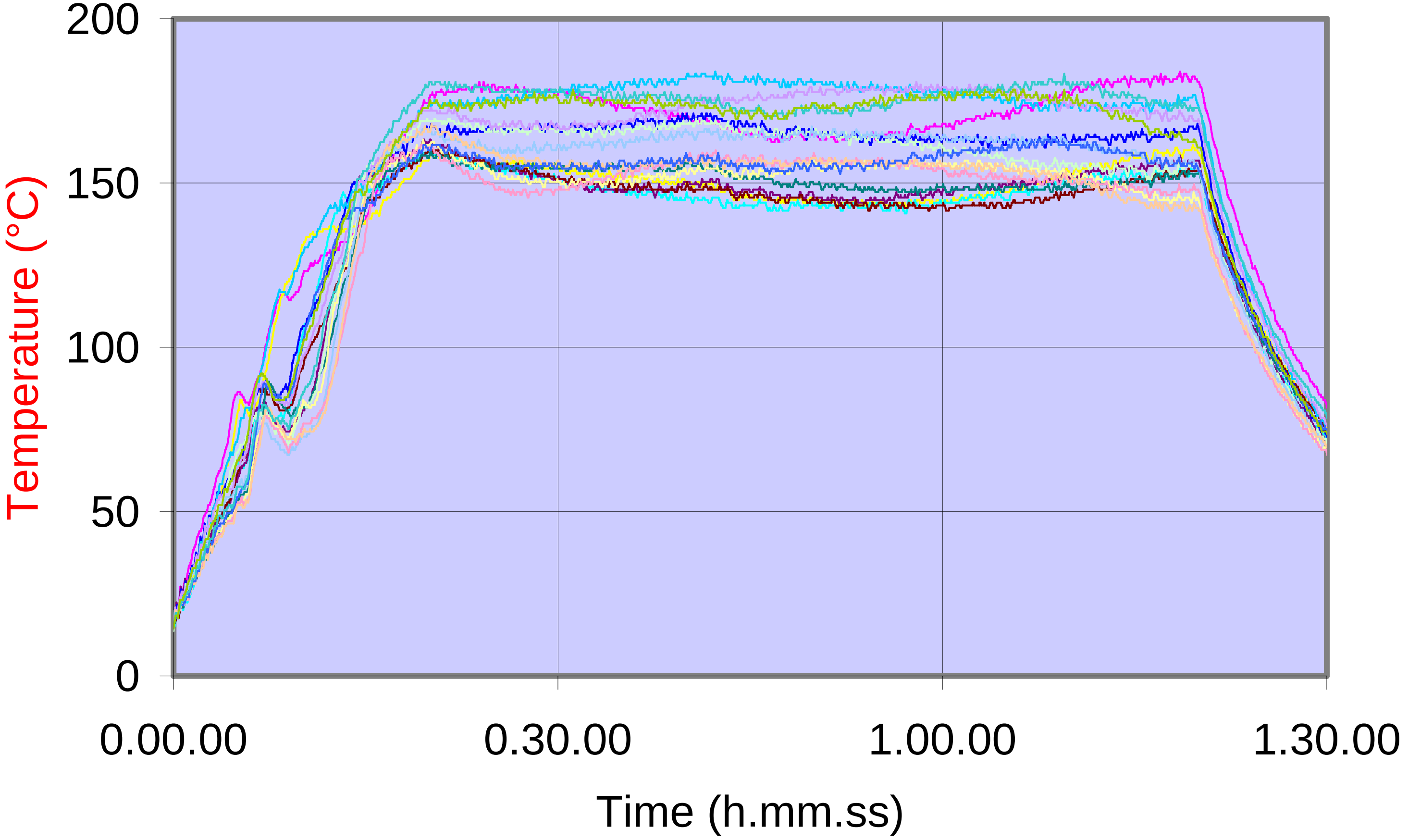
Temperature Control in All Vessels



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Direct pressure control

- Direct pressure monitoring and control in a reference vessel
- Suitable for ‘unknown’ samples to maintain pressure limits within the vessel’s specifications

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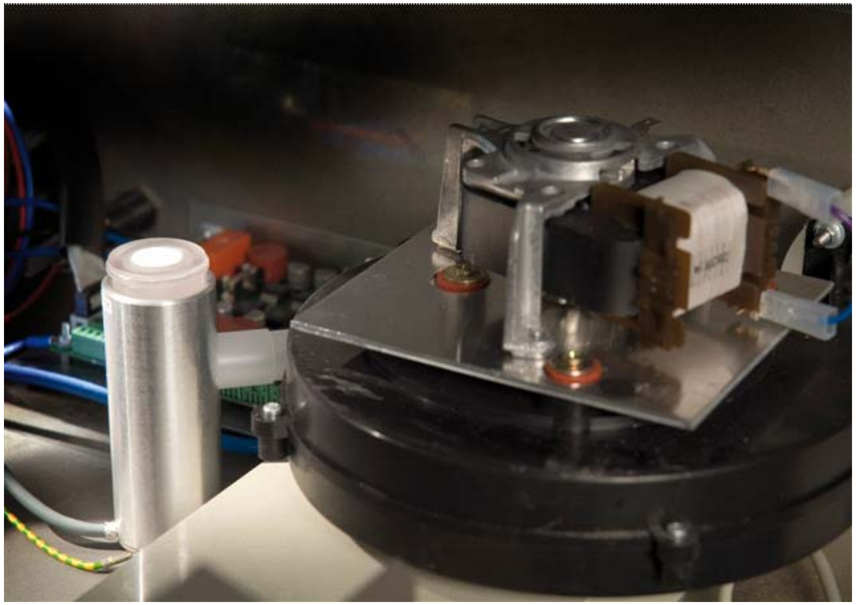
Contact-less pressure control in all vessels



- Sensor monitors all vessels simultaneously
- Prevents leakages and acid diffusion
- Ensures complete and safe digestion without losses of volatiles

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Advanced vessel technology

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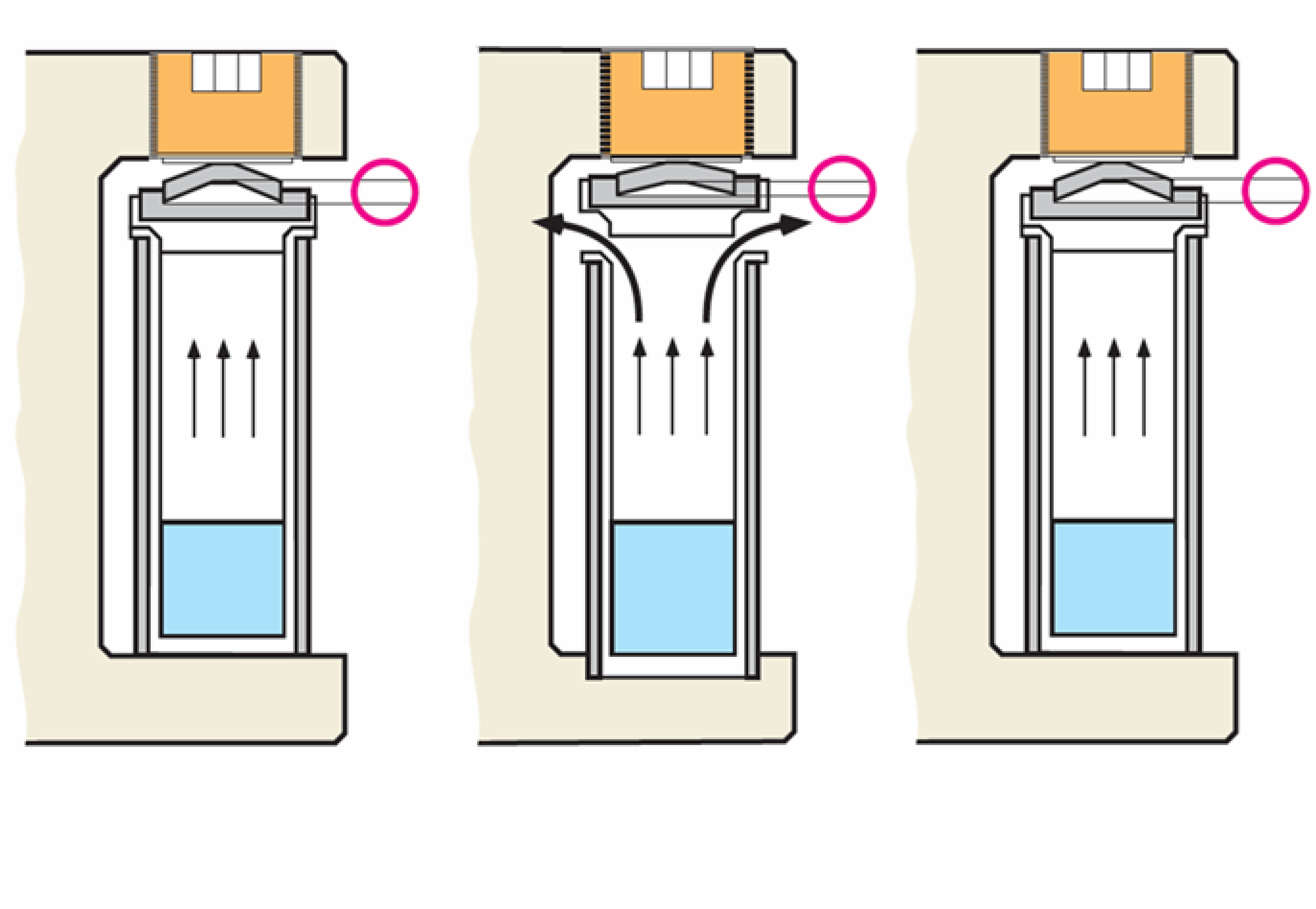
‘Vent-and-reseal’ technology



