

Microwave Sample Preparation for AA and ICP

Milestone Srl



Closed Vessel Acid Digestion

Microwave Sample Preparation
for AA and ICP



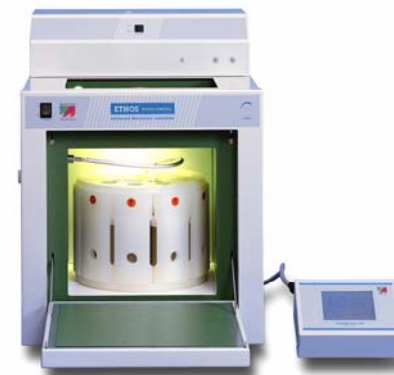
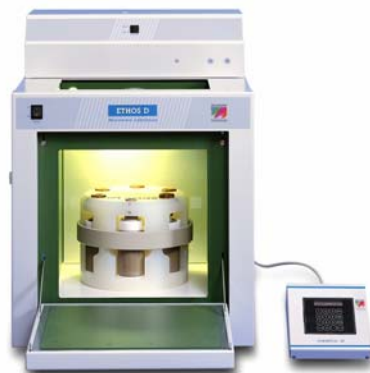
Microwave Instrumentation

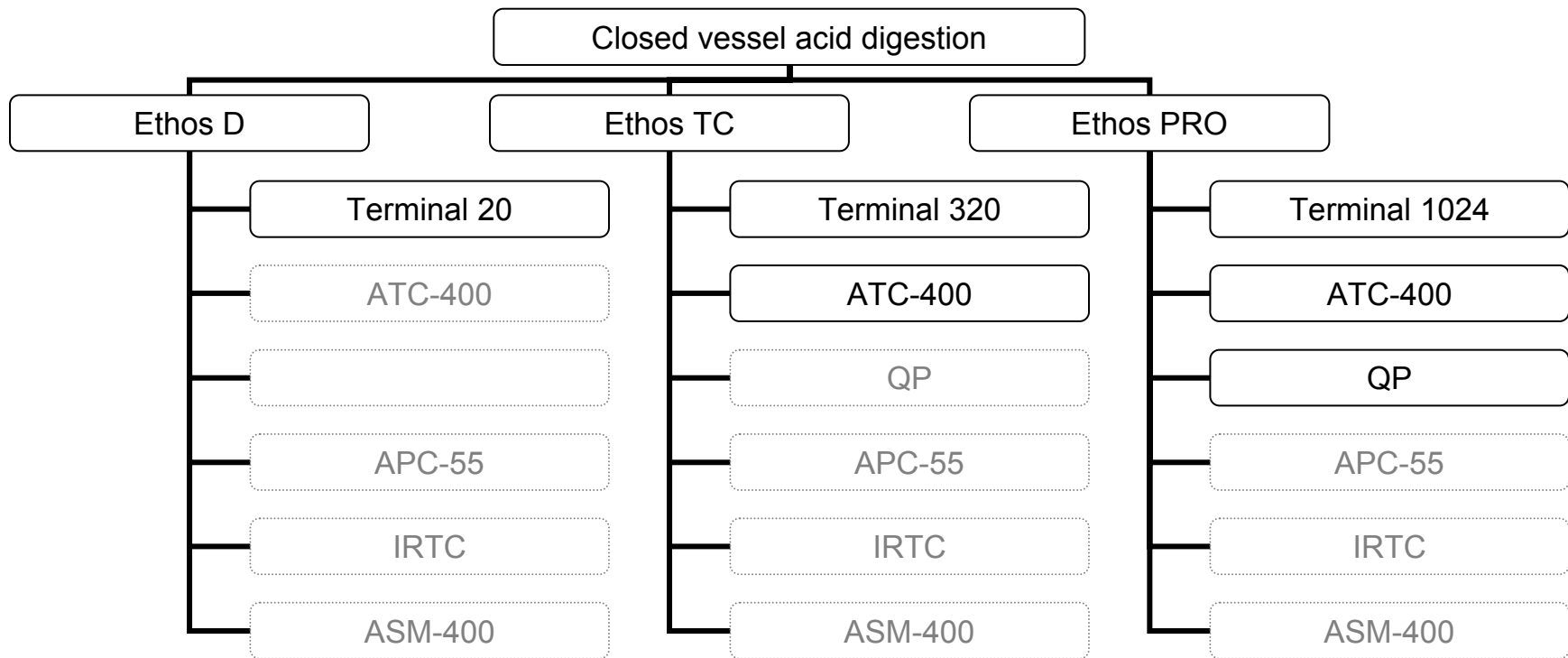
- Microwave oven
- Microwave control system
- Reaction monitoring and control
- Pressure vessels



Milestone Microwave Systems

- One microwave platform
- Three different controllers to fit customer needs
 - Ethos D
 - Ethos TC
 - Ethos PRO

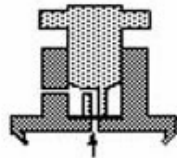




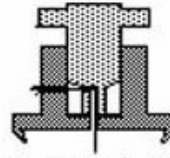
Terminal 1024 Software



Vessel Technology

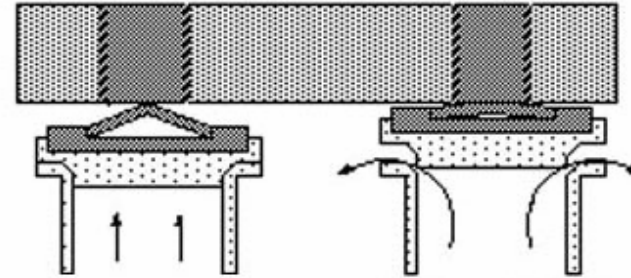


Normal Operating Conditions
Internal Pressure < Burst Disk Strength



Over-Pressurization Condition
Burst Disk Breaks and Excess
Pressure Vents

©"Laboratory Microwave Safety", Kingston, H.M.; Walter, P.J.; Engelhart, W.G.; and Parsons, P.J., Chapter 16 In Microwave-Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications, Kingston, H.M. and S.J. Haswell, Eds.; American Chemical Society: Washington, D.C., 1997: 697-745.



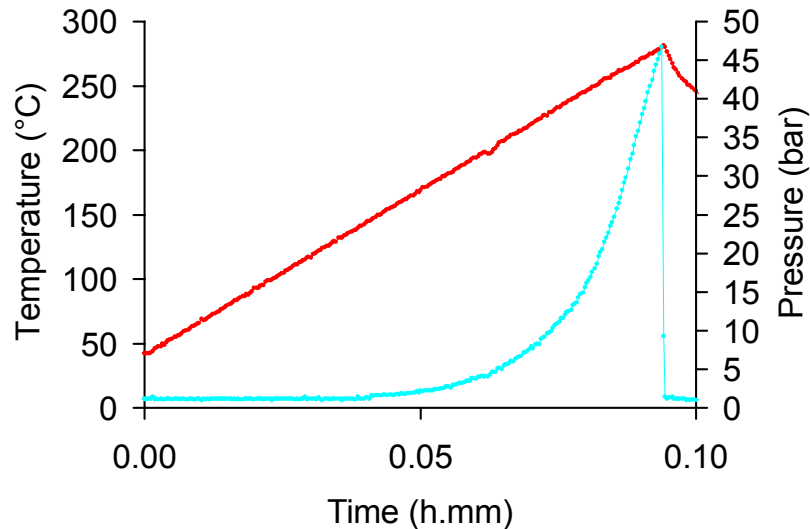
Normal Operating Conditions
Internal Pressure < Force on Cap

Over-Pressurization Condition
Internal Pressure > Force on Cap
Excess Pressure Vents and Reseals Once
Internal Pressure < Force on Cap

©"Laboratory Microwave Safety", Kingston, H.M.; Walter, P.J.; Engelhart, W.G.; and Parsons, P.J., Chapter 16 In Microwave-Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications, Kingston, H.M. and S.J. Haswell, Eds.; American Chemical Society: Washington, D.C., 1997: 697-745.



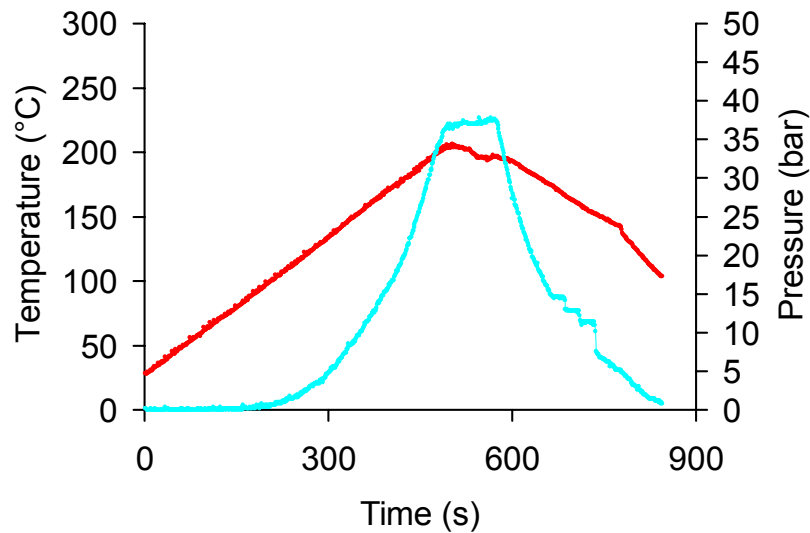
Vessel Technology



- Non re-closing type safety devices
 - Pressure relief device designed to remain open after operation (rupture disks and membranes)
- Limitations
 - The vessel content is expelled and lost for analysis
 - Gas removal rate must be equal or greater than gas or vapor generation
 - Vessel pressure is “transferred” to the microwave cavity

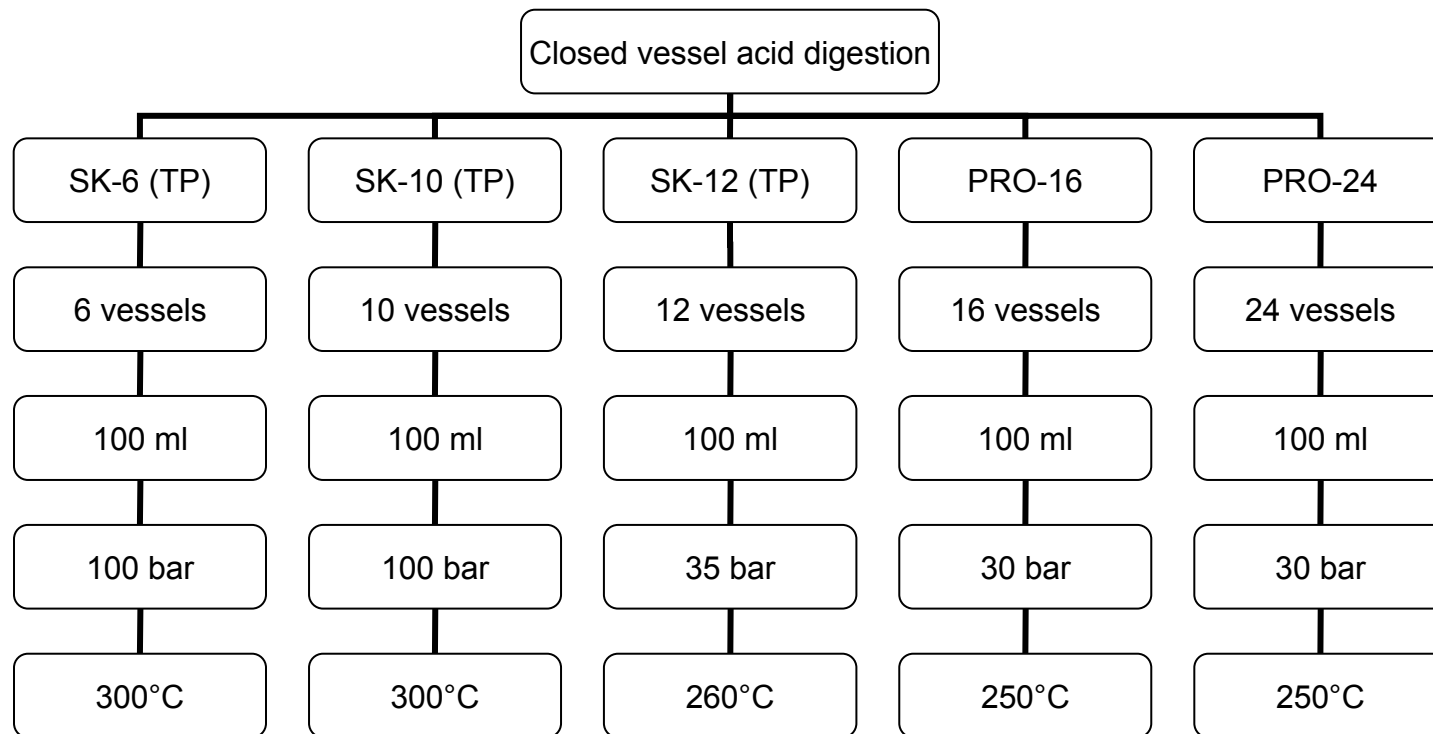


Vessel Technology



- Re-closing type devices
 - Self re-closing pressure relief valve by a safety spring instead of burst discs or membranes
 - Only the excess pressure is released from the vessel

