GUIDELINES FOR MICROWAVE ACID DIGESTION

INTRODUCTION TO THE REAGENTS MOST COMMONLY USED IN MICROWAVE DIGESTION

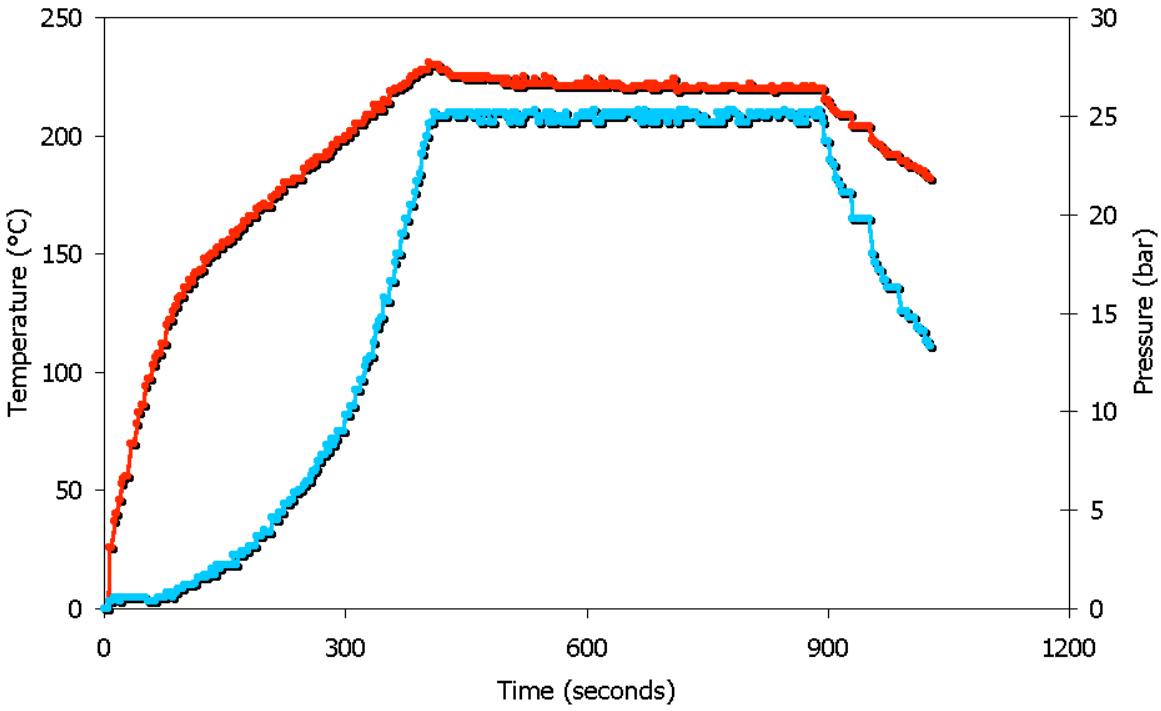
The acids used in microwave digestion may be classified in two main groups:

- non-oxidizing acids, such as hydrochloric acid, hydrofluoric acid, phosphoric acid, diluted sulfuric acid and diluted perchloric acid;
- oxidizing acids, such as nitric acid, hot concentrated perchloric acid, concentrated sulfuric acid and hydrogen peroxide.

NITRIC ACID

Nitric acid has the following properties:

- boiling point is 120°C at 65% concentration;
- poor oxidizing strength at concentrations less than 2M; oxidizing strength increases with concentration and reaction temperature;
- most common acid for oxidation of organic matrices with this typical reaction: $(CH_2)_X + 2HNO_3 \rightarrow CO_2(g) + 2NO + 2H_2O$;
- it dissolves most metals forming soluble nitrates, exceptions are Au and Pt (non oxidized) and Al, B, Cr, Ti and Zr (passivated);
- these metals require acid mixtures or diluted nitric acid;
- often mixed with H_2O_2, HCl and H_2SO_4;
- available in high purity for trace level analysis.



The above graphic represents the temperature and pressure profile of nitric acid up on microwave heating. Notice that pressure has been controlled at 25bar, resulting in a temperature of 225°C.

