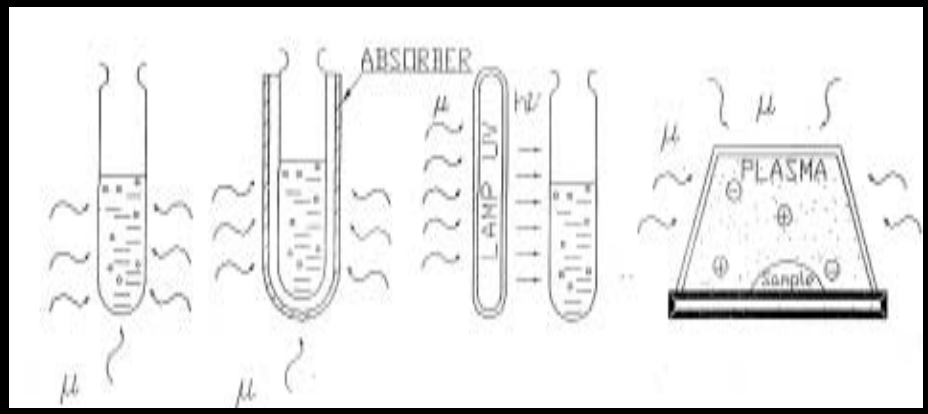
Selmar-GBC Slesin 2004

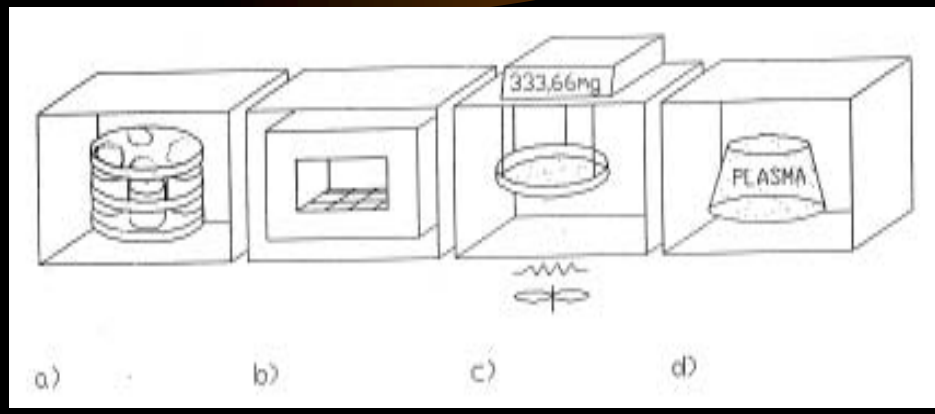
Mikrofale w akredytowanym laboratorium analitycznym