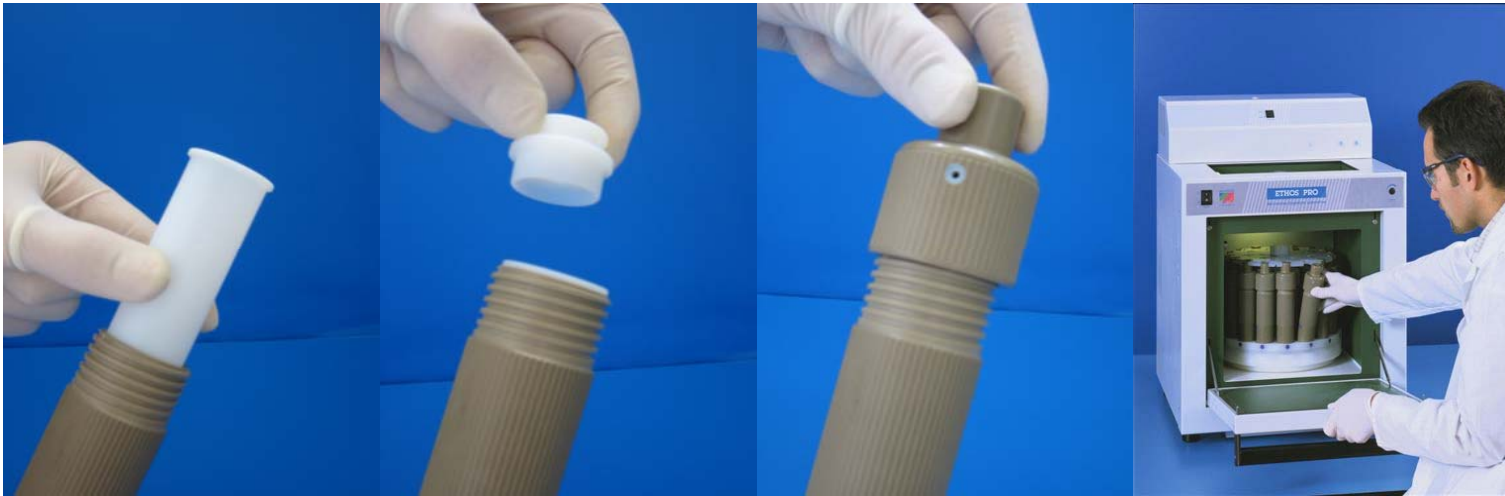




PRO-16/PRO-24 Vessels



Easy Handling



Applications

Microwave Sample Preparation for AA and ICP



Recommended Literature

- “Introduction to Microwave Sample Preparation”
H.M. Kingston, Ed., ACS Professional Reference Book, Washington, DC, 1988
- “Microwave Enhanced Chemistry”
H.M. Kingston and Stephen Haswell, Ed., ACS Professional Reference Book, Washington, DC, 1997



Environmental Samples



- Soil, sediment, sludge, fly-ash, wastewater etc.

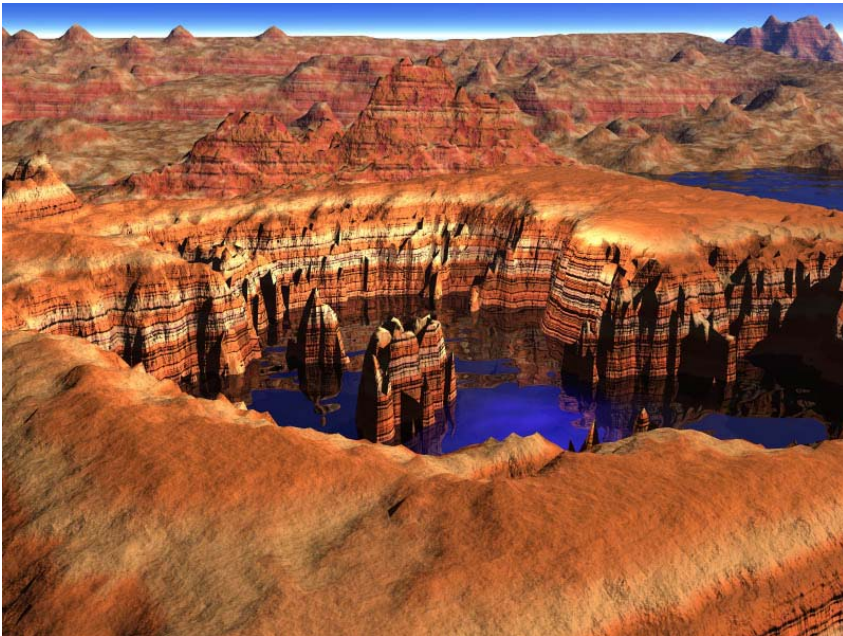




- US-EPA 3015 SW-846 Update II
Microwave-assisted acid digestion of aqueous samples and extracts
- US-EPA 3051 SW-846 Update II
Microwave-assisted acid digestion of sediments, sludges, soils and oils
- US-EPA 3052 SW-846 Update III
Microwave-assisted acid digestion of siliceous and organically based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



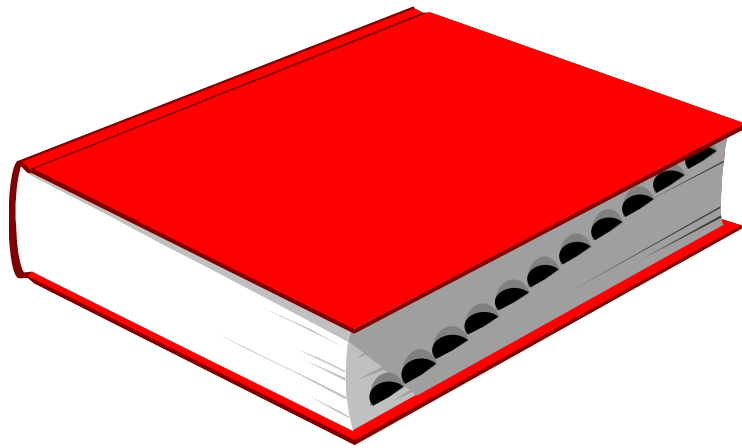
Inorganic Samples



- Metals, alloys, oxides, ores, rocks, slag, ceramics etc.



Our Experience at Your Service



- A library of nearly 400 sample preparation methods is available from Milestone



Organic Samples



- Food, feed, tissues, botanicals, biological samples etc.



Nitric Acid

- Nitric acid is the most common oxidizing agent used to digest organic samples, according to the following reaction



- Metals are converted into soluble nitrates, available for analysis



Target Digestion Temperature of Biological Samples

- Based on sample decomposition with HNO_3
 - 180°C for high fat samples (cheese, butter, vegetable oil etc.)
 - 160°C for high protein samples (bovine, serum, albumin)
 - 140°C for high carbohydrate samples (wheat, sugar etc.)



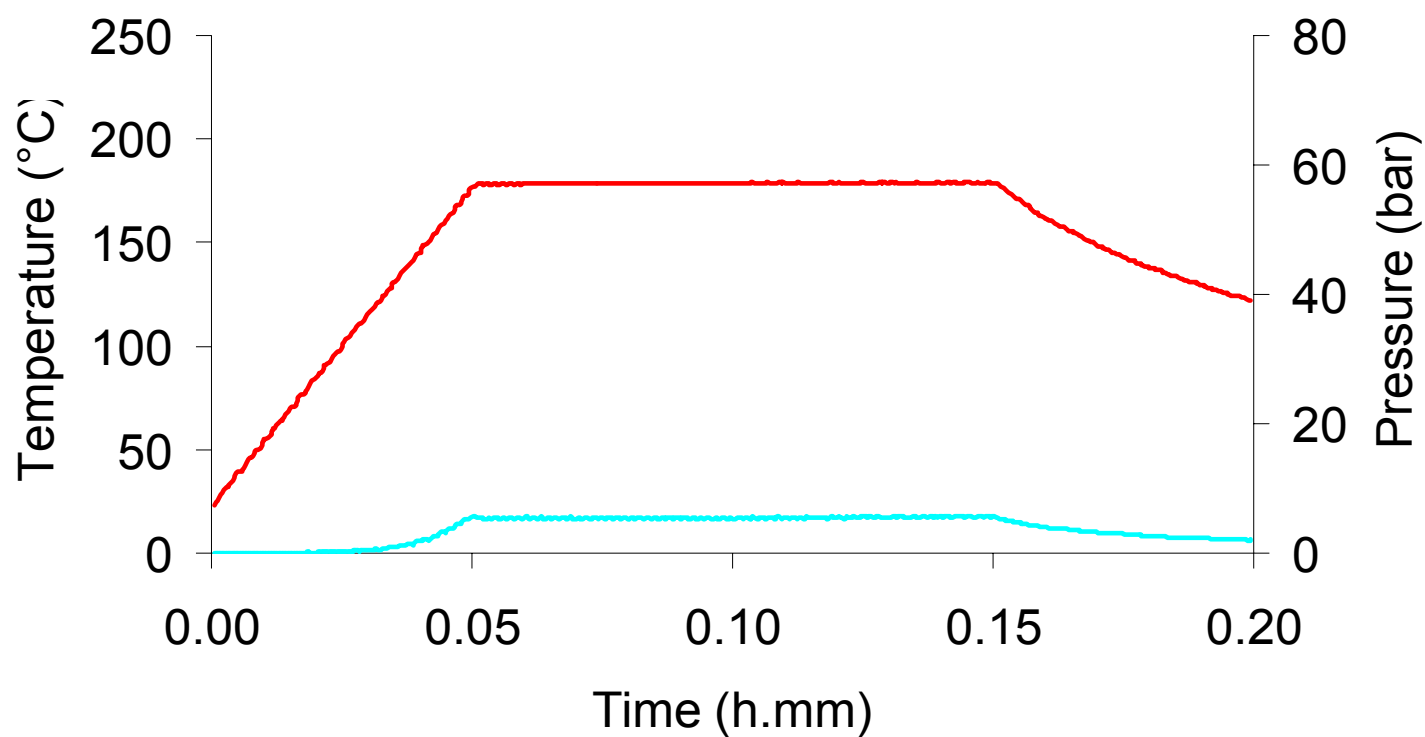
Pressure during Microwave Digestion

- Temperature is key
- Pressure is mean
- Microwave heating raises acid temperature and vapor pressure
- Gaseous products (CO_2 and NO_x) are formed from sample decomposition