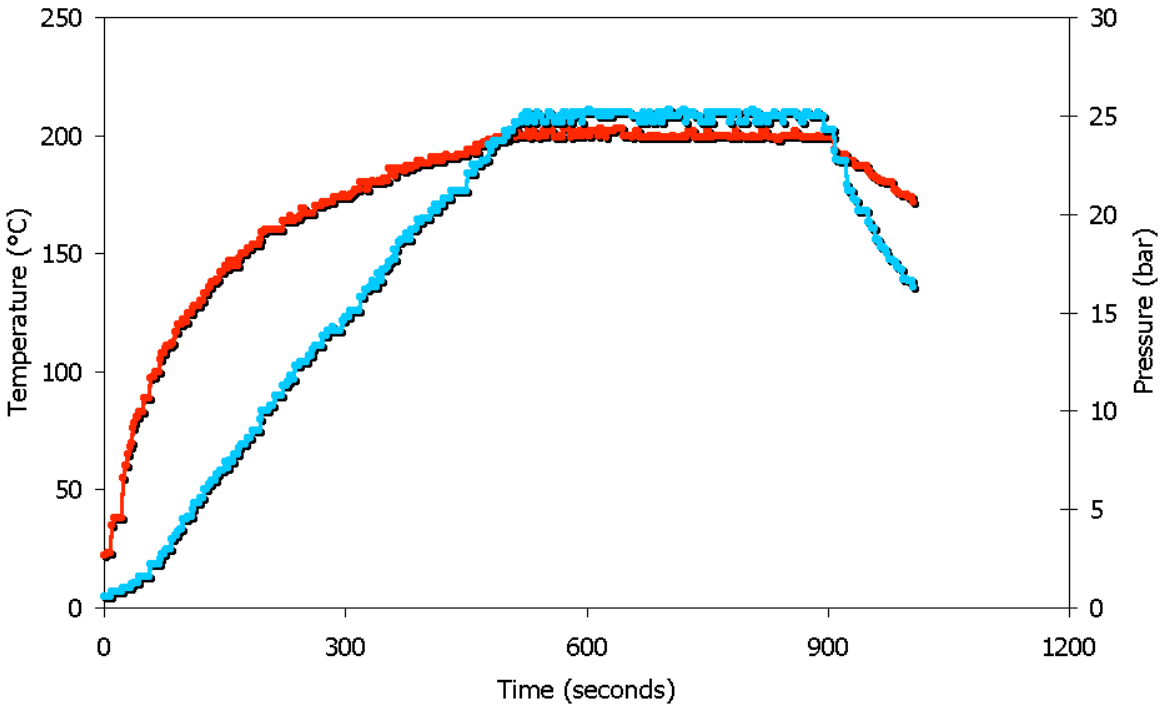
HYDROGEN PEROXIDE

Hydrogen peroxide is an oxidizing agent ($2H_2O_2 \rightarrow 2H_2O + O_2$); added to nitric acid it reduces the nitrous vapors and it accelerates the digestion of organic samples by raising the temperature.
A typical mixture ratio is HNO_3:H_2O_2= 4:1 (volume/volume).

HYDROCHLORIC ACID

Hydrochloric acid has the following properties:

- boiling point of azeotropic mixture with H_2O with 20,4% HCl is 110°C;
- available with 38% concentration;
- it dissolves salts of weak acids (carbonates, phosphates) and most metals are soluble with the exception of AgCl, HgCl and TiCl;
- excess of HCl improves the solubility of AgCl, converted into $AgCl_2^-$;
- strong complex nature;
- widely used for iron-based alloys because of its ability to hold large amounts of chloro-complex in solution;
- other complexes formed are Ag (I), Au (II), Hg (II), Ga (III), Tl (III), Sn (IV), Fe (II) and Fe (III);
- it does not dissolve oxides of Al, Be, Cr, Ti, Zr, Sn and Sb; sulphates of Ba and Pb, group II fluorides, SiO_2, TiO_2 and ZrO_2.



The graphic above represents the temperature and pressure profile of hydrochloric acid up on microwave heating.
Notice that pressure has been controlled at 25bar, resulting in a temperature of 205°C.