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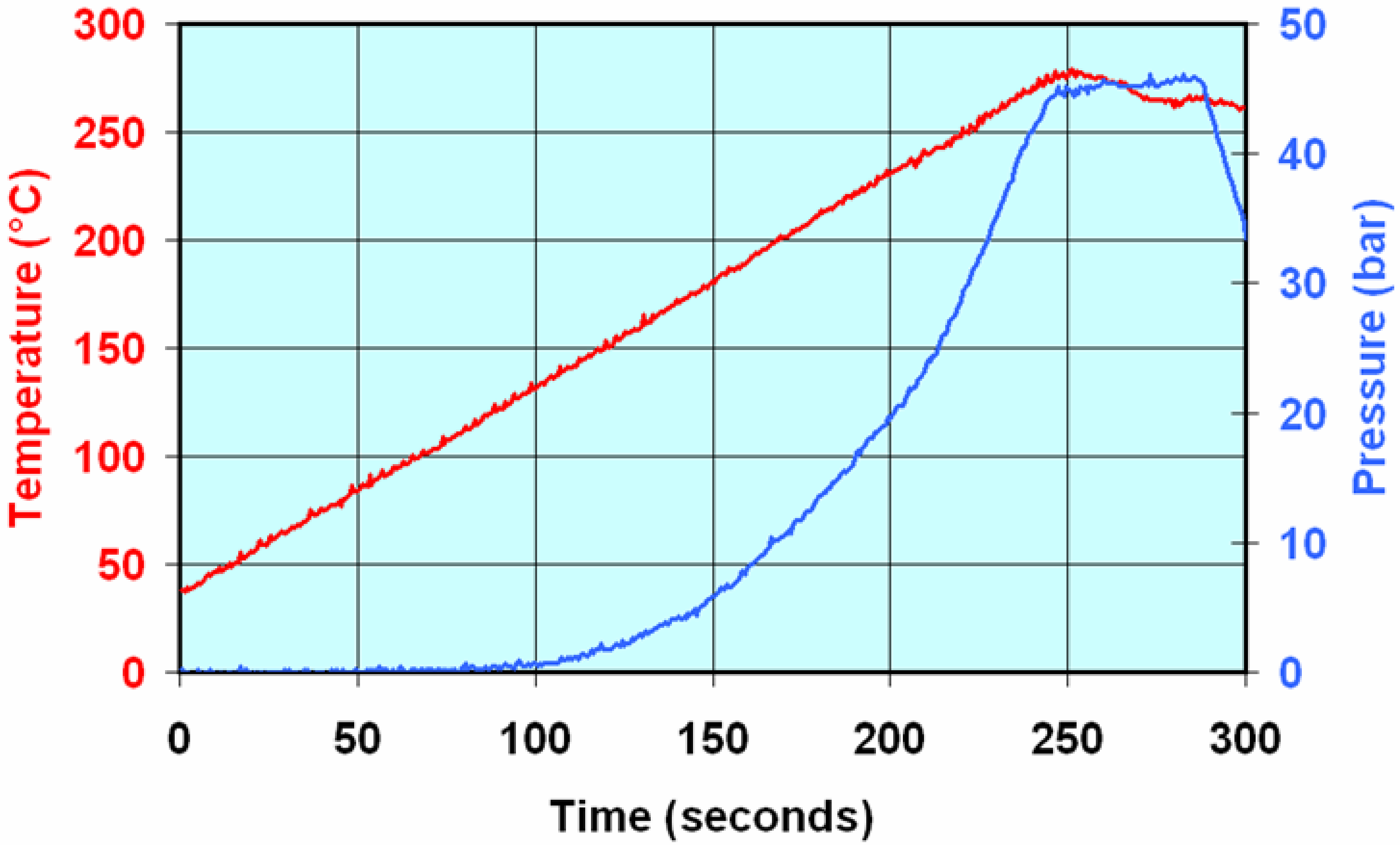
‘Vent-and-reseal’ technology



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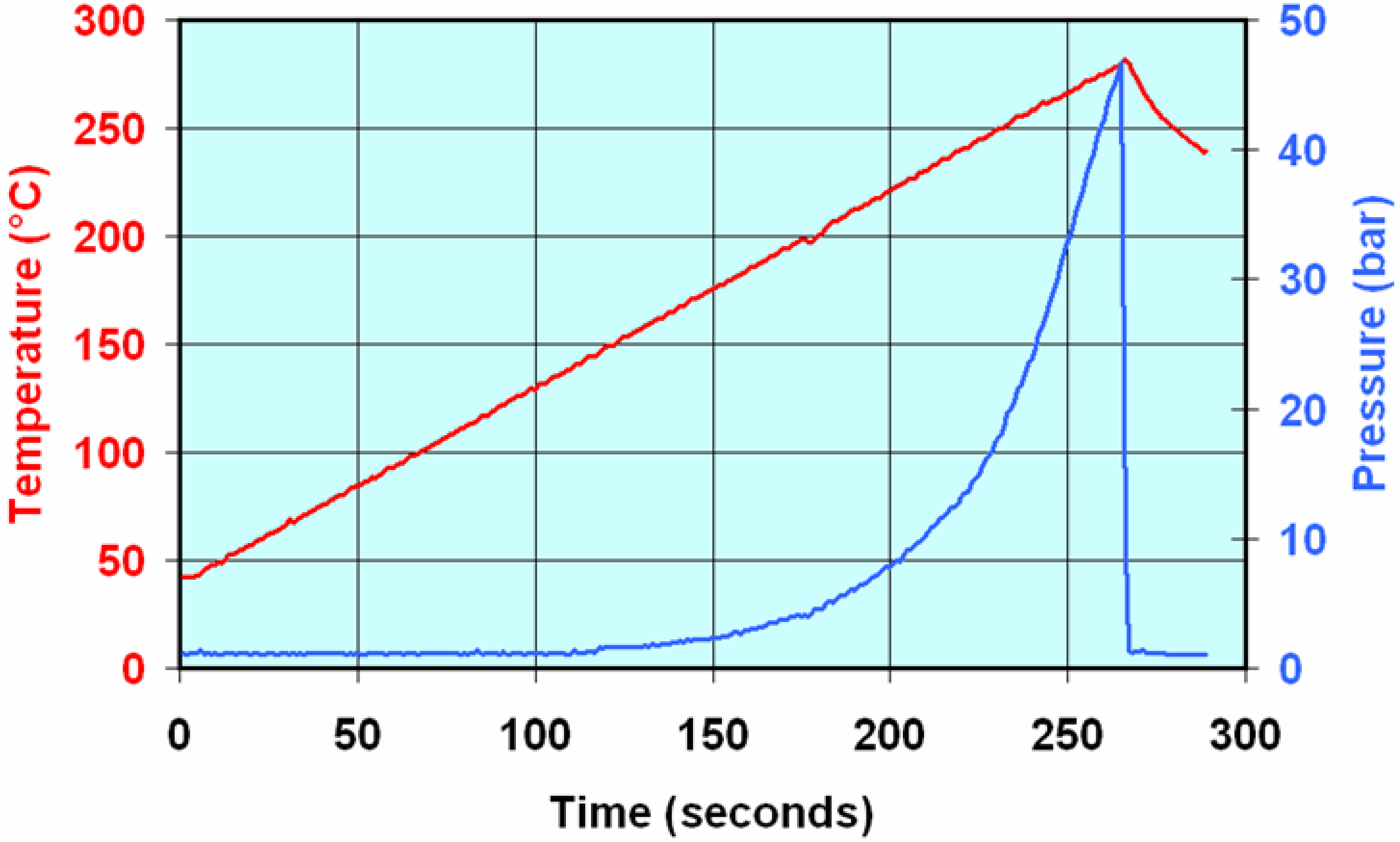
‘Burst-disk’ technology