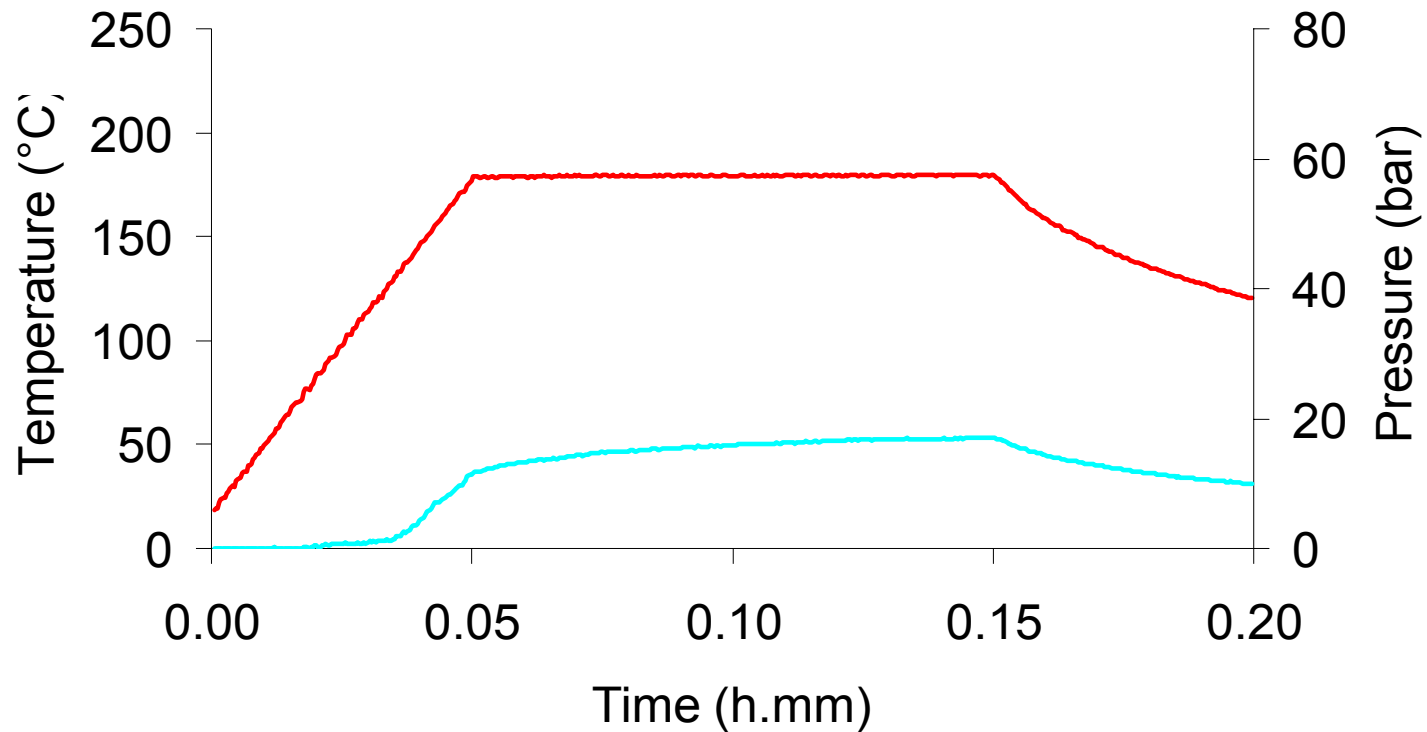
Nitric Acid Vapor Pressure

10 ml HNO₃



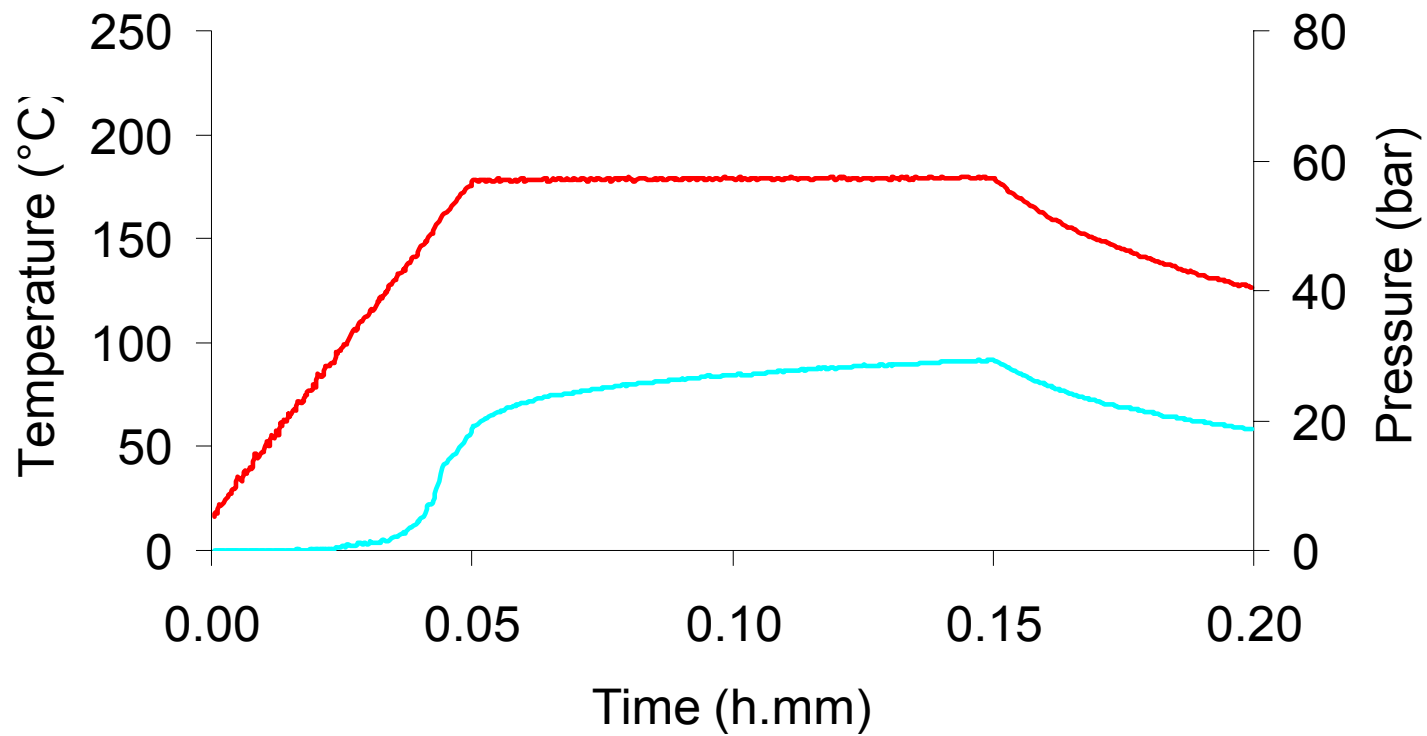
0,25 g Organic Sample

0,25 g BCR 185 Bovine Liver with 10 ml HNO₃



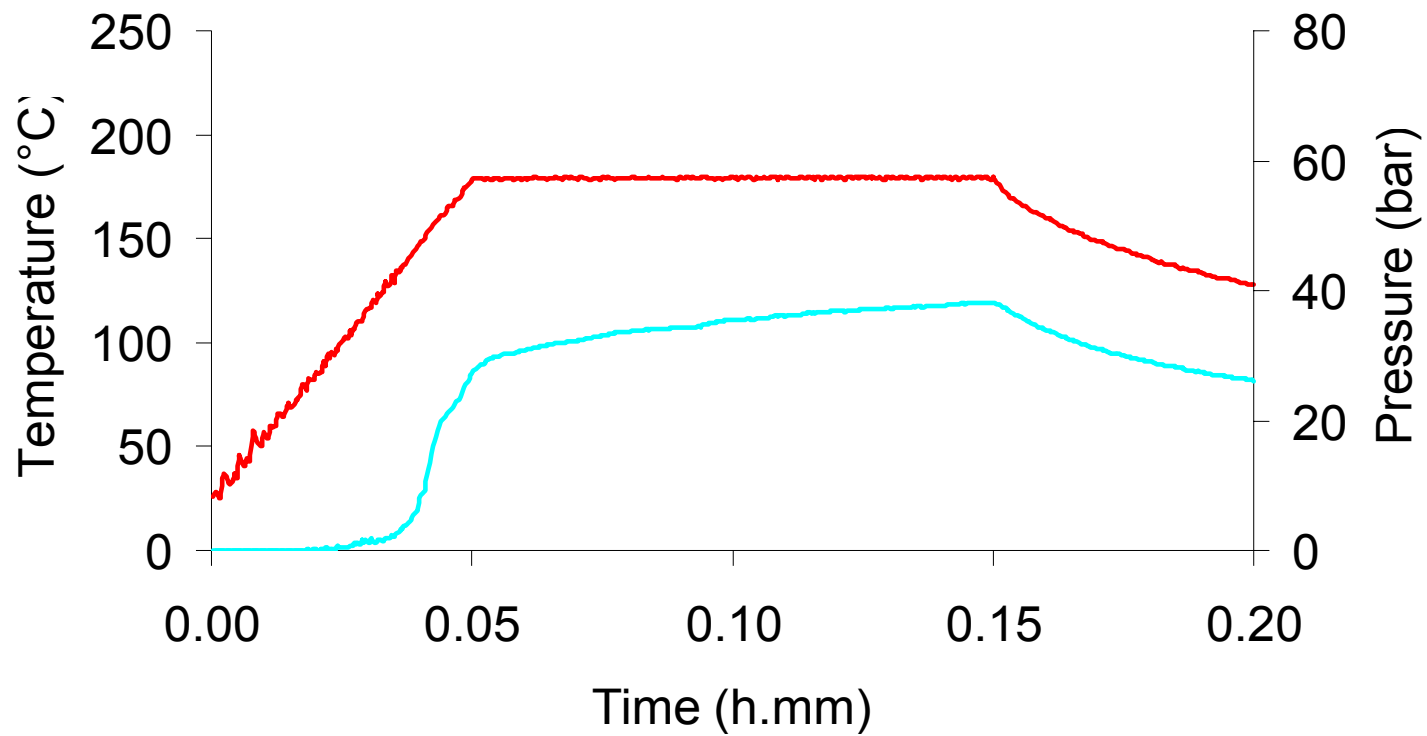
0,50 g Organic Sample

0,50 g BCR 185 Bovine Liver with 10 ml HNO₃



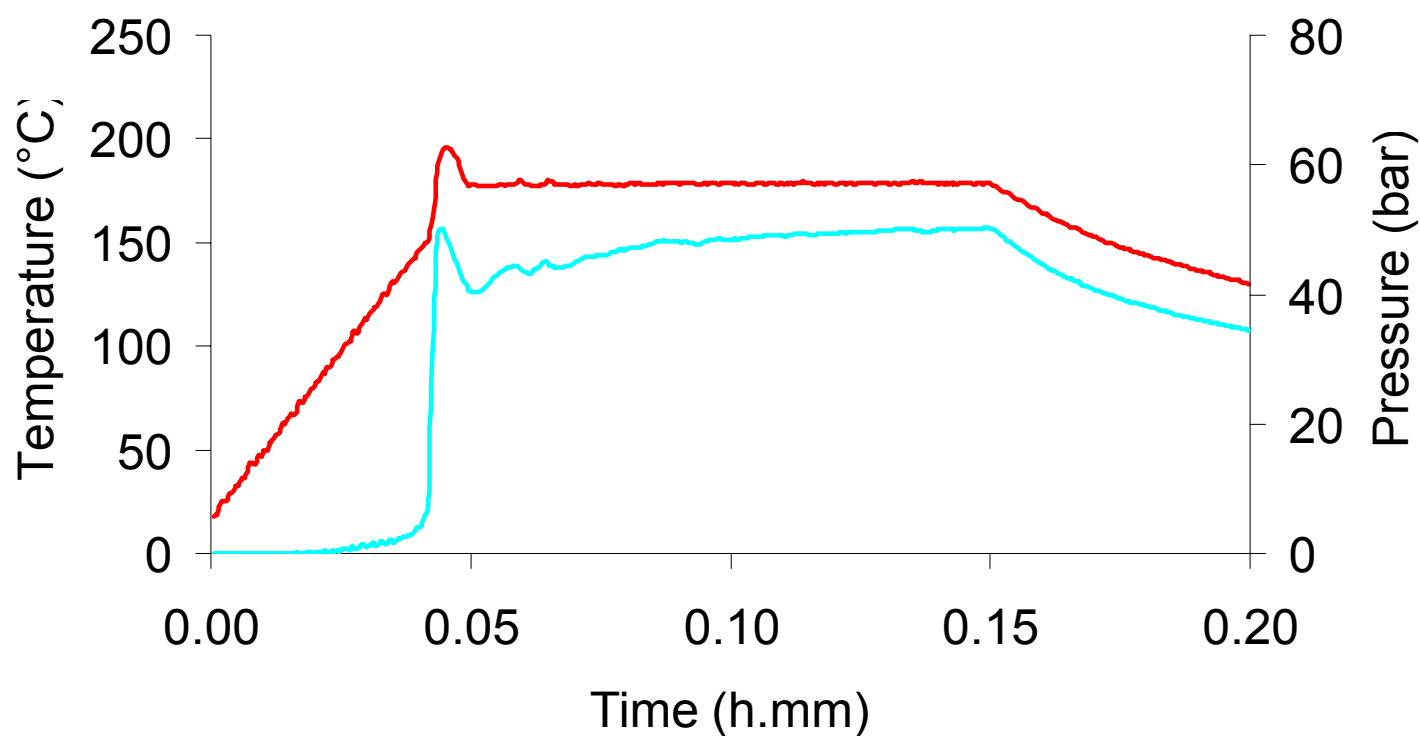
0,75 g Organic Sample

0,75 g BCR 185 Bovine Liver with 10 ml HNO₃



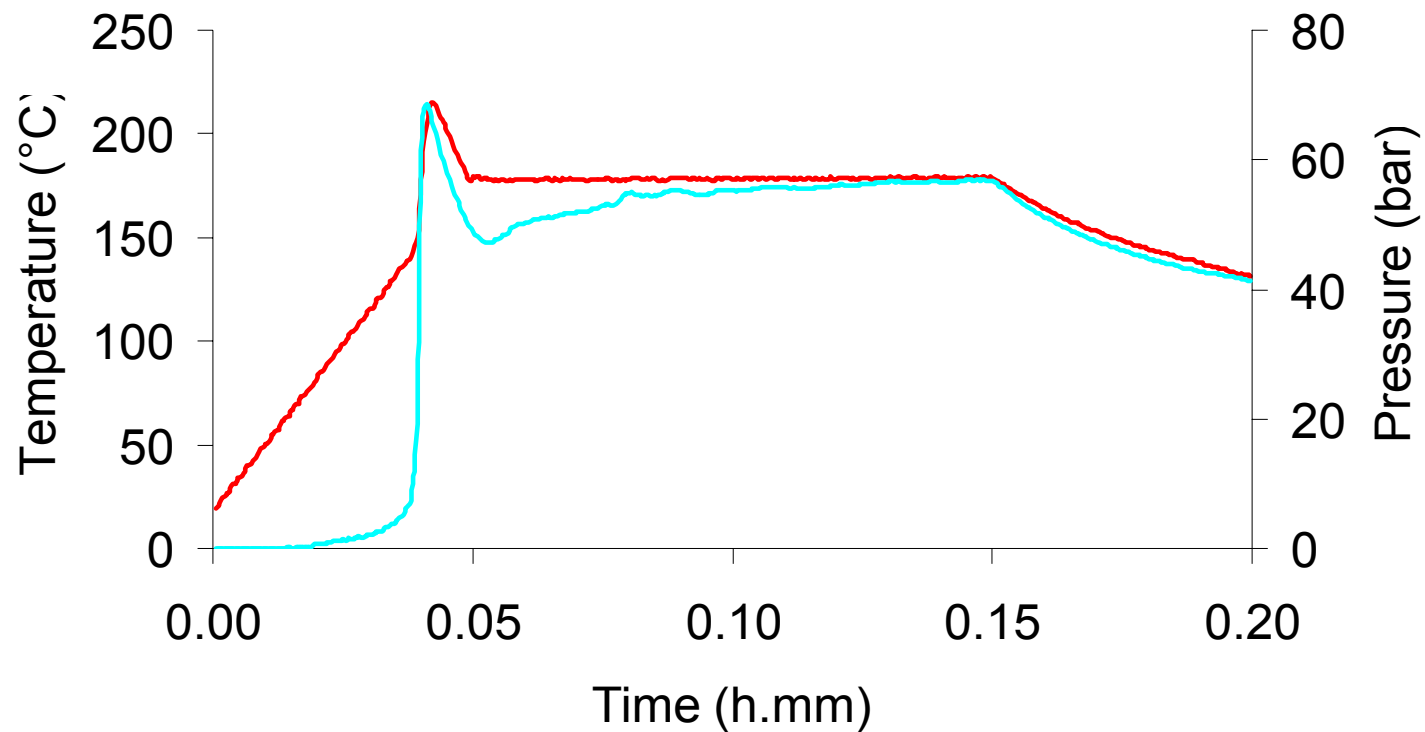
1,00 g Organic Sample

1,00 g BCR 185 Bovine Liver with 10 ml HNO₃

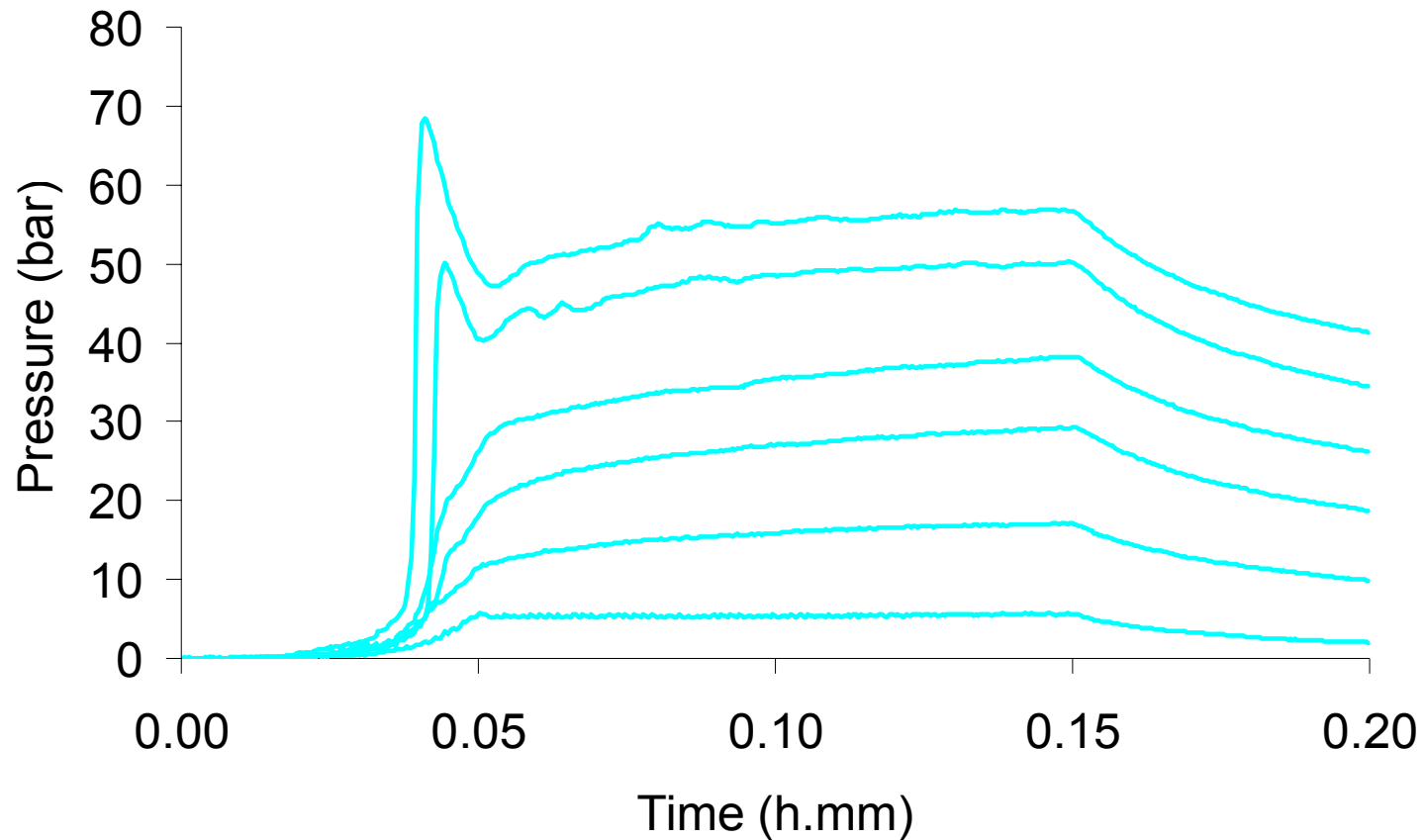


1,25 g Organic Sample

1,25 g BCR 185 Bovine Liver with 10 ml HNO₃



Sample Weight Effect on Decomposition Pressure



Effect of Sample Amount

- Higher pressure conditions
- More exothermic reactions
- Vessel and microwave system have to be capable of withstand or handle such over-pressurization
- Vessel design and materials are key factors for safe microwave digestions



Ethos MOD

Microwave Open Digestion

Milestone Srl



Sample Size

- Many applications require the digestion of the largest possible sample mass
 - Larger samples provide increased sensitivity to extend detection limit
 - Larger samples are more representative aliquot of a large sample bulk
 - Plastics, polymers, inorganic and organic chemicals, food and feed, pharmaceuticals, composites, photo-resist and other semiconductor compounds, resins, wastes and other highly reactive compounds
 - Sample size represents the main limitation of the closed vessel microwave digestion technology



Ethos MOD 320



Ethos MOD 1024



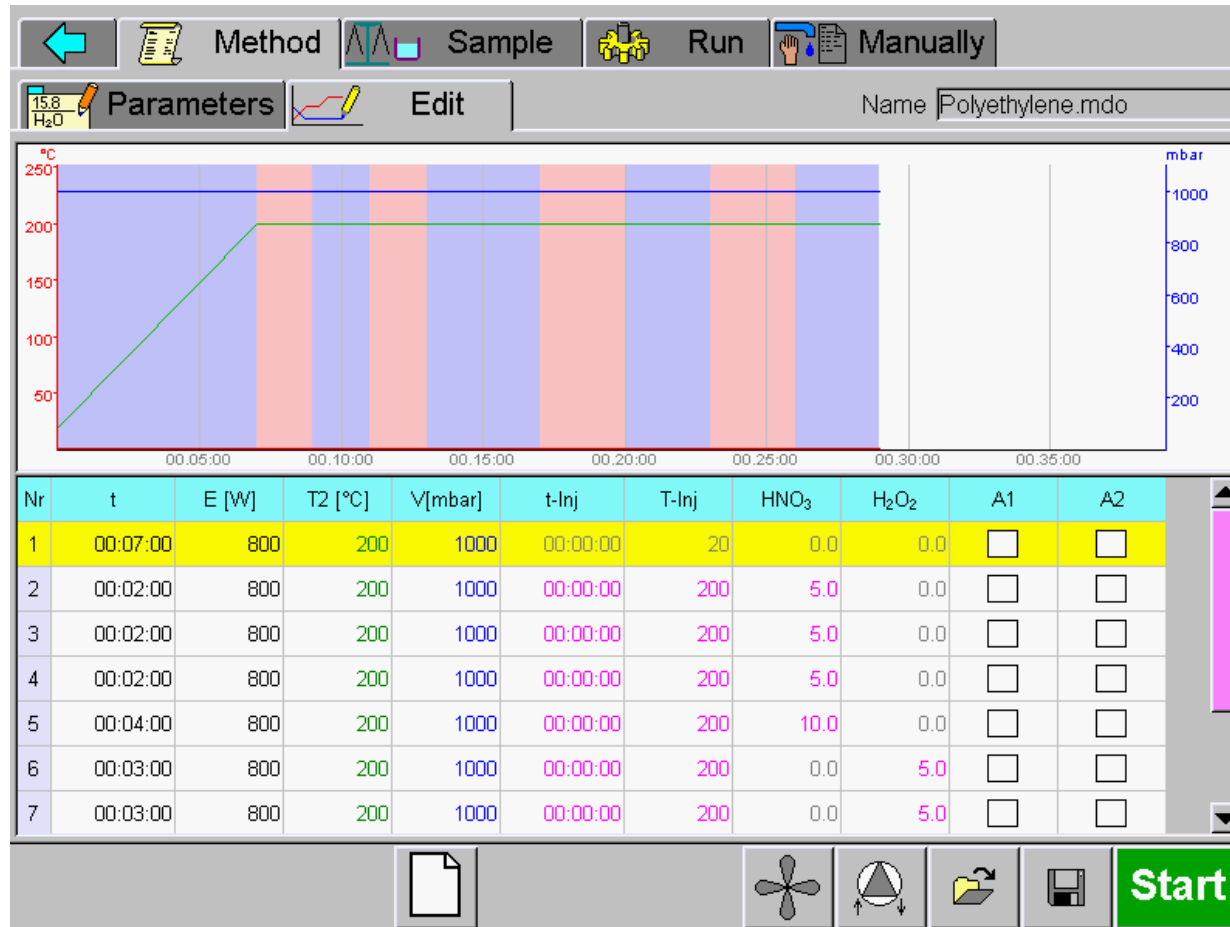
Ethos MOD 320/1024