HYDROFLUORIC ACID

Hydrochloric acid has the following properties:

ACID DIGESTION

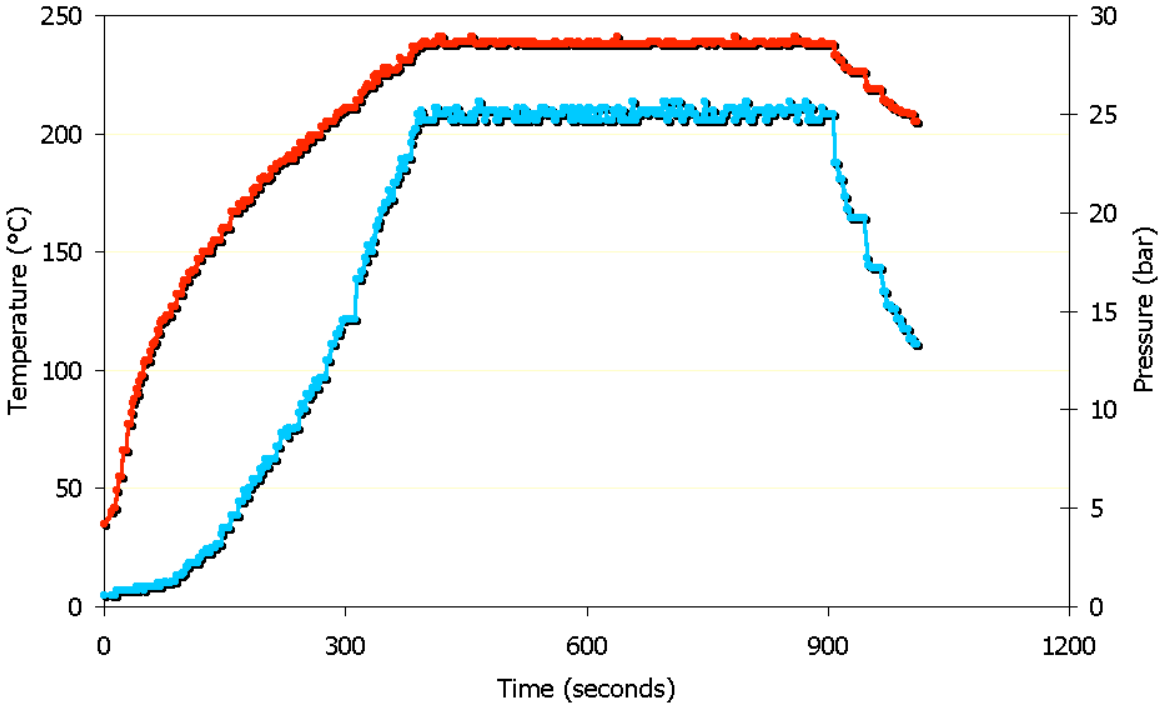
- Boiling point is 108°C at 40% concentration;
- non-oxidizing, strong complex nature;
- used in digestion of minerals, ores, soils, rocks and even vegetables containing silicates;
- major use is the decomposition of silicates according with this reaction: $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$;
- often used in combination with HNO_3 or $HClO_4$.

EVAPORATION/CONCENTRATION

- Following dissolution, many analyses require removal of HF to prevent equipment damage or to resolubilize insoluble fluorides;
- many analytes such as As, B, Se, Sb, Hg and Cr may volatilize.

COMPLEXATION

- Alternative approach to remove HF from the solution, by addition of Boric acid;
- the following reactions take place: $H_3BO_3 + 3HF \rightarrow HBF_3(OH) + 2H_2O$ and $HBF_3(OH) + HF \rightarrow HBF_3 +$ H2O;
- 10-50 times excess Boric acid enhances reaction rate.