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‘Vent-and-reseal’ advantages

- Highest temperature and pressure
- Highest safety standards
- Easy of use
- Fast air cooling

Environmental Samples

Resource Library

U.S. EPA Methods

EPA Method 3052

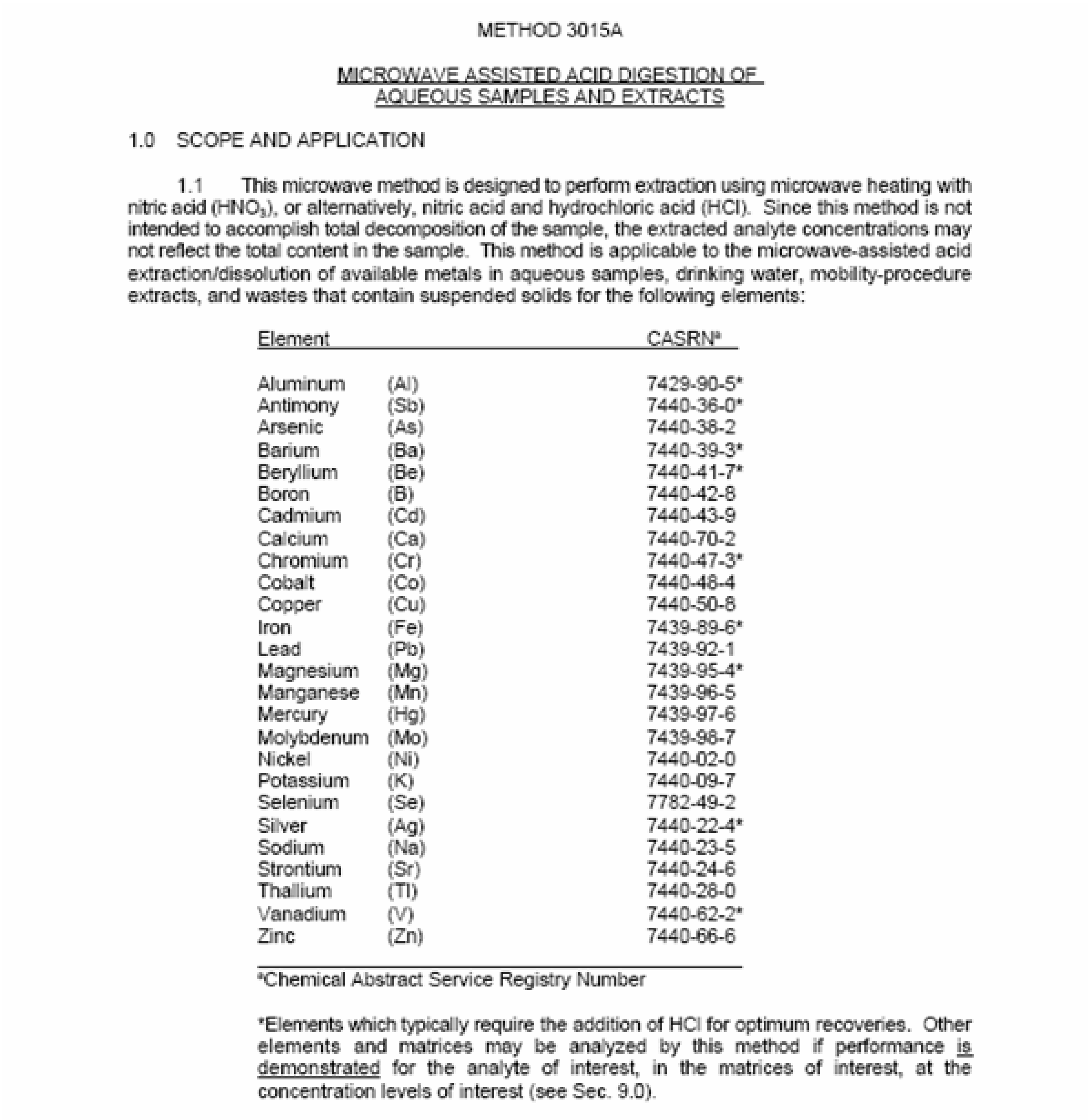
Microwave-Assisted Acid Digestion of Siliceous and Organically Based Matrices

EPA Method 3051a

Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

EPA Method 3015a

Microwave-Assisted Acid Leach of Aqueous Samples and Extracts



METHOD 3015A

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This microwave method is designed to perform extraction using microwave heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl). Since this method is not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution of available metals in aqueous samples, drinking water, mobility-procedure extracts, and wastes that contain suspended solids for the following elements:

Element		CASRN[a]
Aluminum	(Al)	7429-90-5*
Antimony	(Sb)	7440-36-0*
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3*
Beryllium	(Be)	7440-41-7*
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3*
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6*
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4*
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4*
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2*
Zinc	(Zn)	7440-66-6

[a] Chemical Abstract Service Registry Number

*Elements which typically require the addition of HCl for optimum recoveries. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 9.0).

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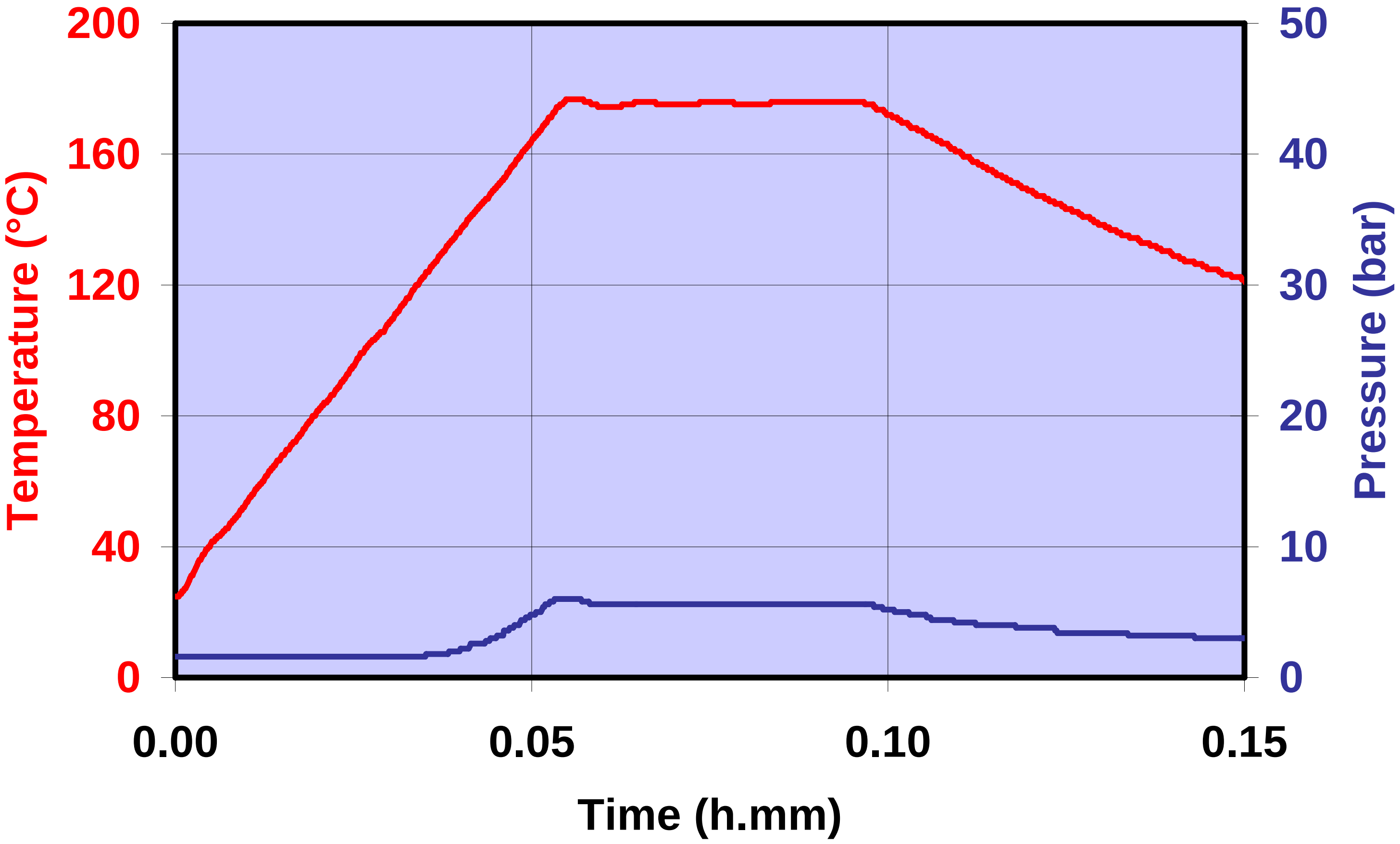
2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is extracted in 5 mL concentrated nitric acid or, optionally, 4 mL concentrated nitric acid and 1 mL concentrated hydrochloric acid, for 20 minutes using microwave heating with a suitable laboratory microwave unit. The temperature of the acid-sample mixture is brought to 170 ± 5 °C in 10 minutes, and maintained at 170 ± 5 °C for 10 minutes to accelerate the leaching process. The sample and acid(s) are placed in a fluorocarbon polymer (such as PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method.