- Terminal 320/1024
 - Full procedure control, including automatic acids dosing
- Glass door
 - Easy viewing of all vessels during digestion
- Infrared sensor
 - Non-contact temperature control in all vessels
- Automatic vacuum control
 - Digestion procedure optimization



Open Vessel Digestion Editing with Automatic Dosing



MOD-8 Rotor



- Simultaneous open vessel digestion of up to 8 samples
- Glass bottle with 200 ml volume for large sample amount
- Individual connections to exhaust line
- Separate individual connections to dosing system
- Entirely made of inert plastic material (PTFE and PP)



Metrohm Dosing System (plus Interface Kit)



- Metrohm dosing system
 - N. 1 Liquino 711
 - N. 2 Dosino 700 complete with 50 ml burette cylinder
- Controlled and operated by 320/1024 terminal software
- Interface Kit
 - RS-232 connecting cable
 - Tubing connection



VAC-4000 Vacuum System



- Provides exhaust and neutralization of acid vapors
- Four operating steps
 - Water-cooled PTFE condenser (over 90% recovery HNO_3 and other low boiling acids)
 - PFA Teflon collecting bottle
 - Sodium Hydroxide neutralizing solution
 - Acid resistant all-PTFE vacuum pump with maximum vacuum 20 mbar, flow rate of 40 l/minute



Ethos Flexibility

Closed to open vessel digestion

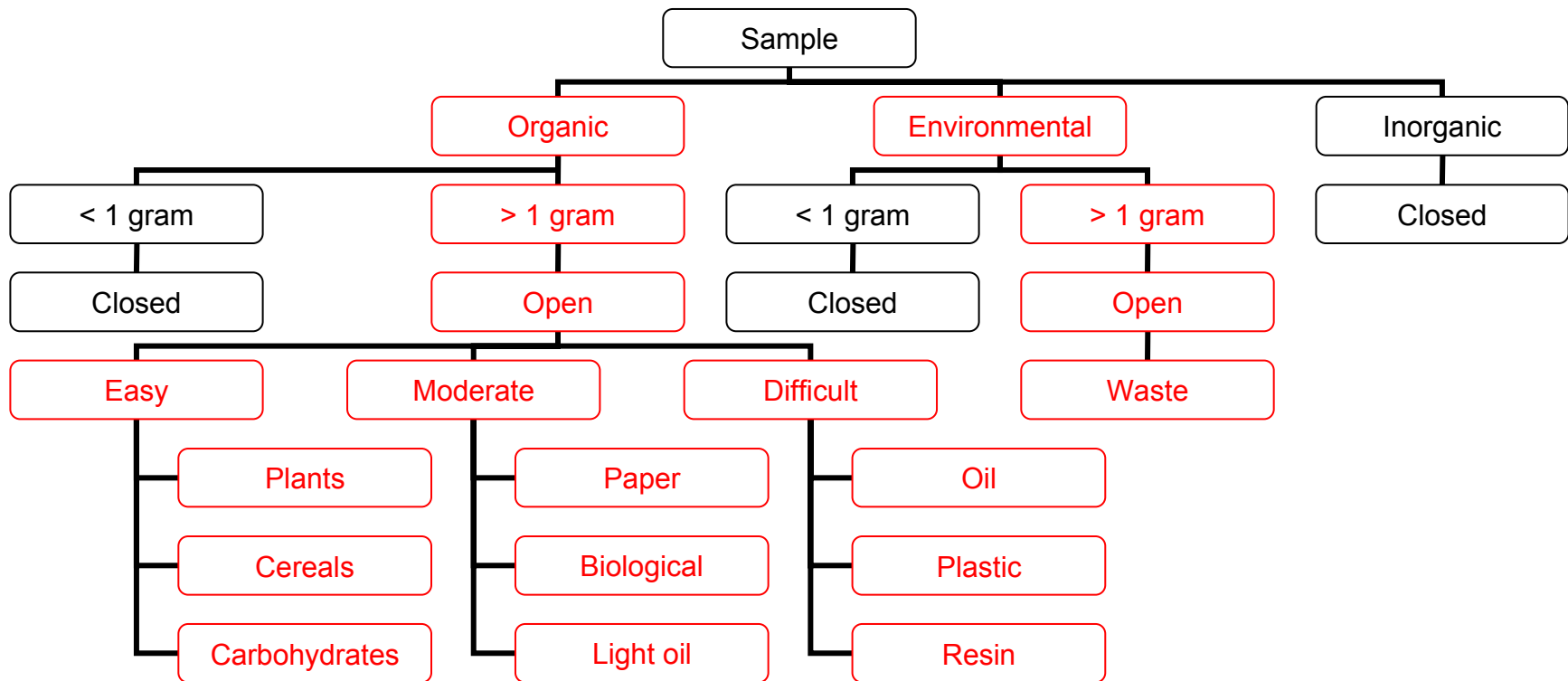
- Ethos TC → Ethos MOD 320
 - Add...
 - IRT infrared temperature control
 - AVC-2000 automatic vacuum control
 - MOD-8/VAC-1000/Metrohm system
- Ethos PRO → Ethos MOD 1024
 - Add...
 - IRT infrared temperature control
 - AVC-2000 automatic vacuum control
 - MOD-8/VAC-1000/Metrohm system