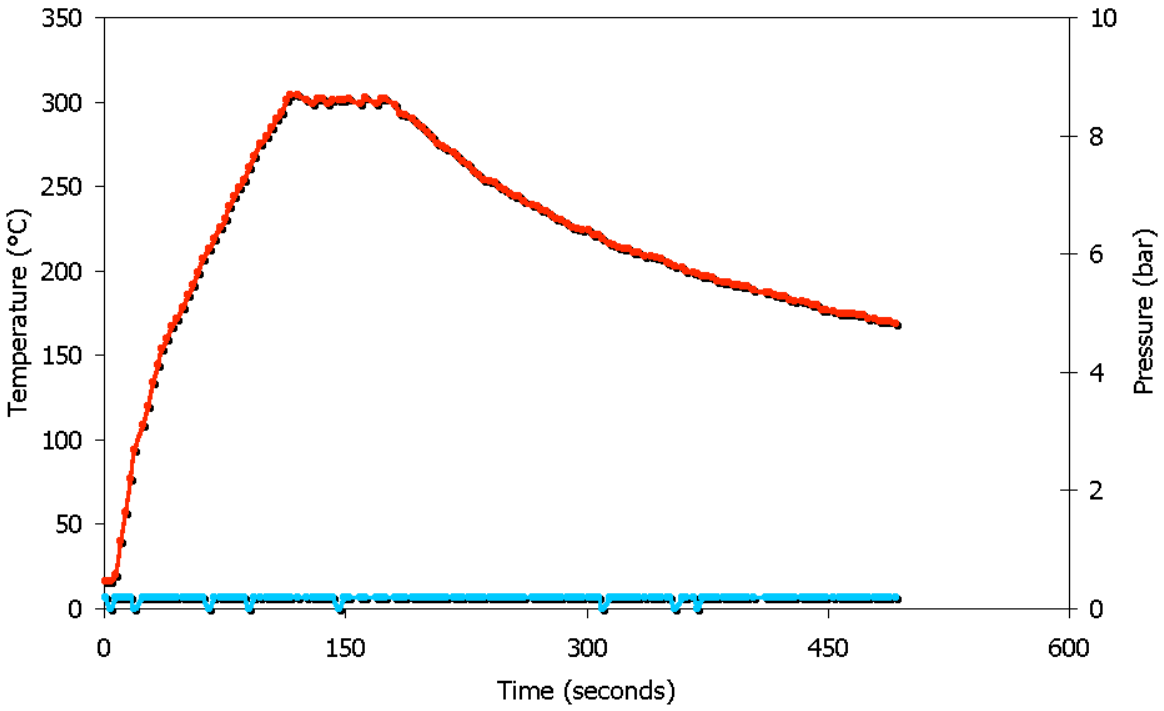


The above graphic represents the temperature and pressure profile of hydrofluoric acid up on microwave heating. Notice that pressure has been controlled at 25bar, resulting in a temperature of 240°C.

SULFURIC ACID

Sulfuric acid has the following properties:

- boiling point is 340°C at 98% concentration, exceeding the maximum working temperature of TFM Teflon vessels;
- careful reaction monitoring is required to prevent vessel damages;
- it destroys organics by dehydrating action;
- many sulfates are insoluble (Ba, Sr, Pb).



The above graphic represents the temperature and pressure profile of sulfuric acid up on microwave heating.
Notice that temperature has been controlled at 300°C (for 1 minute only), without any pressure increase.
It is clear that the use of concentrated sulfuric acid in the MDR rotors poses significant problems because of its high boiling point.
300°C are critical for TFM Teflon vessels and simply too high for PFA Teflon vessels (they melt down at such temperature).
It is therefore advisable to use sulfuric acid only with a strict temperature control.

PERCHLORIC ACID

Perchloric acid has the following properties:

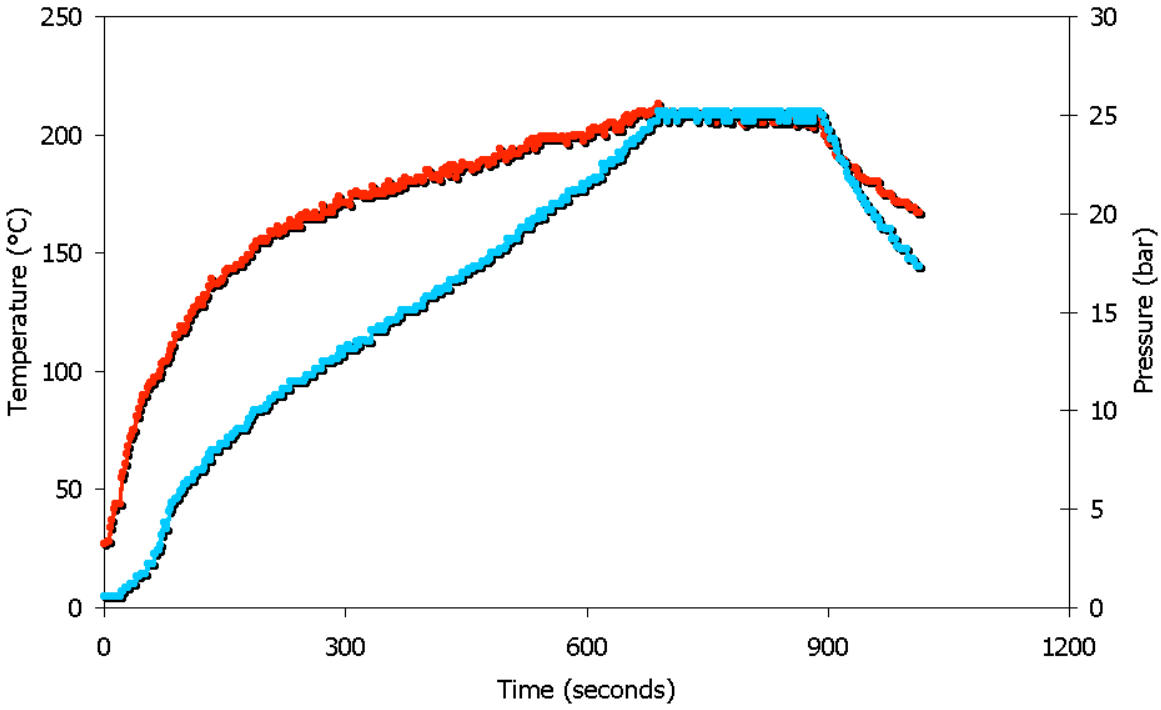
- boiling point is 203°C at 72% concentration;
- hot and concentrated is the strongest oxidizing acid;
- rapid, sometimes explosive, reaction with organic matrices;
- often mixed with nitric acid for a controllable digestion of organic matrices;
- all perchlorate are soluble with the exception of $KClO_4$;
- perchloric acid decomposes at 245°C in a closed microwave vessel, developing gaseous by-products and a tremendous excess pressure.

WARNING
Special care has to be taken when the use of perchloric acid is required.
Do not use at all perchloric acid with organic samples.
It may be possible to use perchloric acid with inorganic samples when the temperature does not exceed 200°C and when the amount of perchloric acid is below 20% (volume/volume) of the total solution volume.

AQUA REGIA

Aqua regia properties are the following:

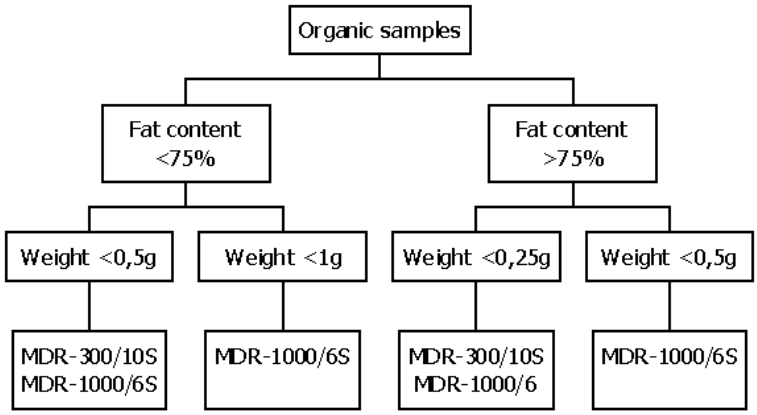
- made up by hydrochloric acid and nitric acid in a 3:1 (volume/volume) mixture;
- it produces NOCl (nitrosyl chloride), which decomposes in NO and Cl_2 up on heating;
- it dissolves precious metals;
- it must be freshly prepared and used immediately, otherwise it evolves chlorine gas overpressurizing and venting the vessel



The above graphic represents the temperature and pressure profile of aqua regia up on microwave heating. Notice that pressure has been controlled at 25bar, resulting in a temperature of 200°C.

MICROWAVE ACID DIGESTION OF ORGANIC SAMPLES

Organic samples group includes food, feed, tissues, botanicals, biological etc.
Nitric acid is the most common oxidizing agent used to digest organic samples, according to the following reaction: ORG + HNO_3 -> NO_X + CO_2 + H_2O.
Metals are converted into soluble nitrates, available for analysis.
When operating the ETHOS with ATC-400CE Automatic Temperature Control device, set the digestion temperature at 140°C or higher for samples rich in carbohydrates (wheat, sugar etc.), at 150°C or higher for samples rich in proteins (serum, albumin etc.) and at 170°C or higher for fatty samples (cheese, butter, vegetable oil etc.).
Those temperature represent minimum target digestion temperature for the above matrices.
The sample amount directly influence the pressure generated inside the vessel, as sample is decomposed into CO_2 gas.
Therefore some limitation in regards to the sample amount may apply.
Follow the scheme below.