US EPA 3051a



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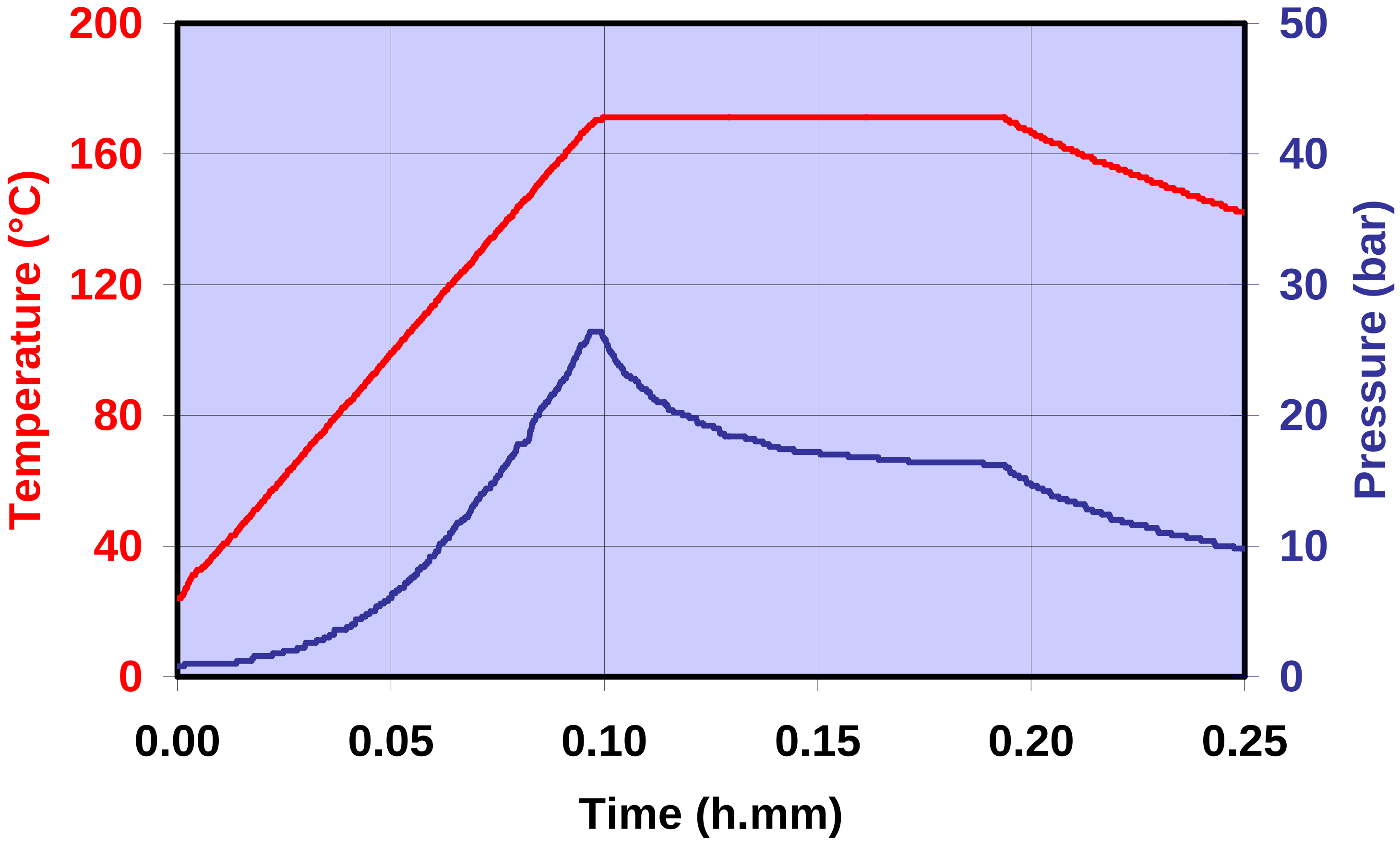
US EPA 3015a



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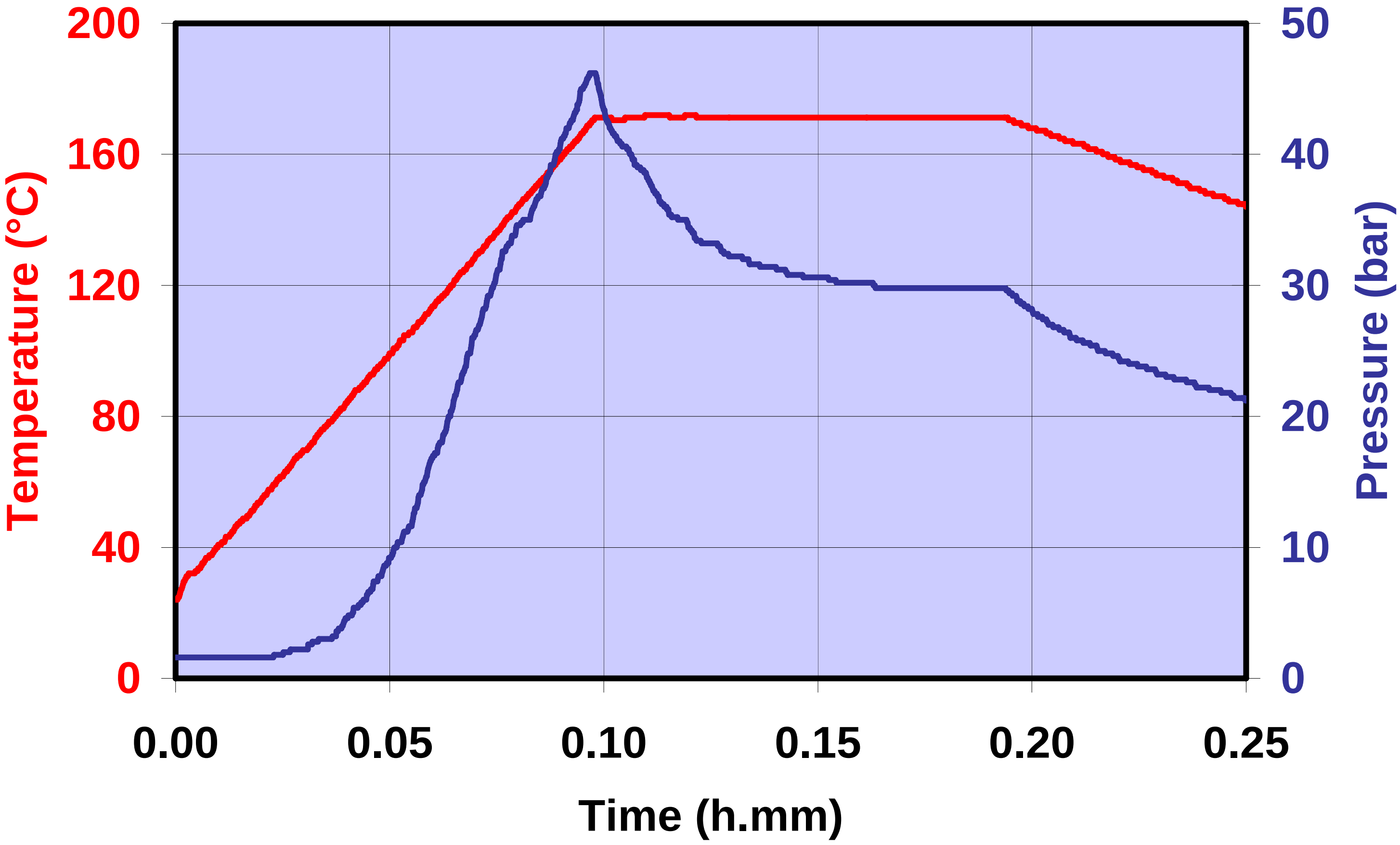
US EPA 3015a