Open to closed vessel digestion

- Ethos MOD 320 → Ethos TC
 - Add...
 - ATC-400 automatic temperature control
 - SK-6T/SK-10T/SK-12T
- Ethos MOD 1024 → Ethos PRO
 - Add...
 - ATC-400 automatic temperature control
 - SK-6T/SK-10T/SK-12T



Method Development Guidelines



Method Development Notes

- H_2SO_4
 - Used for moderate and difficult samples to shorten digestion time
 - Usually added only once at beginning of digestion
 - Use less possible volume
- HNO_3
 - Widely used for all organic samples
 - Starting reagent for easy samples
 - Added at high temperature for moderate and difficult samples
- H_2O_2
 - Added at the end of digestion to clarify the solution
 - Foaming is reduced by using small volumes and slow additions



Method Development Notes

Step			
1	2	3	4
Carbonization/ Charring	Oxidation	Evaporation (if required)	Acid re-treatment (if required)
Acids			
HNO ₃ and/or H ₂ SO ₄	Dosing of HNO ₃ and/or H ₂ O ₂		
Notes			
Homogeneous black residue/solution	Clear/Yellowish solution	Small amount of acid left	Clear solution

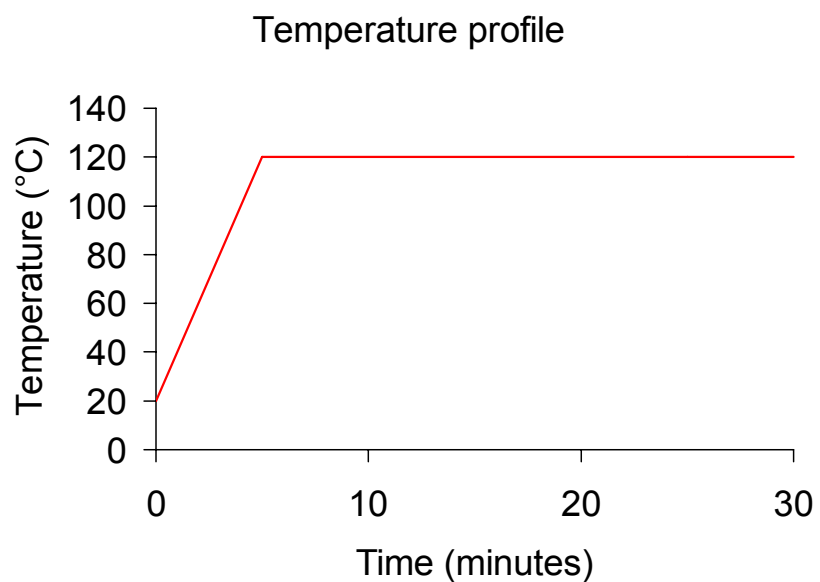


Applications

- Food and feed
- Plastics, polymers, resins, inorganic and organic chemicals
- Pharmaceuticals
- Photo-resist and other semiconductor compounds
- Wastes and other highly reactive environmental compounds



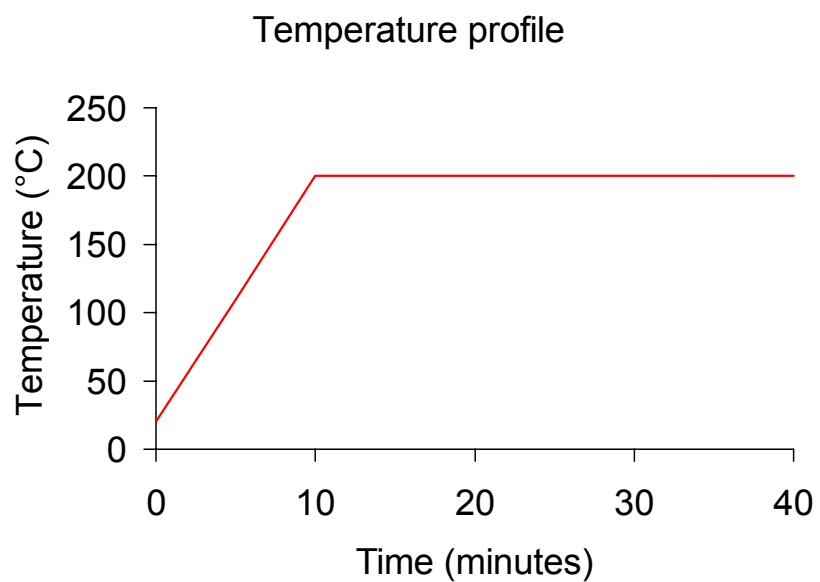
Easy Samples



Acids addition			
Time (minutes)	T (°C)	Acid	Volume (ml)
0	20	HNO ₃	20
5	120	HNO ₃	10
10	120	HNO ₃	10
15	120	HNO ₃	10
20	120	H ₂ O ₂	5
25	120	H ₂ O ₂	5
30	120	H ₂ O ₂	5



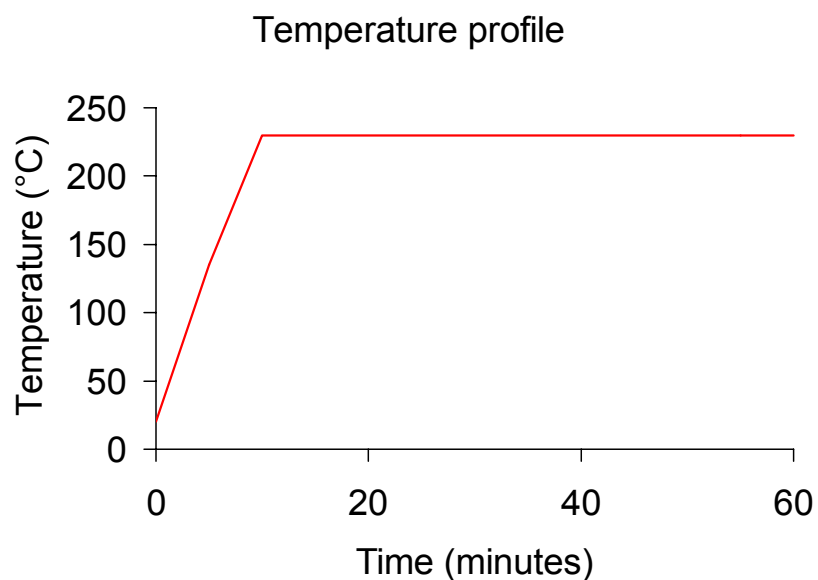
Moderate Samples



Acids addition			
Time (minutes)	T (°C)	Acid	Volume (ml)
0	20	H ₂ SO ₄	10
5	120	HNO ₃	10
10	200	HNO ₃	10
20	200	HNO ₃	10
30	200	H ₂ O ₂	5
35	200	H ₂ O ₂	5
40	200	H ₂ O ₂	5



Difficult Samples



Acids addition			
Time (minutes)	T (°C)	Acid	Volume (ml)
0	20	H ₂ SO ₄	10
5	120	HNO ₃	10
10	240	HNO ₃	10
20	240	HNO ₃	10
30	240	HNO ₃	10
40	240	HNO ₃	10
50	240	H ₂ O ₂	5
55	240	H ₂ O ₂	5
60	240	H ₂ O ₂	5



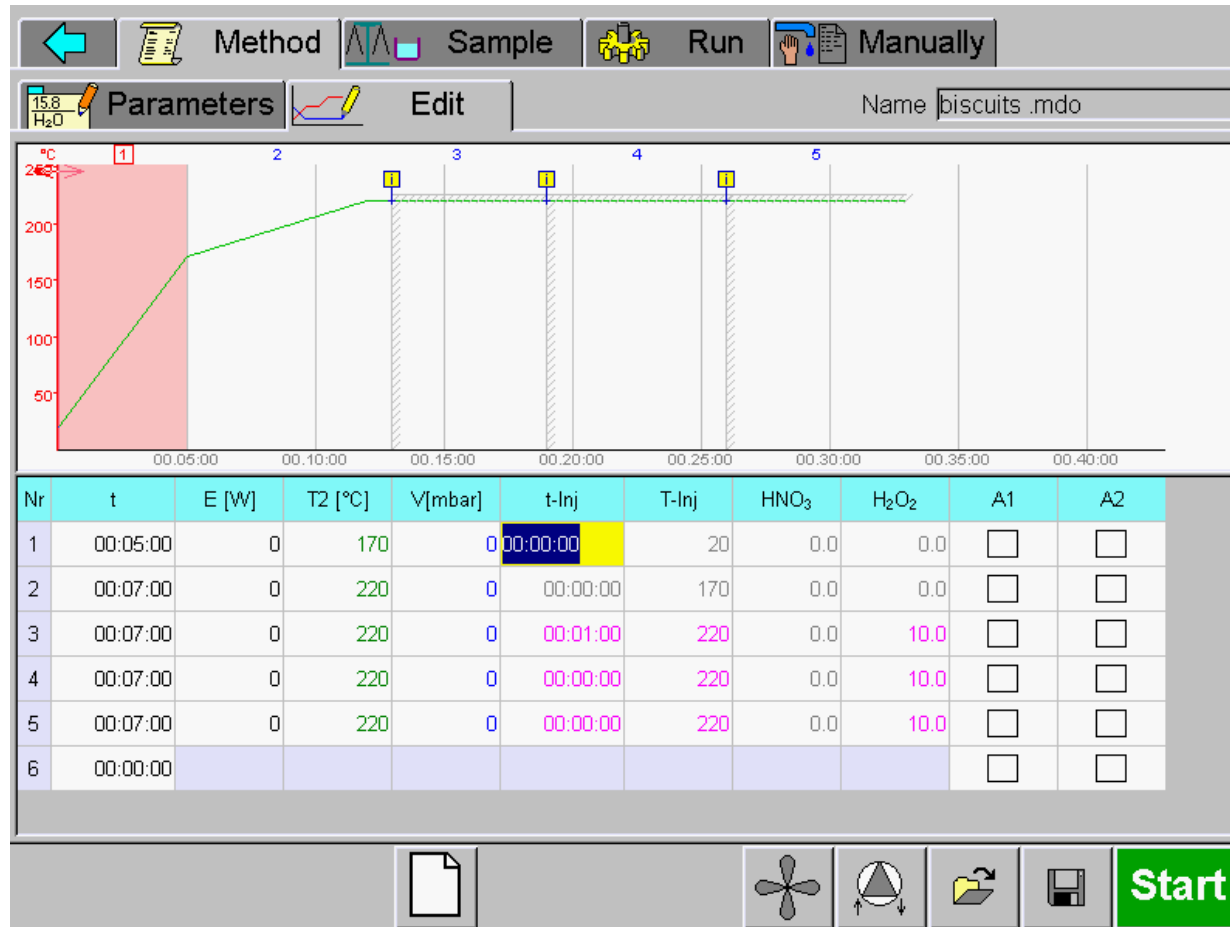
Biscuits



Sample size	2 grams (dry)
Reagents	HNO_3 and H_2O_2
Total time	35 minutes
Highest temperature	115°C



Biscuits



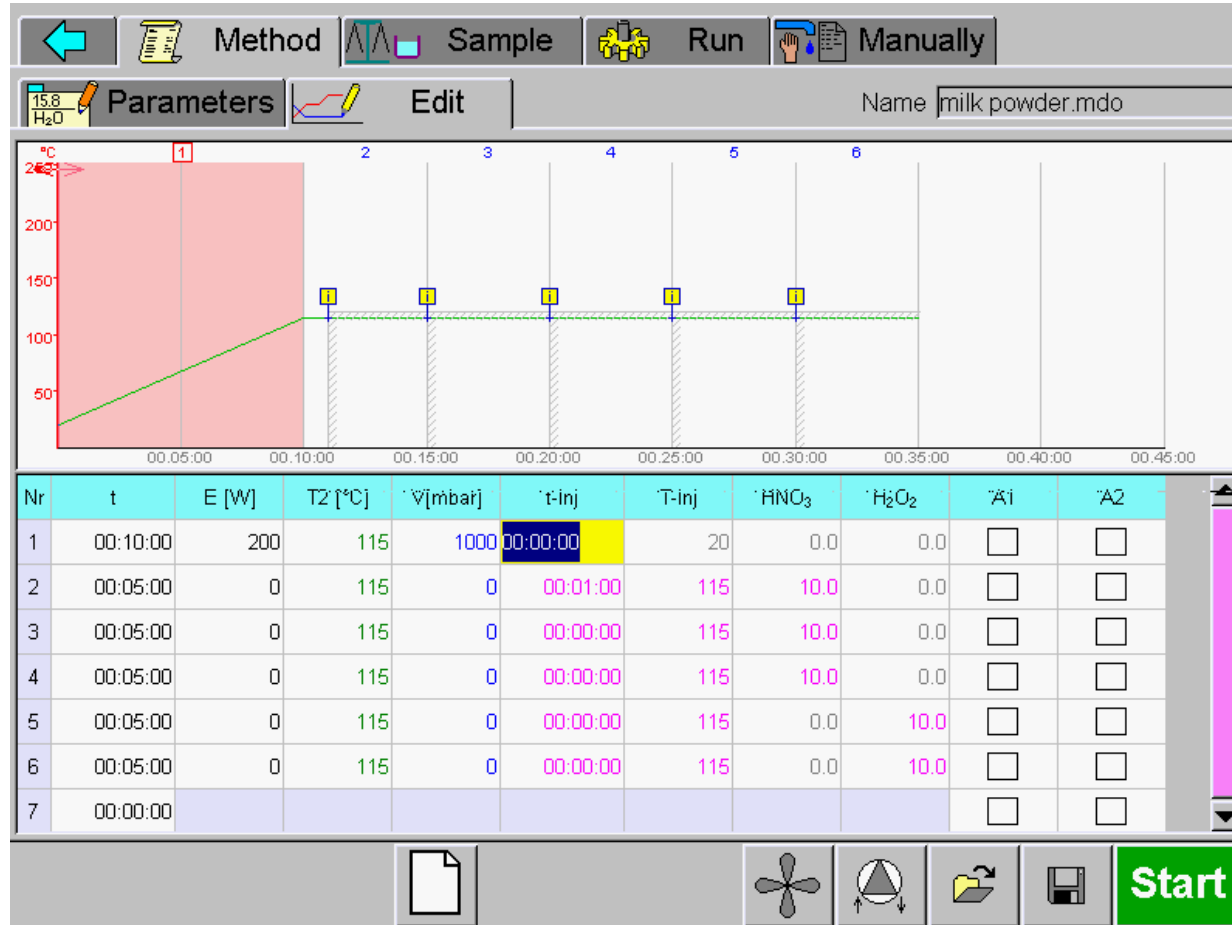
Milk Powder



Sample size	2 grams (dry)
Reagents	HNO_3 and H_2O_2
Total time	35 minutes
Highest temperature	115°C