Note that the above sample amounts do refer to organic matter.
Therefore the moisture content of the sample should not be considered (for instance, if a sample contains about 80% of moisture, up to 5 gram could be digested).
When operating the ETHOS without ATC-400CE Automatic Temperature Control, follow the basic programs recommended by Milestone.
Microwave power and heating time strictly depend on the number of samples being prepared simultaneously.
To organic samples 4-8mL of nitric acid (depending on sample amount) should be added, as well as 1-2mL of hydrogen peroxide.

BASIC PROGRAM FOR 3 SAMPLES

Step	Time (minutes)	Power (Watt)
1	5	250
2	3	600
3	2	300

BASIC PROGRAM FOR 6 SAMPLES

Step	Time (minutes)	Power (Watt)
1	5	250
2	5	500
3	5	650

BASIC PROGRAM FOR 12 SAMPLES

Step	Time (minutes)	Power (Watt)
1	8	250
2	8	500
3	8	750

MICROWAVE ACID DIGESTION OF ENVIRONMENTAL SAMPLES

A number of microwave digestion methods for environmental samples have been approved by the US EPA (Environmental Protection Agency).

- US EPA 3015 SW-846 Update II
  Microwave assisted acid digestion of aqueous samples
- US EPA 3051 SW-846 Update II
  Microwave assisted acid digestion of sediments, slugs, soils and oils
- US EPA 3052 SW-846 Update III
  Microwave assisted acid digestion of siliceous and organically based matrices

A brief explanation of the methods is given here; more detailed information are available from your Milestone local supplier up on request.

US EPA METHOD 3015

- Sample amount 45mL.
- Reagents 2,5mL HNO_3 and 2,5mL HCl when analyzing the solution with FLAA or ICP, 5mL HNO_3 only when analyzing the solution with FLAA, GFAA, ICP or ICP-MS.
- Microwave digestion time 20 minutes.
- Temperature to reach 160°C within 10 minutes and to remain between 165-170°C for other 10 minutes.

US EPA METHOD 3051

- Sample amount 0,5g.
- Reagent 10mL HNO_3.
- Acid leaching method.
- Microwave digestion time 10 minutes.
- Temperature to reach 170°C within 5,5 minutes and to remain between 170-180°C for the balance of 10 minutes.

US EPA METHOD 3052

- Sample amount up to 1,0g.
- Basic reagents 9mL HNO_3 and 3mL HF.
- Alternative combinations include HCl (for Erg, BA, SB, Fe and Al determination), H_2O_2 (for organic samples) and H_2O (to slow down exothermal reaction).
- Goal is total sample decomposition.
- Microwave digestion time 15 minutes.
- Temperature to reach 180°C within 5 minutes and to remain between 175-185°C for 10 minutes.

MICROWAVE ACID DIGESTION OF INORGANIC SAMPLES

Inorganic samples group includes metals, alloys, oxides, ores, rocks, slags, ceramics etc.

CHEMISTRY

Sample preparation procedures are strongly dependent on the chemical nature of the material to be digested and on the elements to be determined.
The microwave acid(s) choice is often the same as used with “conventional” methods.

MICROWAVE PROGRAM

Most inorganic samples show non-exothermal reactions and do not produce large amount of gases.
The sample amount does not affect the ratio temperature/pressure as much as with organic samples.
The digestion efficiency strongly depends on the digestion temperature; therefore the target is to bring the solution to the highest temperature in the shortest time (first step) and to hold this temperature until the digestion is complete (second step).
For difficult samples, requiring temperatures higher than 200°C, a high pressure rotor MDR-1000/6S should be used, while for easier samples, requiring temperature below 200°C, a medium pressure rotor MPR-300/12S is enough.
As a matter of fact, when samples such as sand (1g) are to be digested with 4mL HF and 1mL HNO_3, a suitable program would be:

Step	Time (minutes)	Power (Watt)
1	10	650
2	10	350

The above program refers to the simultaneous digestion of 6 samples.
A library of nearly 400 sample preparation methods is available from your local Milestone distributor.