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COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~ 0.35 G SRM 2704 (BUFFALO RIVER SEDIMENT) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

Element	**5 mL HNO_3 digest**	**4 mL HNO_3 + 1 mL HCl digest**	**Total Analyte Concentration**
Ag	0.31 ± 0.05	0.41 ± 0.09	<4
B	23.8 ± 3.1	30.6 ± 8.3	---*
Be	0.81 ± 0.13	0.91 ± 0.19	---*
Co	12.0 ± 0.30	11.5 ± 0.98	14.0 ± 0.6
Hg	----	1.49 ± 0.03	1.44 ± 0.07
Mo	2.97 ± 0.72	3.15 ± 0.28	---*
Ni	39.6 ± 2.5	41.3 ± 1.7	44.1 ± 3.0
Sr	41.9 ± 1.3	49.0 ± 1.6	(130)
V	6.18 ± 2.5	14.6 ± 2.4	95 ± 4
Zn	418 ± 12	412 ± 31	438 ± 12

Results reported in µg/g analyte (mean ± 95% confidence limit).
Total concentrations are taken from NIST SRM Certificate of Analysis.
Values in parenthesis are reference concentrations.
* The total concentration of this analyte in SRM 2704 is not certified.

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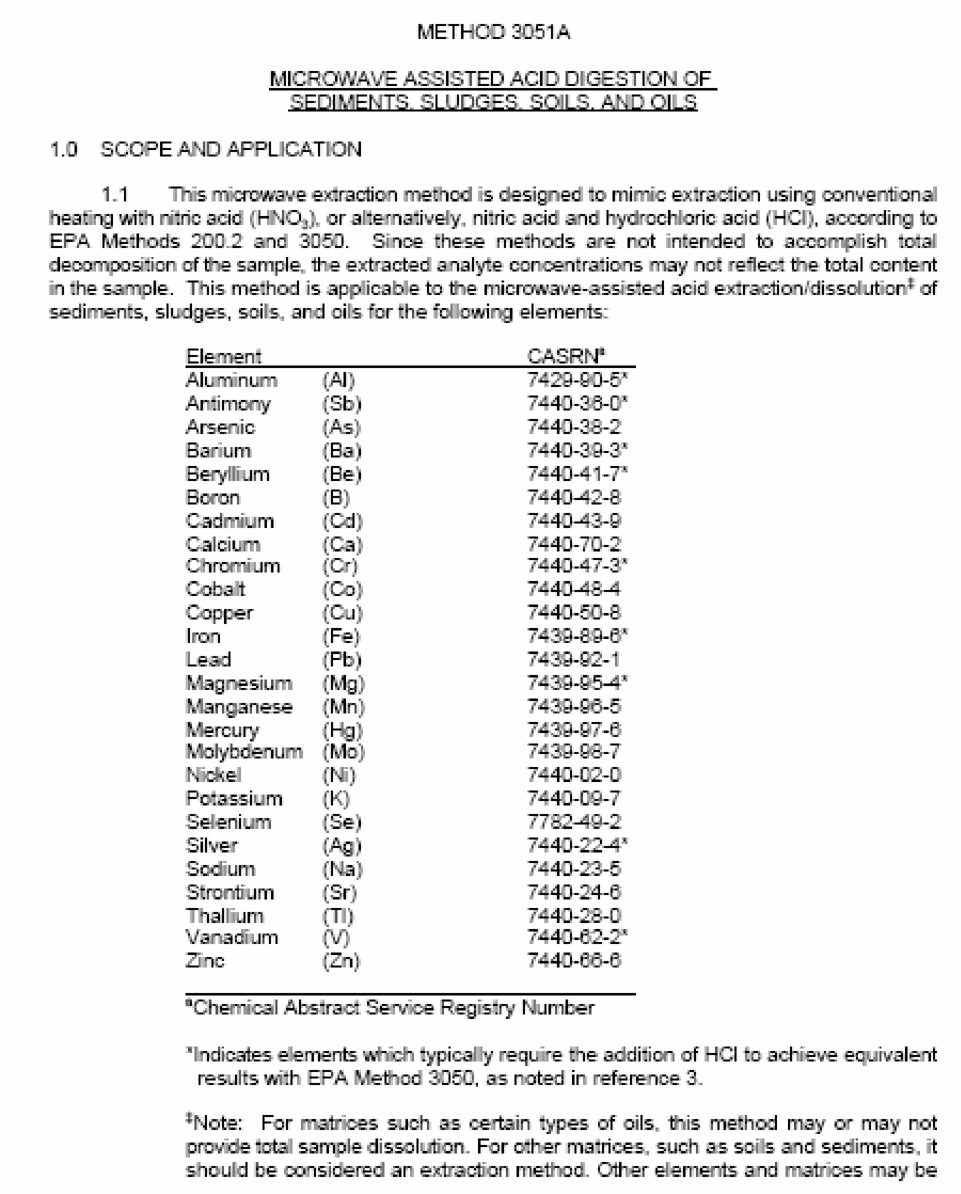
COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~0.35 G SRM 4355 (PERUVIAN SOIL) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

Element	**5 mL HNO_3 digest**	**4 mL HNO_3 + 1 mL HCl digest**	**Total Analyte Concentration**
Ag	1.31 ± 0.12	1.62 ± 0.11	(1.9)*
B	32.9 ± 2.1	31.8 ± 2.7	(63)*
Co	10.5 ± 0.34	10.4 ± 0.41	14.8 ± 0.76
Mo	0.99 ± 0.06	1.1 ± 0.11	(1.7)*
Ni	12.2 ± 1.2	13.1 ± 1.9	(13)*
Pb	135 ± 4	136 ± 4	129 ± 26
Sb	3.7 ± 0.30	5.2 ± 0.53	14.3 ± 2.2
Sr	140 ± 6	143 ± 7	(330)

Results reported in µg/g analyte (mean ± 95% confidence limit).
Total concentrations are taken from NIST SRM Certificate of Analysis.
* Values in parenthesis are reference concentrations.



METHOD 3051A

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This microwave extraction method is designed to mimic extraction using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Methods 200.2 and 3050. Since these methods are not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution[‡] of sediments, sludges, soils, and oils for the following elements:

Element		CASRN[a]
Aluminum	(Al)	7429-90-5*
Antimony	(Sb)	7440-36-0*
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3*
Beryllium	(Be)	7440-41-7*
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3*
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6*
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4*
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4*
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2*
Zinc	(Zn)	7440-66-6

[a] Chemical Abstract Service Registry Number

*Indicates elements which typically require the addition of HCl to achieve equivalent results with EPA Method 3050, as noted in reference 3.

[‡] Note: For matrices such as certain types of oils, this method may or may not provide total sample dissolution. For other matrices, such as soils and sediments, it should be considered an extraction method. Other elements and matrices may be