Milk Powder



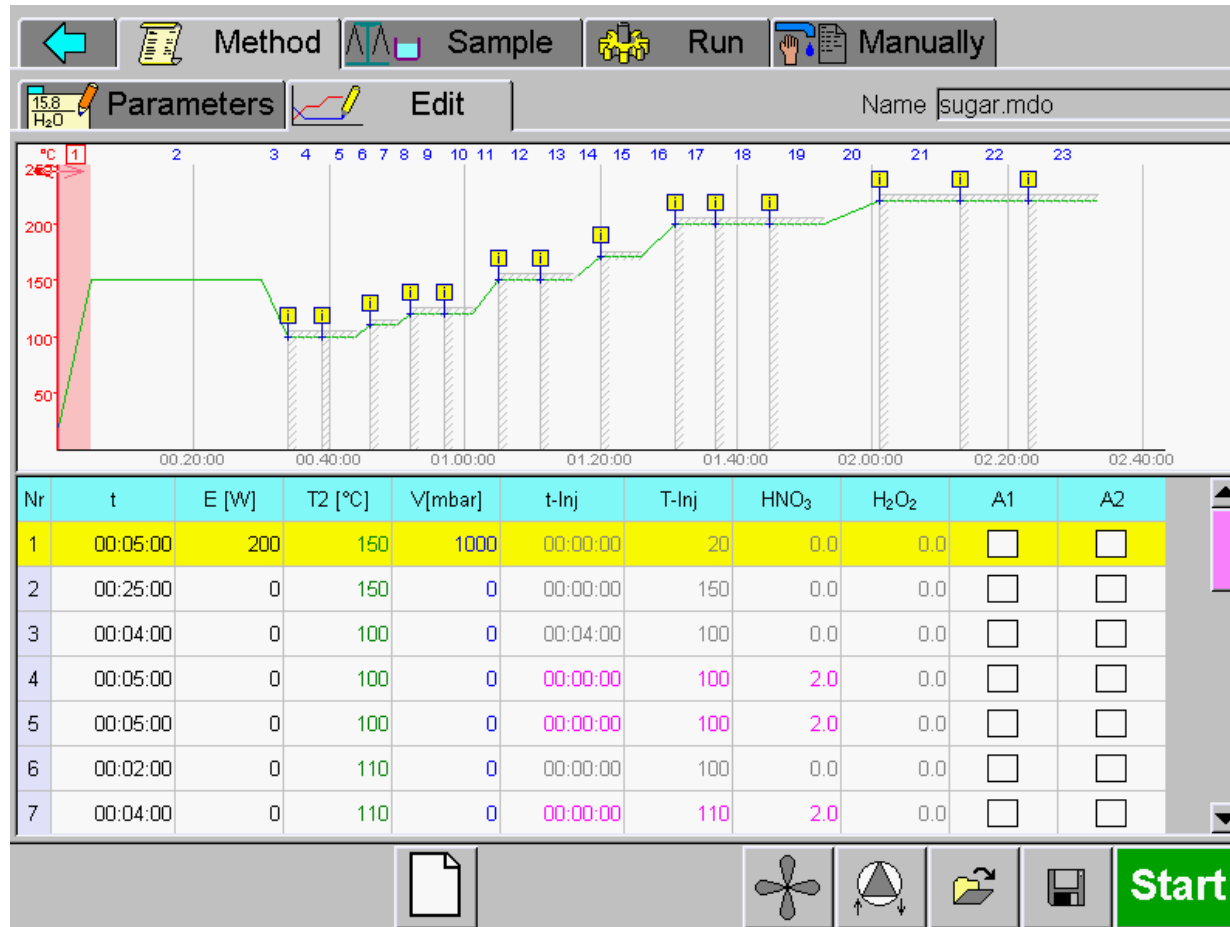
Sugar



Sample size	5 grams (dry)
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	2 hours+
Highest temperature	220°C



Sugar



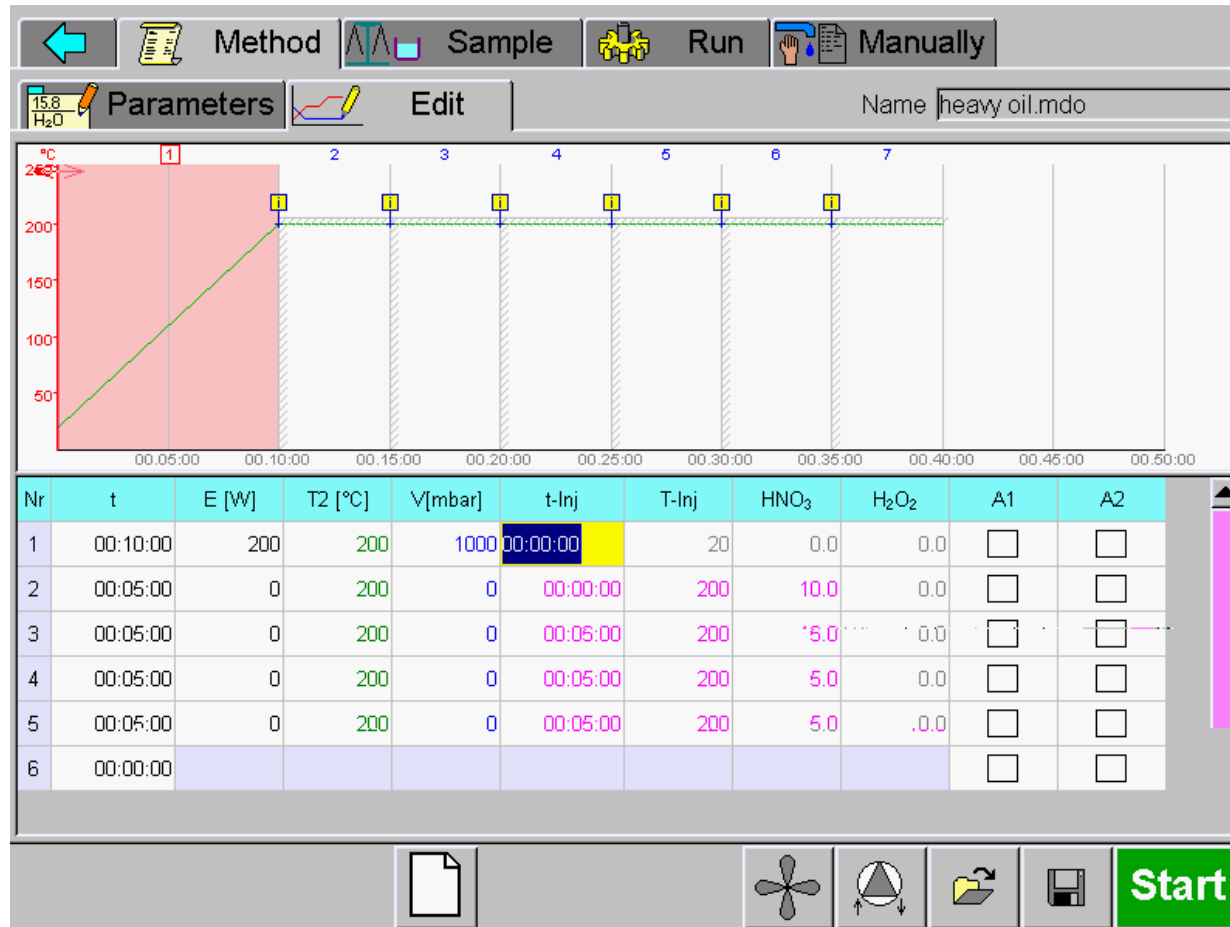
Heavy Oil



Sample size	2 grams
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	40 minutes
Highest temperature	200°C



Heavy Oil



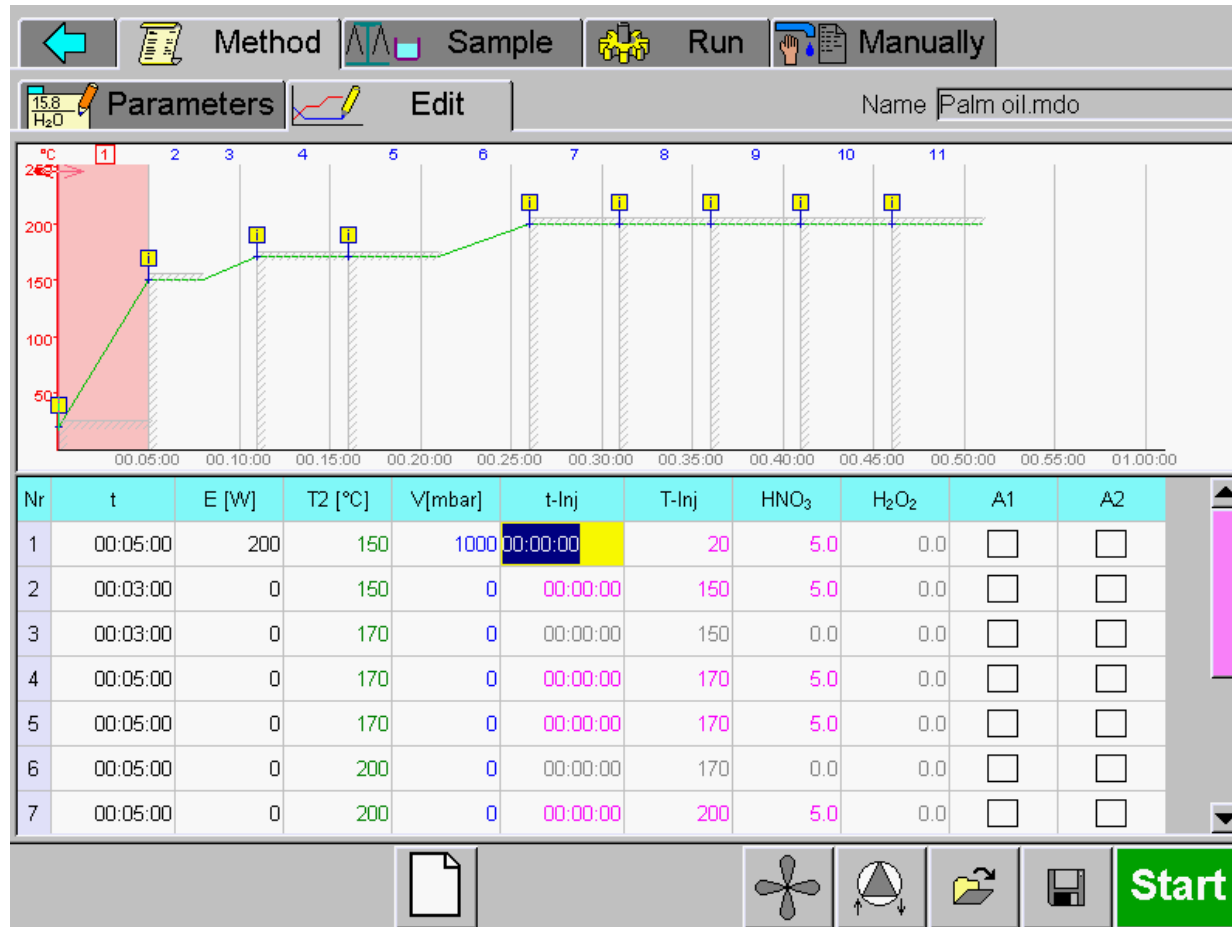
Palm Oil



Sample size	4 grams
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	50 minutes
Highest temperature	115°C