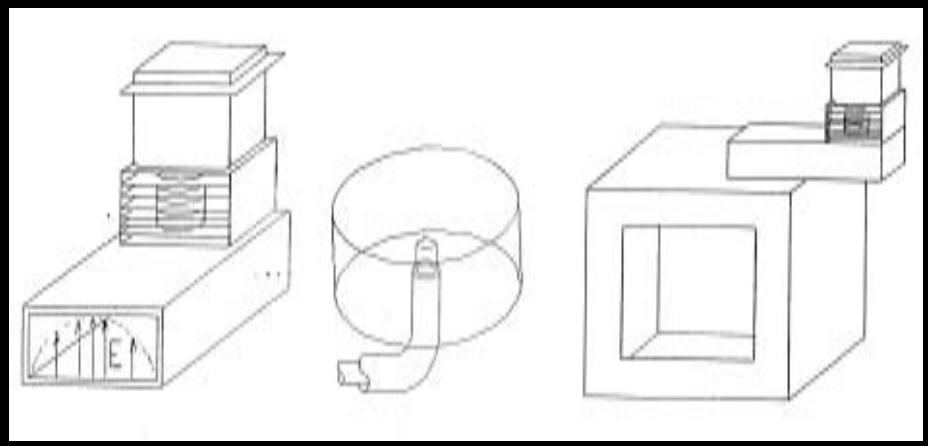
Edward Reszke
ERTEC-Poland

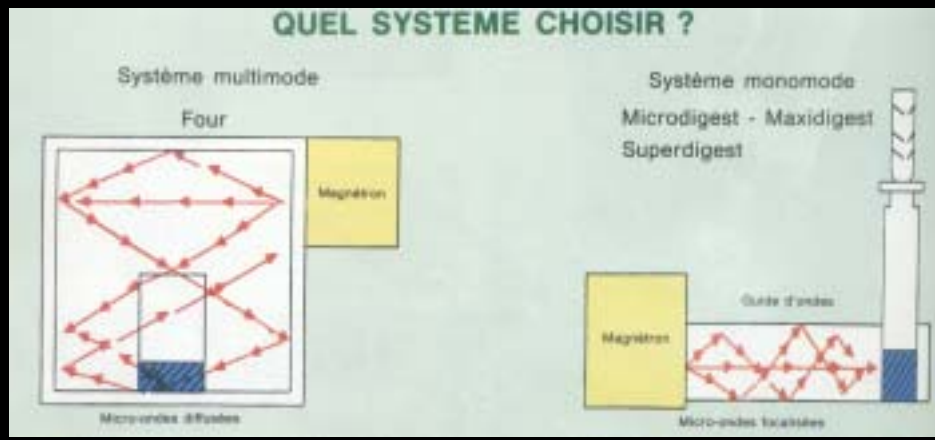
May 2004

Mikrofale w laboratorium









Just for the beginning

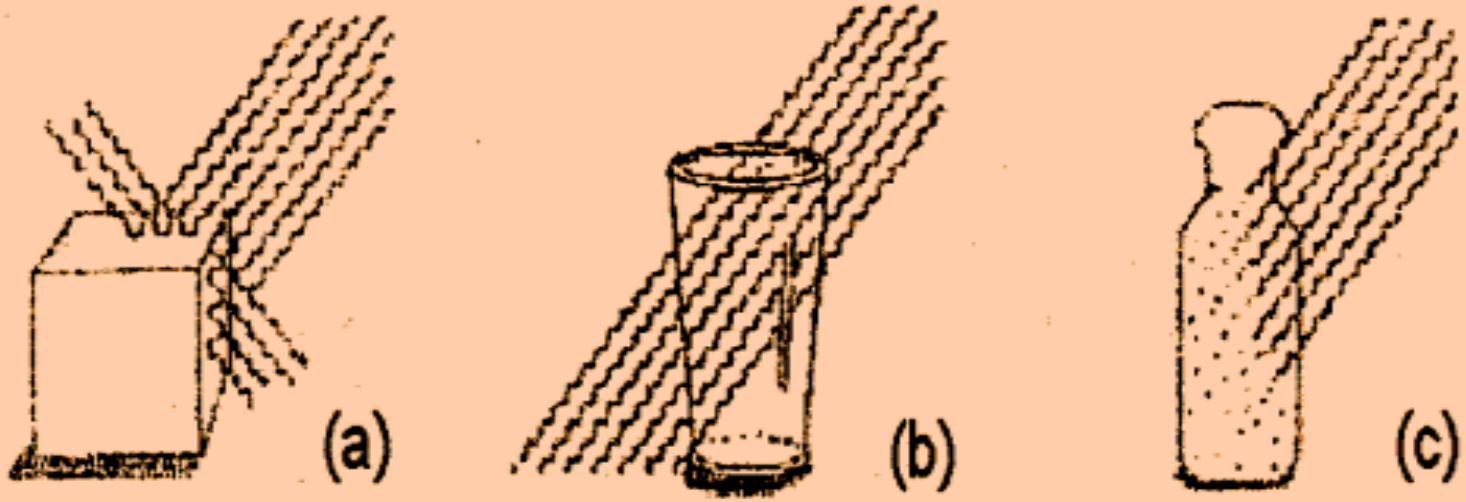


Fig. 2. Interaction of materials with microwaves
(a) conductor - reflects microwave energy
(b) insulator - transparent to microwave energy
(c) dielectric - absorbs microwaves

Piec mikrofalowy Milestone'a

Dry ahsing of analytical samples

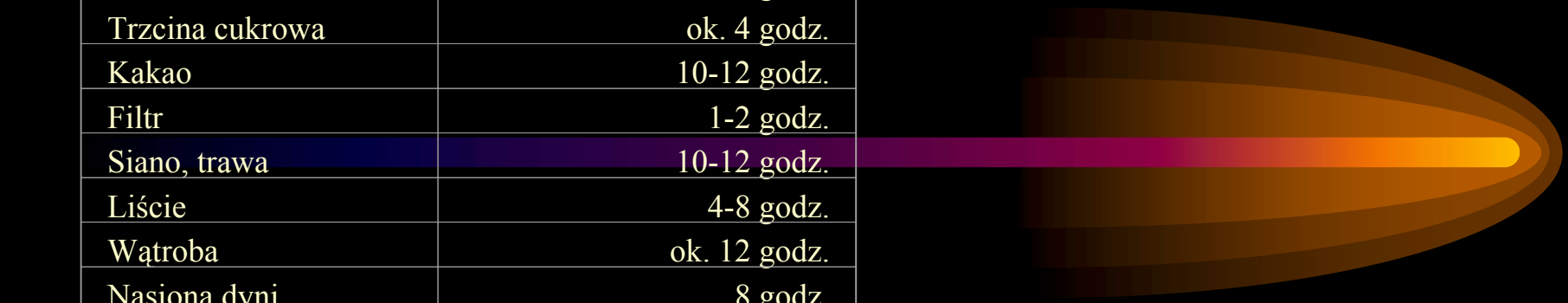
Why you need a Milestone Pyro Ashing System