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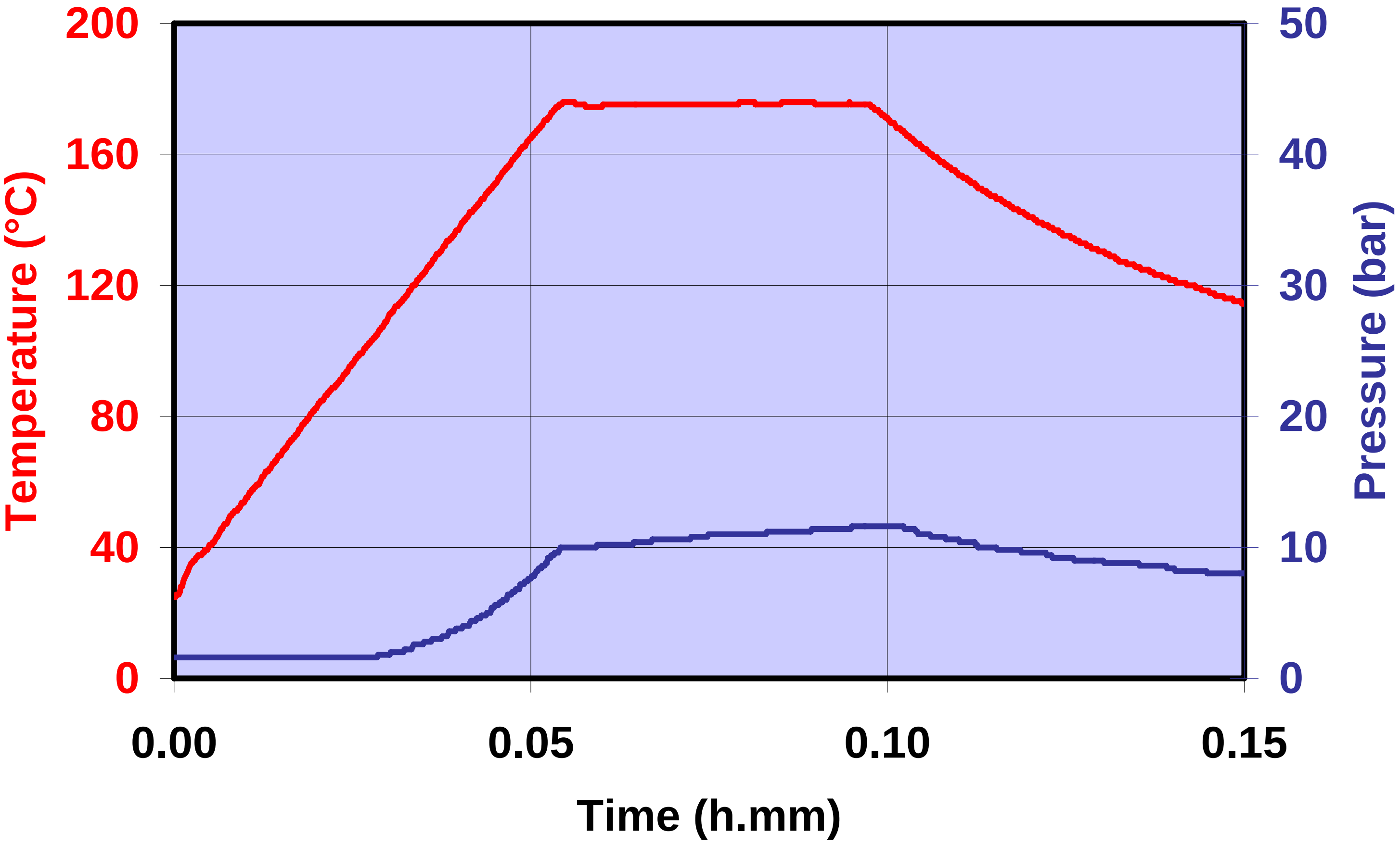
2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is extracted and/or dissolved in 10 mL concentrated nitric acid, or alternatively, 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid for 10 minutes using microwave heating with a suitable laboratory microwave unit. The sample and acid(s) are placed in a fluorocarbon polymer (PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method.

11.3.5 This method is a performance based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 175 ± 5 °C in approximately 5.5 ± 0.25 minutes and remain at 175 ± 5 °C for 4.5 minutes, or for the remainder of the ten minute digestion period (see Refs. 2, 3, and 4 and the document listed in 13.3.4). The time versus temperature and pressure profile is given for a standard sediment sample in Figure 2. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of vessels that can be heated by the magnetron of the microwave unit according to the heating profile specified previously in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss from the vessels (Ref. 3)).

US EPA 3051a



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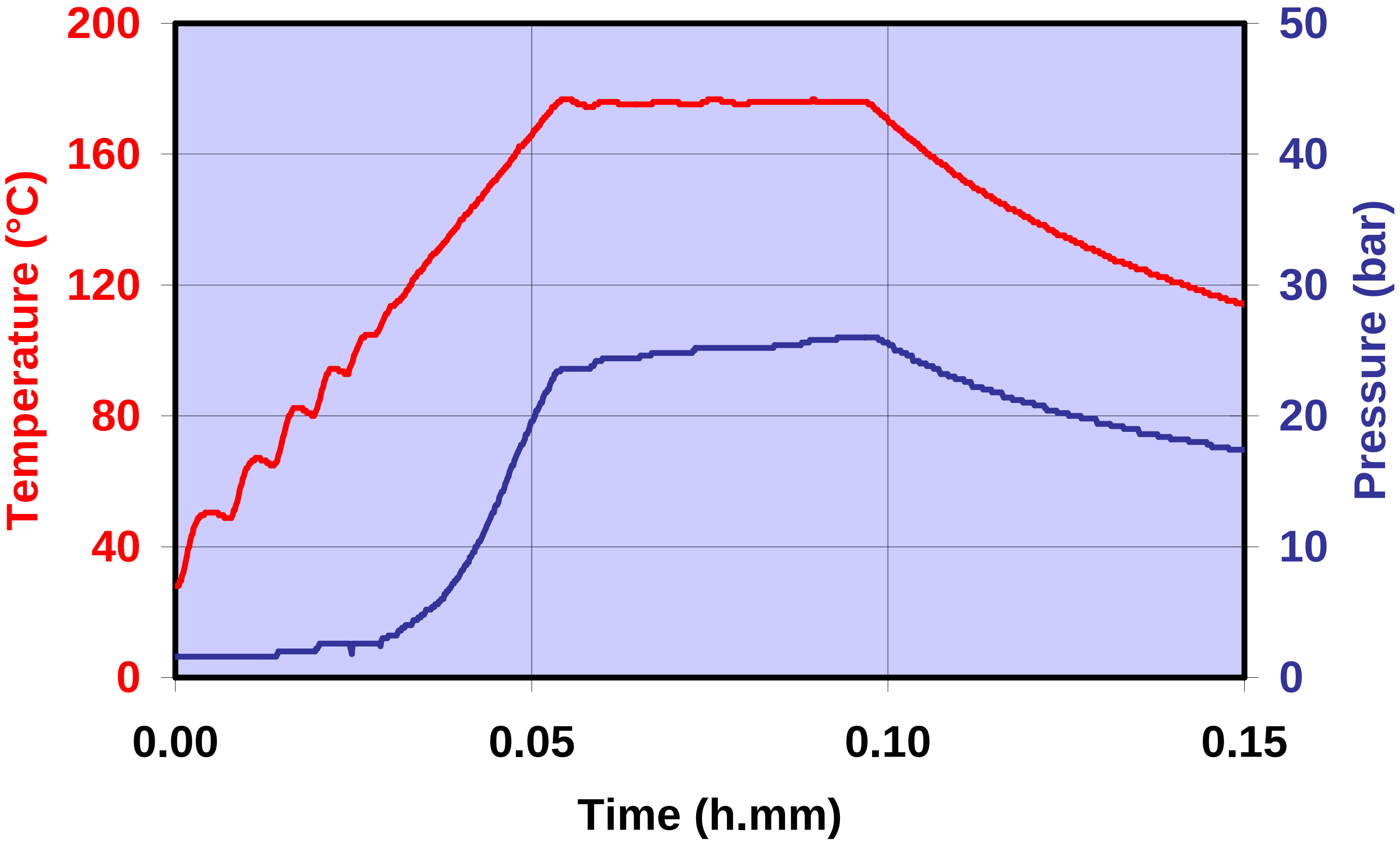

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METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices. If a total decomposition analysis (relative to the target analyte list) is required, the following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. This method is applicable for the following elements:

Aluminum
Antimony
Arsenic
Boron
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Potassium
Selenium
Silver
Sodium
Strontium
Thallium
Vanadium
Zinc

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 8.0).

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid for 15 minutes using microwave heating with a suitable laboratory microwave system. The method has several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method has provisions for scaling up the sample size to a maximum of 1.0 g. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 ºC in approximately less than 5.5 minutes and remaining at 180 ± 5 ºC for 9.5 minutes for the completion of specific reactions (Ref. 1, 2, 3, 4). After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method.