Palm Oil



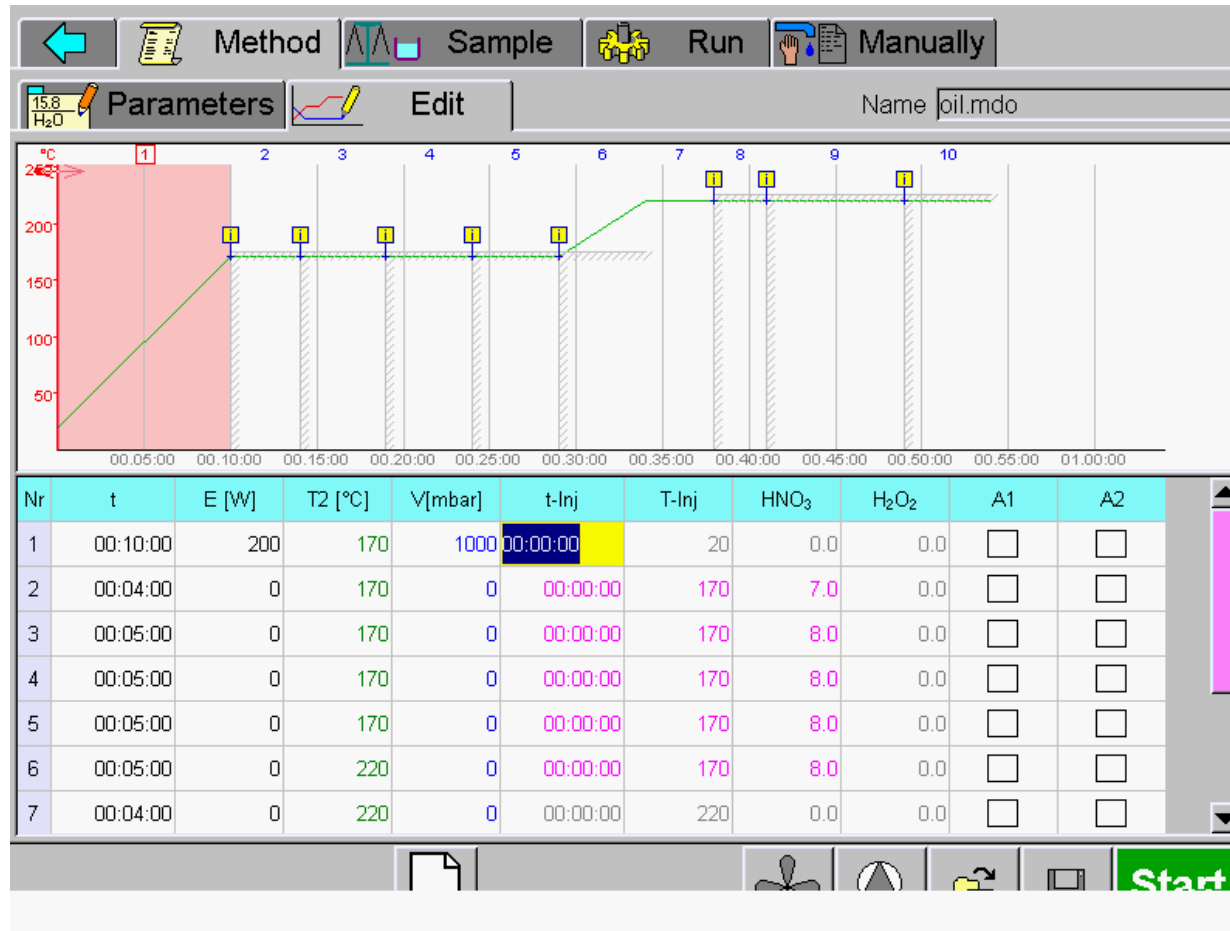
Lubricant Oil



Sample size	1 gram
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	50 minutes
Highest temperature	220°C



Lubricant Oil



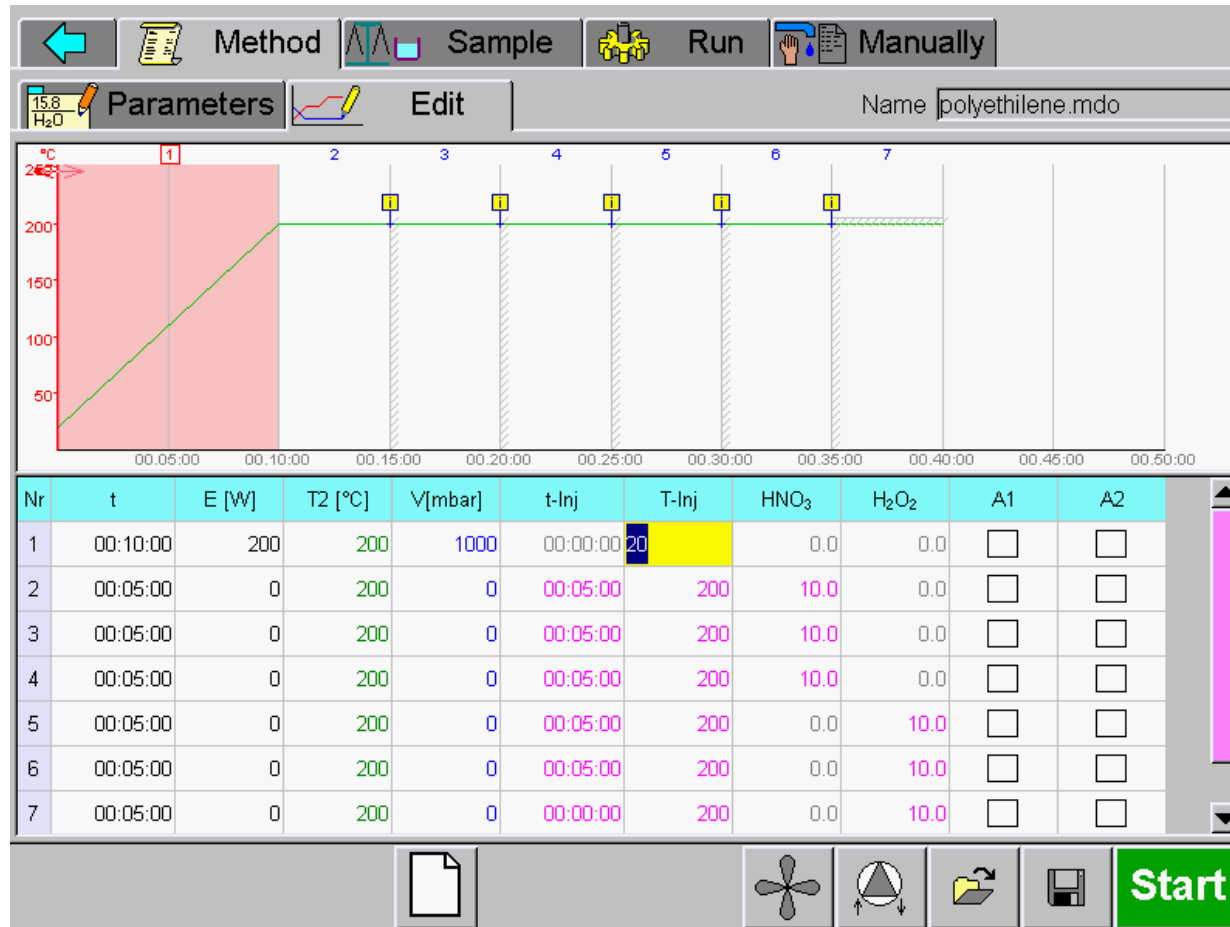
Polyethylene



Sample size	2 grams (dry)
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	40 minutes
Highest temperature	200°C



Polyethylene



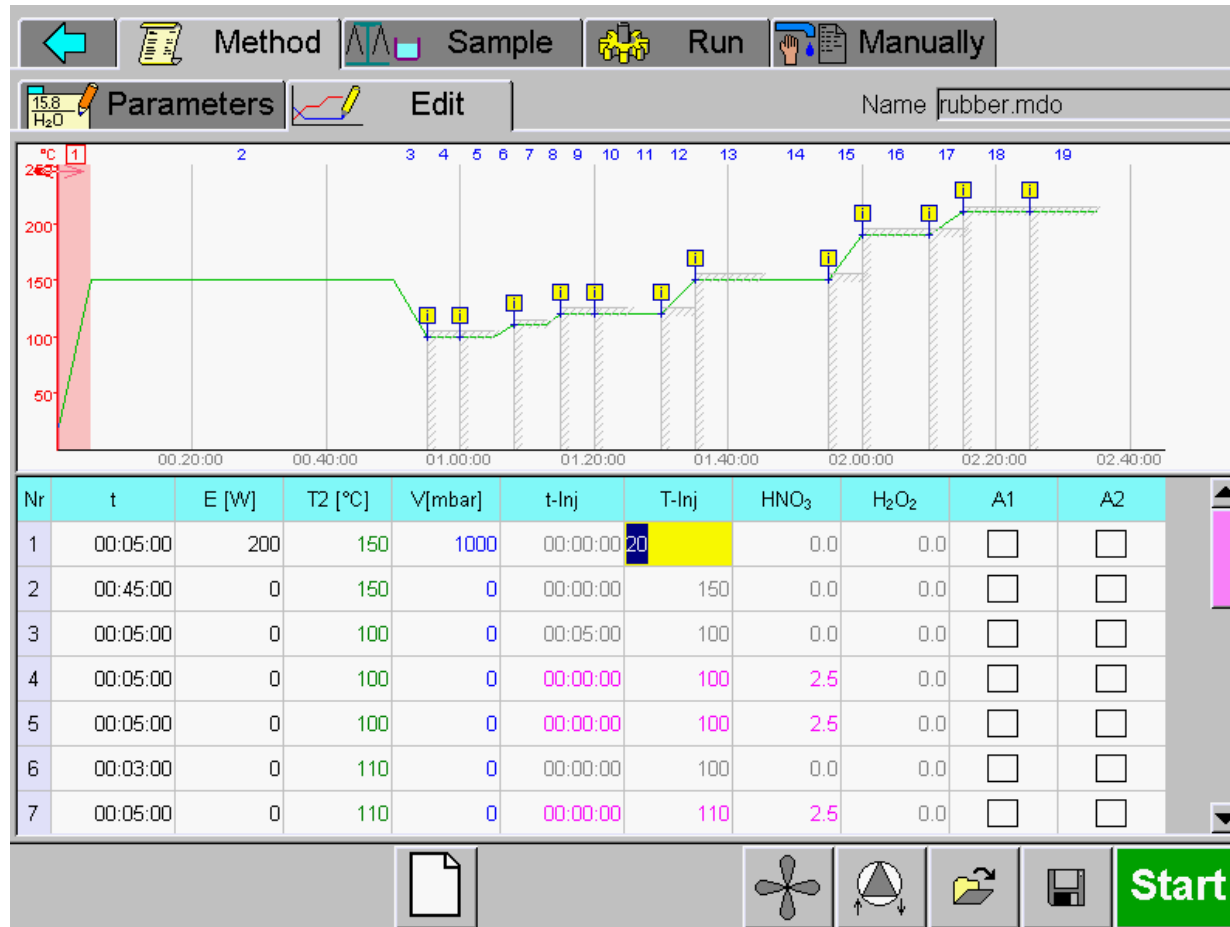
Rubber



Sample size	1 gram
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	2 hours+
Highest temperature	210°C



Rubber



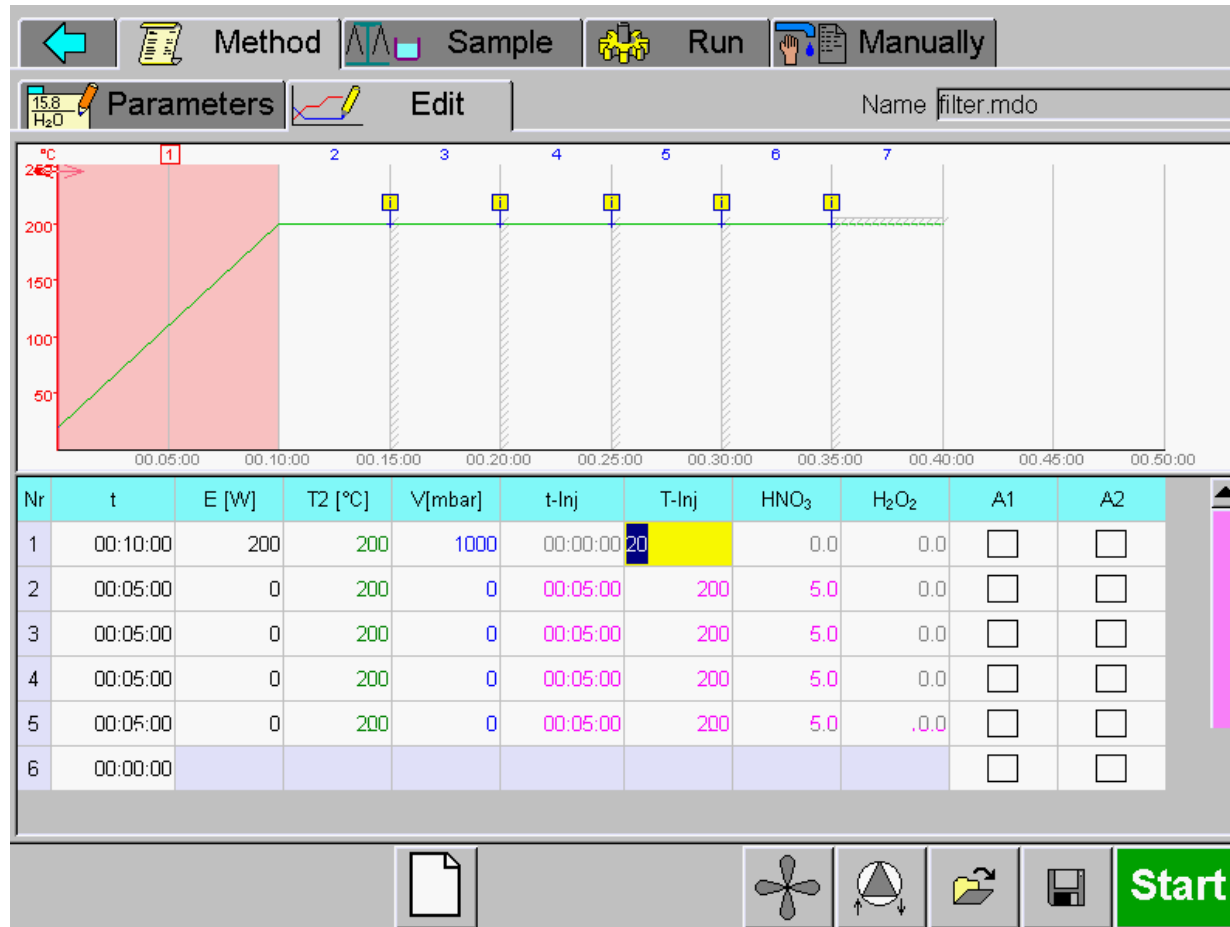
Air Monitor Filter



Sample size	2 grams (dry)
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	40 minutes
Highest temperature	200°C