ANALYSIS OF NIST SRM 2704 (COMPILATION OF REFS. 2 AND 3)[a]
BUFFALO RIVER SEDIMENT

Element	Analyzed (µg/g)	Certified (µg/g)
Arsenic (n=4)	23.4 ± 2.6	23.4 ± 0.8
Cadmium (n=6)	3.5 ± 1.2	3.45 ± 0.22
Chromium (n=6)	132.9 ± 1.3	135 ± 5
Copper (n=6)	98.0 ± 4.2	98.6 ± 5.0
Lead (n=6)	155 ± 9.2	161 ± 17
Mercury (n=4)	1.49 ± 0.14	1.44 ± 0.07
Nickel (n=6)	43.6 ± 3.9	44.1 ± 3.0
Phosphorus (n=4)	1.016 ± 0.016 mg/g	0.998 ± 0.028 mg/g
Selenium (n=4)	1.13 ± 0.9	(1.1)
Sulfur (n=4)	3.56 ± 0.16	-----
Thallium (n=4)	1.15 ± 0.22	1.2 ± 0.2
Uranium (n=4)	2.97 ± 0.04	3.13 ± 0.13
Zinc (n=6)	441.9 ± 0.8	438 ± 12

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Section 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

FUMING OFF HYDROFLUORIC ACID WITH MICROWAVE EVAPORATION SYSTEM (REF 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=4)

Element	Direct (µg/g)	Fumed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9	39.4 ± 0.9	38.4 ± 3.0
Cadmium	21.9 ± 0.7	23.3 ± 1.6	21.8 ± 0.2
Chromium	34.0 ± 3.2	32.4 ± 0.4	(39)
Copper	2902 ± 83	2870 ± 150	2950 ± 130
Lead	5425 ± 251	5502 ± 106	5532 ± 80
Nickel	13.5 ± 1.0	13.5 ± 0.8	14.3 ± 1.0
Silver	36.6 ± 0.5	38.9 ± 1.1	35.3 ± 1.5
Zinc	7007 ± 111	3992 ± 132	6952 ± 91

[a] Direct - Digestion used 9 mL HNO_3 and 3 mL HCl or 9 mL HNO_3, 3 mL HF, and 2 mL HCl
Fumed - Digestion used 9 mL HNO_3 and 3 mL HCl followed by the removal of the HF.
Temperature and pressure conditions are as described in 7.3.6 of the method and similar to Figure 1. The digest solution was fumed in a microwave system under vacuum to ~1 mL and 3 mL HCl added. The digest solution was fumed to ~1 mL and 3 mL HNO_3 was added. The solution was fumed for a final step to ~1 mL and quantitatively transferred and diluted to final volume. Data reported with 95% confidence intervals.

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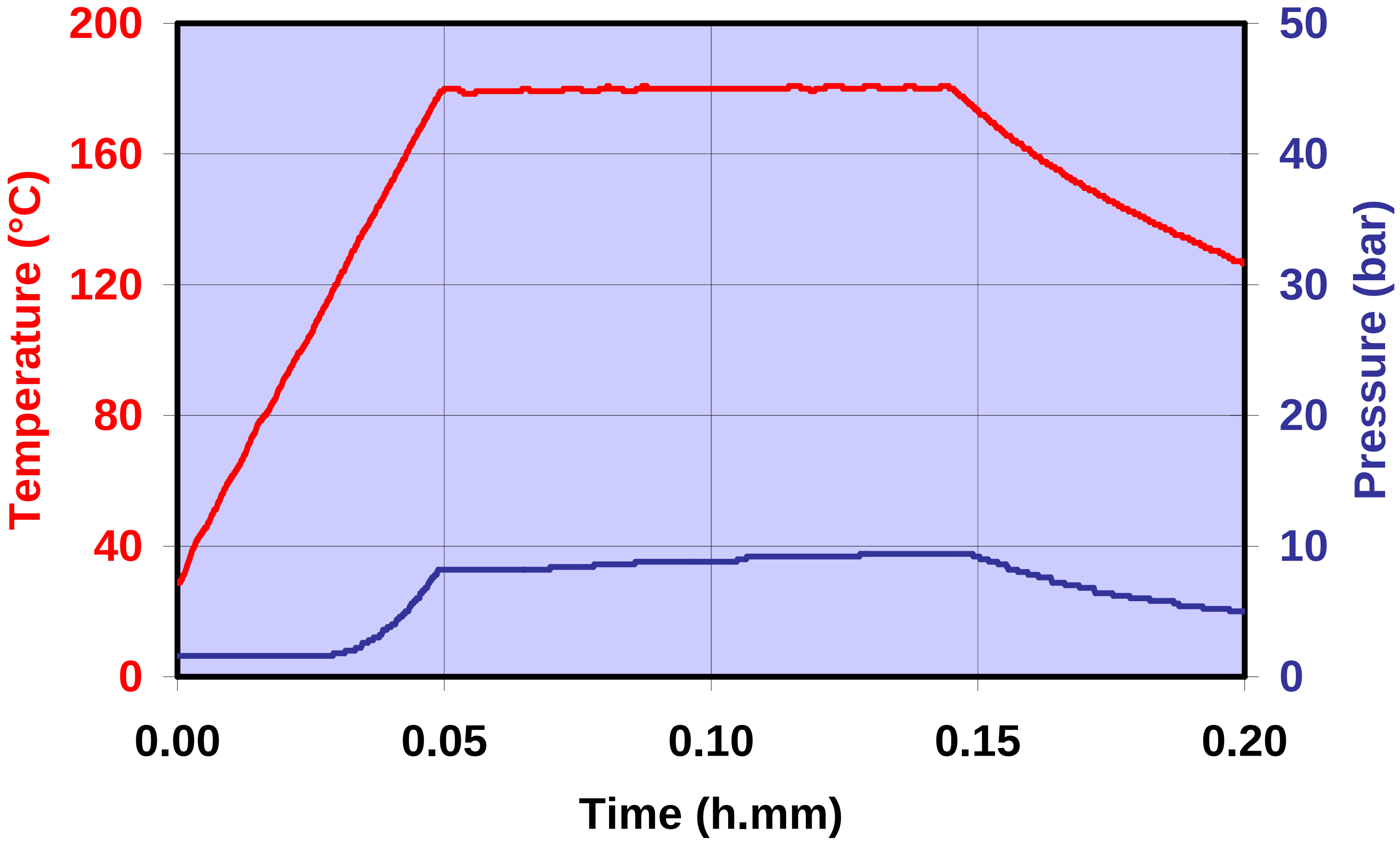
US EPA 3052



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Milestone MULTIPREP-41

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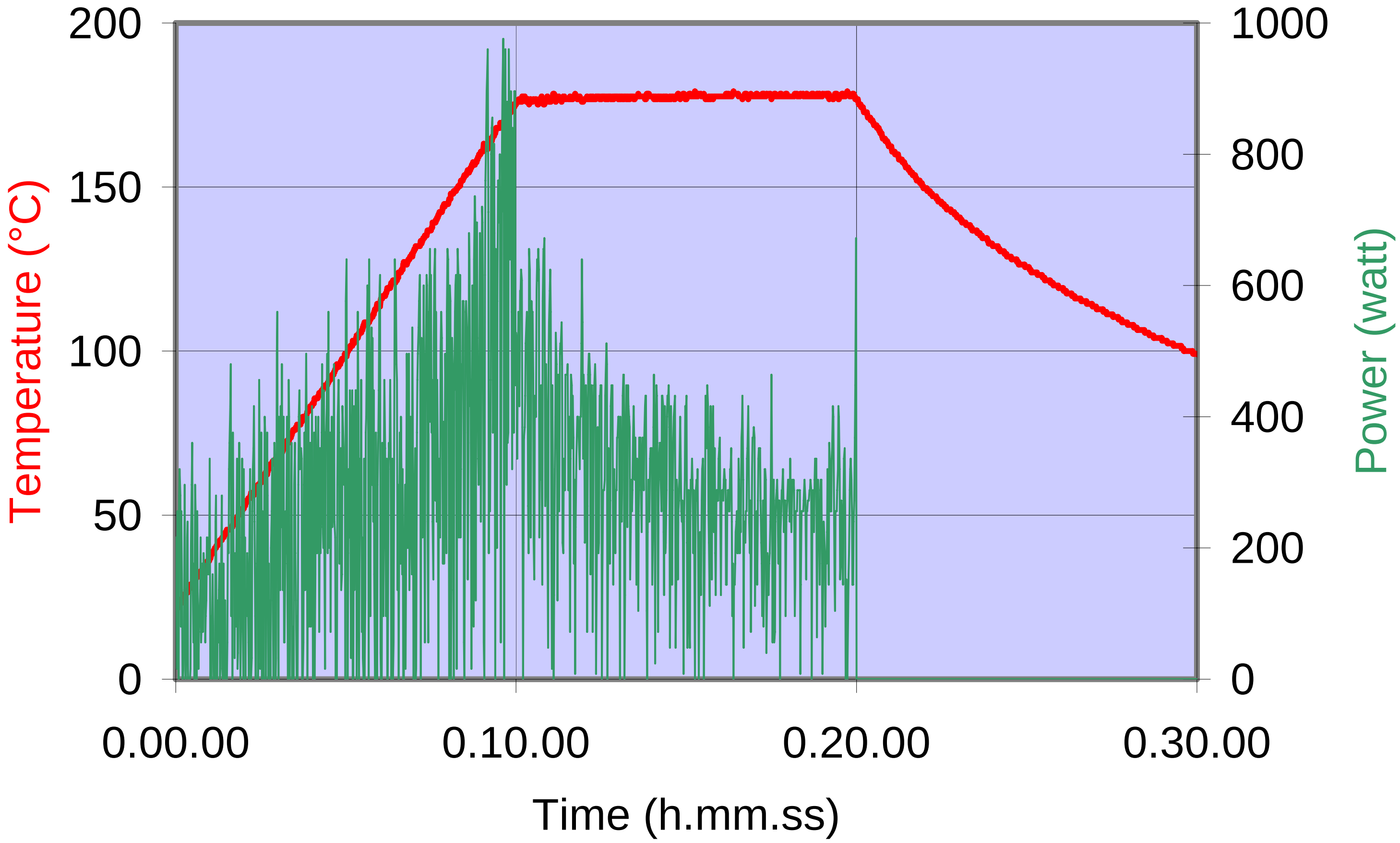
Technical Specifications

Number of vessels	Up to 41
Vessels material	PFA or TFM
Vessels volume	70 ml
Maximum pressure	20 bar
Maximum temperature	200°C

Environmental Samples



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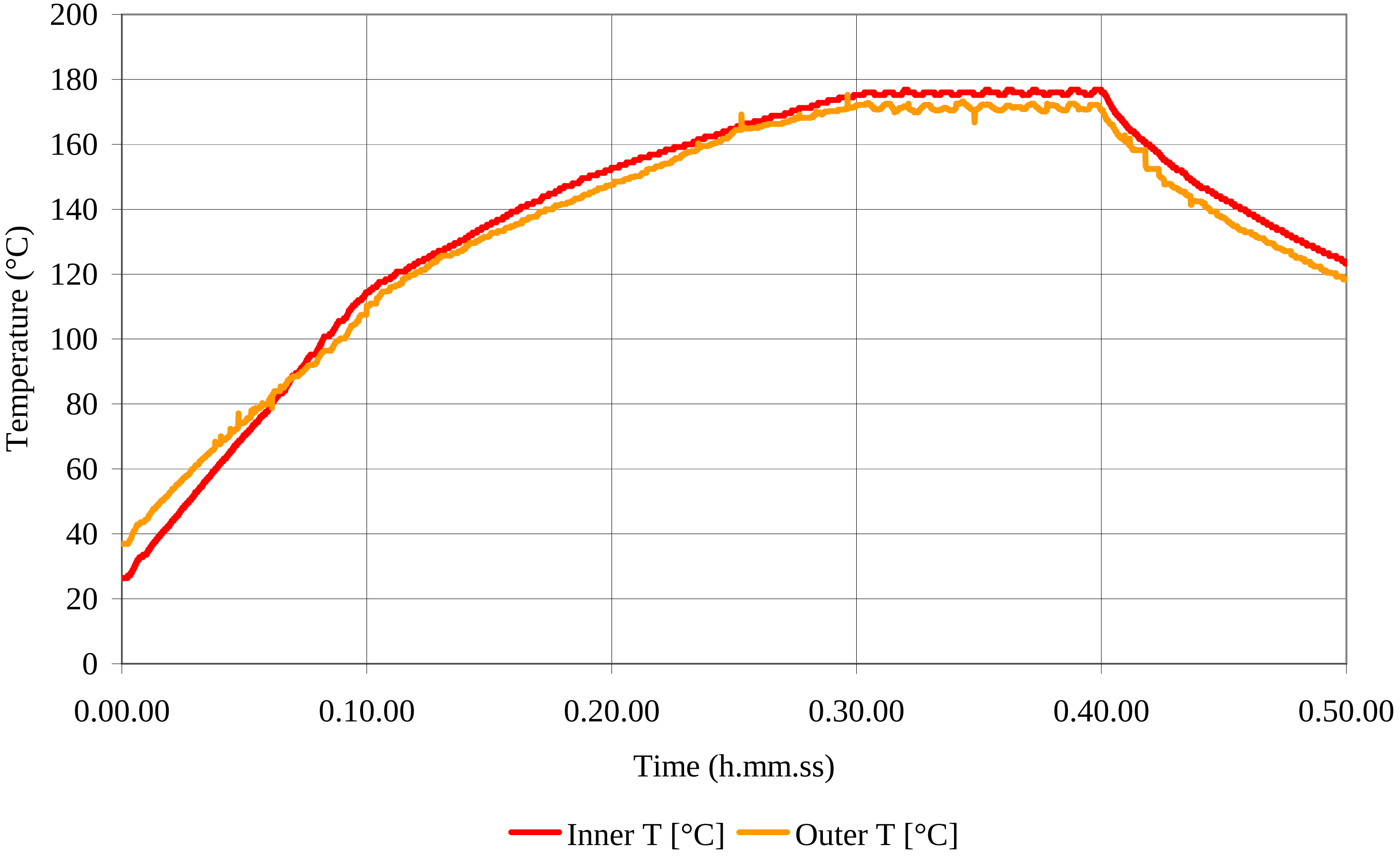
Inner vs. Outer Vessels Temperature



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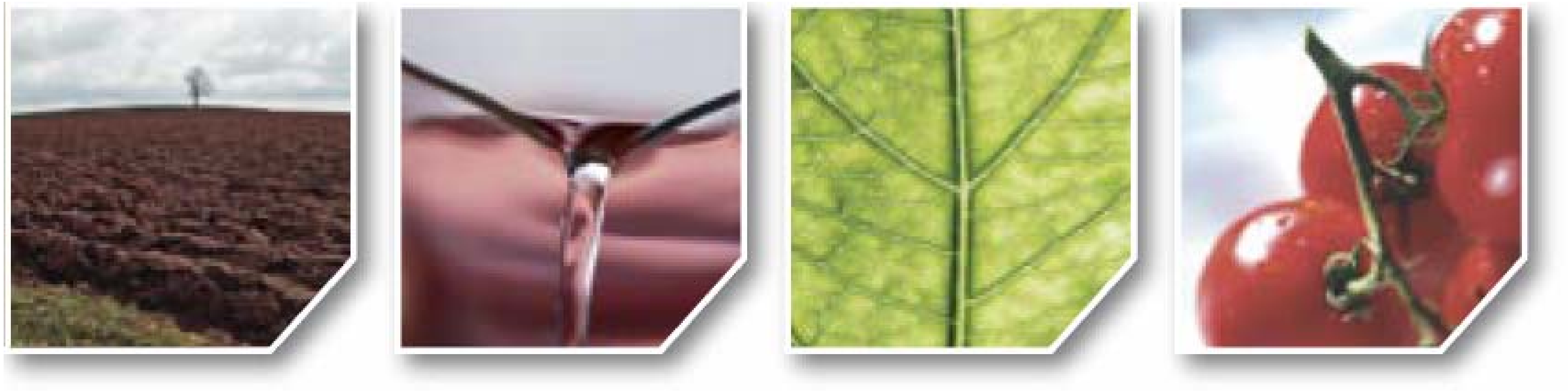
Applications



NIST SRM 2711 Montana Soil

Element	Certified	MULTIPREP-41
Al(1)	6,53 ± 0,09	5,48
As	105 ± 8	108
Cd	41,7 ± 0,25	42,7
Cu	114 ± 2	117
Fe	2,89 ± 0,06	2,84
Hg	6,25 ± 0,19	6,1
Ni	20,6 ± 1,1	21,0
Se	1,52 ± 0,14	1,55
Zn	350,4 ± 4,8	363

All concentrations in µg/kg, except Fe (wt%).

(1) A higher recovery is expected with the addition of HCl.

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NIST SRM 1573a Tomato Leaves

Element	Certified	MULTIPREP-41
Al	598 ± 12	640
As	0,112 ± 0,006	0,102
Cd	1,52 ± 0,04	1,42
Cr	1,99 ± 0,06	1,98
Cu	4,7 ± 0,14	4,82
Mn	246 ± 8	253
Ni	1,59 ±0,07	1,57
Zn	30,9 ± 0,7	32,2
All concentrations in mg/kg.		

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