Air Monitor Filter



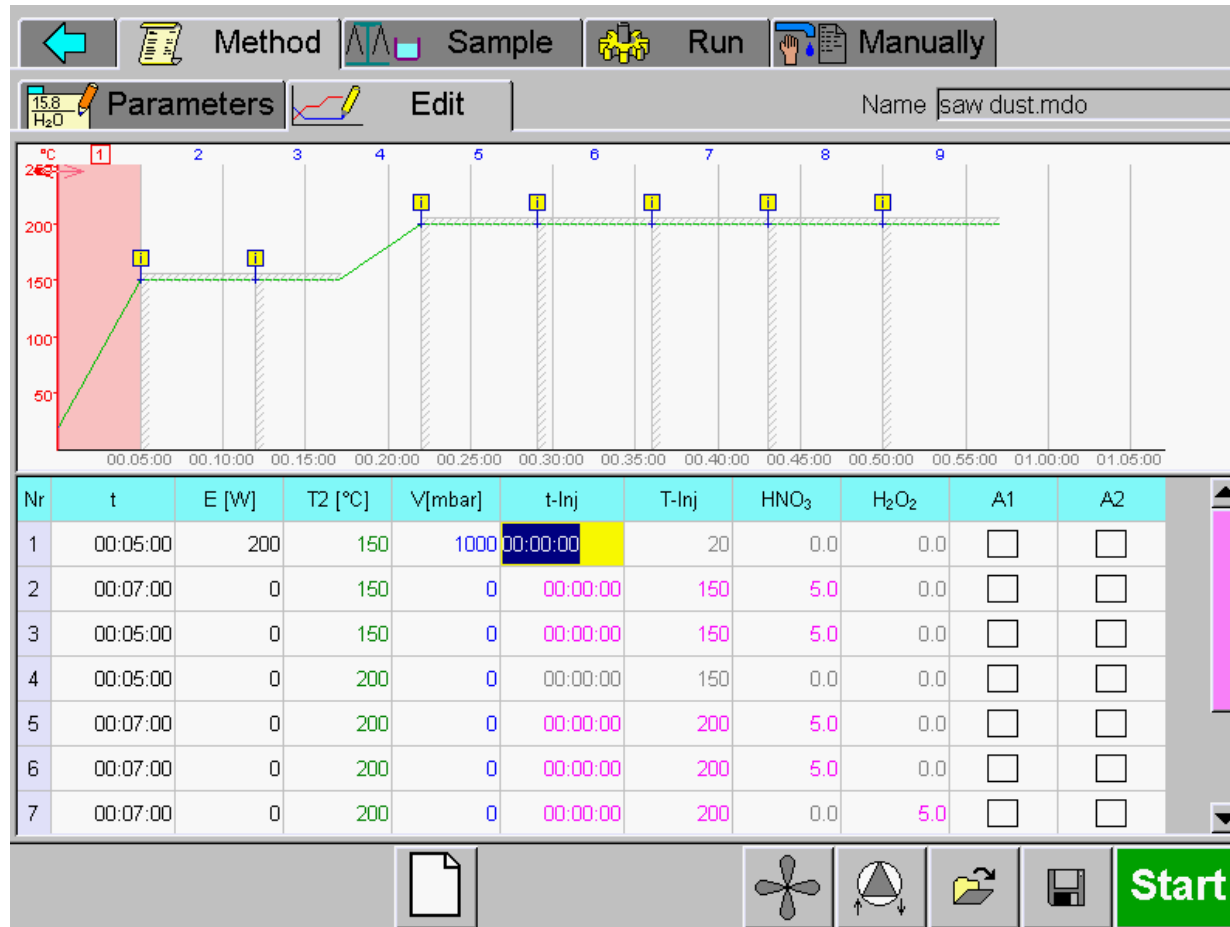
Saw Dust



Sample size	2 grams (dry)
Reagents	H_2SO_4 , HNO_3 and H_2O_2
Total time	55 minutes
Highest temperature	200°C



Saw Dust



Ethos MOD vs. Kjeldhal

Method	Ethos MOD	Kjeldhal
Sample weight	7-9 g	
Catalyst	-	7 g of (2,37 g $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ + 150 g Na_2SO_4)
Reagents	16 ml H_2SO_4 96% and 30 ml H_2O_2 30%	20 ml H_2SO_4 96% and 8 ml H_2O_2 30%
Temperature	235°C	390°C
Total time	1 hours and 15 minutes	4-5 hours

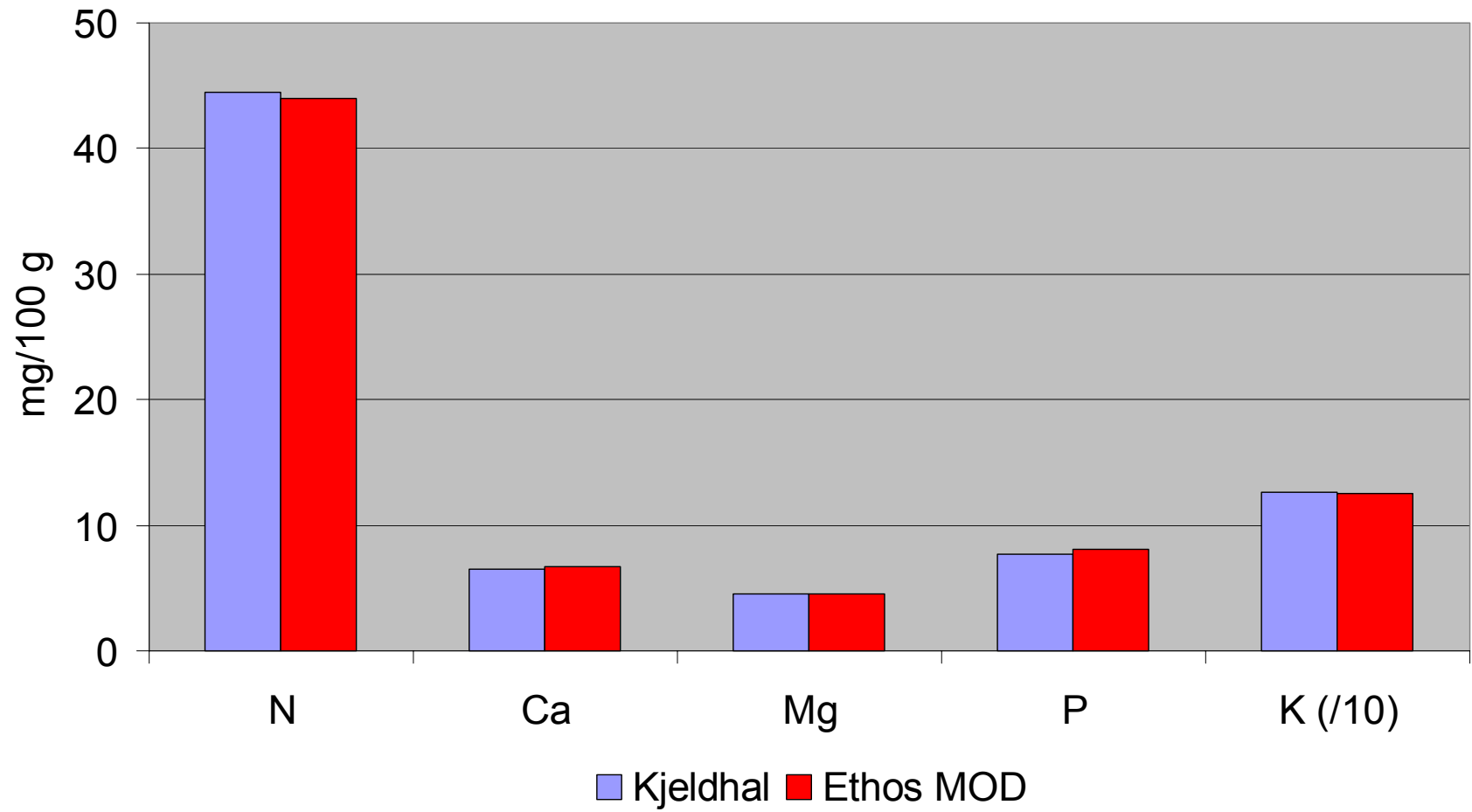


Results



Method	Ethos MOD	Kjeldhal
N	44,0 ± 2,0	44,5 ± 2,3
Ca	6,75 ± 0,48	6,48 ± 0,51
Mg	4,52 ± 0,21	4,56 ± 0,23
P	8,13 ± 0,53	7,67 ± 0,48
K	124,8 ± 2,3	125,9 ± 3,8
Results in mg/100 g		
n	12	18



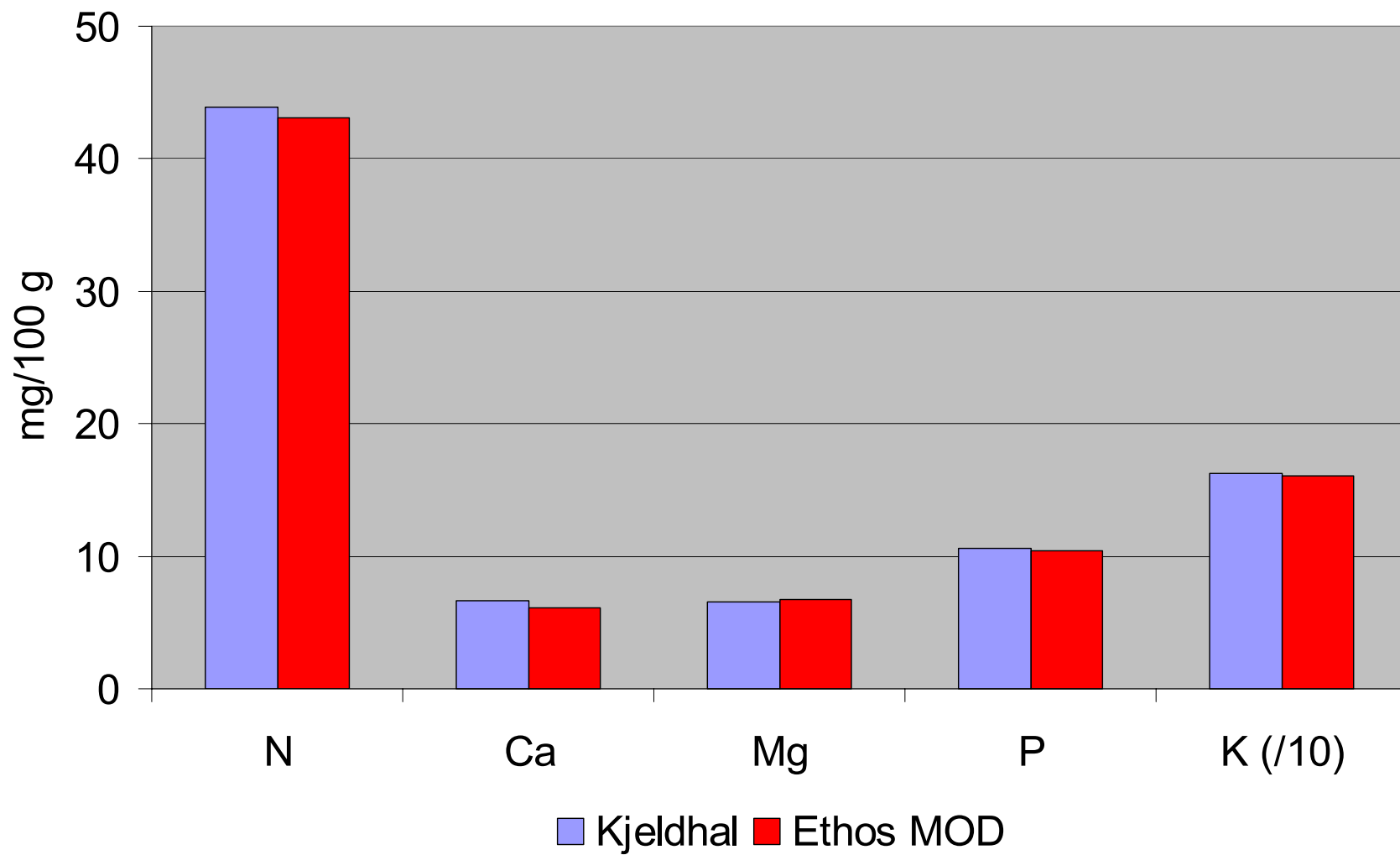


Results



Method	Ethos MOD	Kjeldhal
N	43,1 ± 1,6	43,9 ± 1,5
Ca	6,01 ± 0,34	6,65 ± 0,67
Mg	6,62 ± 0,30	6,58 ± 0,53
P	10,2 ± 0,3	10,6 ± 0,7
K	161,1 ± 1,8	162,1 ± 9,4
Results in mg/100 g		
n	12	18





Complete Solutions for AA and ICP Sample Preparation

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