REDUCED ASHING TIMES: FROM HOURS TO MINUTES

Sample	*Microwave Ashing Temperature (°C)*	*Microwave Ashing Time (minutes)*	*Traditional Ashing Time (minutes)*
Pet food (ground)	575	21	90
Cat food	575	15	300
Polypropylene	650	22	80
PVC	900	15	120
Polyester	600	15	480
Polyurethane	900	15	120
Coal standard AR2782	750	20	120
Dried eggs yolk	925	25	240
Activated Coal	750	25	180
Flour	900	50	360
Salami	600	60	300

Spopielarka plazmowa firmyOrbis Technologies Ltd

Karma dla zwierząt	ok. 10 godz.
Próbki krwi	2-4 godz.
Trzcina cukrowa	ok. 4 godz.
Kakao	10-12 godz.
Filtr	1-2 godz.
Siano, trawa	10-12 godz.
Liście	4-8 godz.
Wątroba	ok. 12 godz.
Nasiona dyni	8 godz.
Olej sałatkowy	ok. 20 godz.
Mąka przenna	2-3 godz.
Papierosy	ok. 1 godz.
Detergent – proszek	ok. 15 godz.
Grafit	3-4 godz.
Tkanina nylonowa	3-5 godz.
Papier	1-2 godz.
Włókna poliamidowe	2-3 godz.
Granulat poliamidowy	6-8 godz.



Orbis-parametry pracy

Poliester	ok. 3 godz.
Polietylen	ok. 25 godz.
PVC	ok. 20 godz.
Próbki gleby	5-15 godz.

Komitet Techniczny ISO/TC-146 : ***Jakość powietrza: Powietrze atmosferyczne. Oznaczanie włókien azbestowych. Metoda transmisyjnej mikroskopii elektronowej z pośrednim przeniesieniem próbki (2003).***

Urządzenia do spopielania próbek azbestu w mikrofalowej plazmie tlenowej

Edward Reszke[1)] , Marta Rożkowicz [2)]

1) Ertec-Poland 54-440 Wrocław ul. Rogowska 146/5 www.ertec.pl, ertec@wp.pl

2) Główny Instytut Górnictwa, 40-166 Katowice Plac Gwarków 1 soxmr@gig.katowice.pl

Celem komunikatu jest przedstawienie projektu budowy pierwszego polskiego spopielacza plazmowego. Projekt dotyczy urządzenia do plazmowego spopielania całych filtrów z estru celulozy o wielkości porów 0,8 µm i średnicy Ø 25 mm wraz z próbką zawierającą włókna azbestu. W celu wykonania badań prototypu nawiązano współpracę badawczą pomiędzy firmą Ertec a Głównym Instytutem Górnictwa, który podjął się przebadania i optymalizacji charakterystyk nowego przyrządu przy pracy z próbkami laboratoryjnymi materiałów azbestowych o różnych matrycach, czyli badań niezbędnych do atestacji nowego aparatu jako legalnego przyrządu laboratoryjnego spełniającego normy europejskie.

Przygotowywanie prób mikroskopowych materiałów zawierających azbest jest problemem, który pojawił się dopiero w ostatnich latach. Nowa analiza wymaga odkrywania struktury niebezpiecznych włókien azbestu i ich rozróżniania w masie

Prototyp plazmowej spopielarki próbek azbestowych

Wnęka prototypowej spalarki

Widok podajnika próbki

(filtr celulozowy z ACM)

Najnowsze źródło wzbudzenia MIP z wnęką typu TEM

An example of MW system with integrated power source, coaxial feeder and two stub tuner placed between MW generator and applicator (a microwave cavity with TEM mode for MIP excitation)

Otwarte systemy mineralizacji „na mokro”

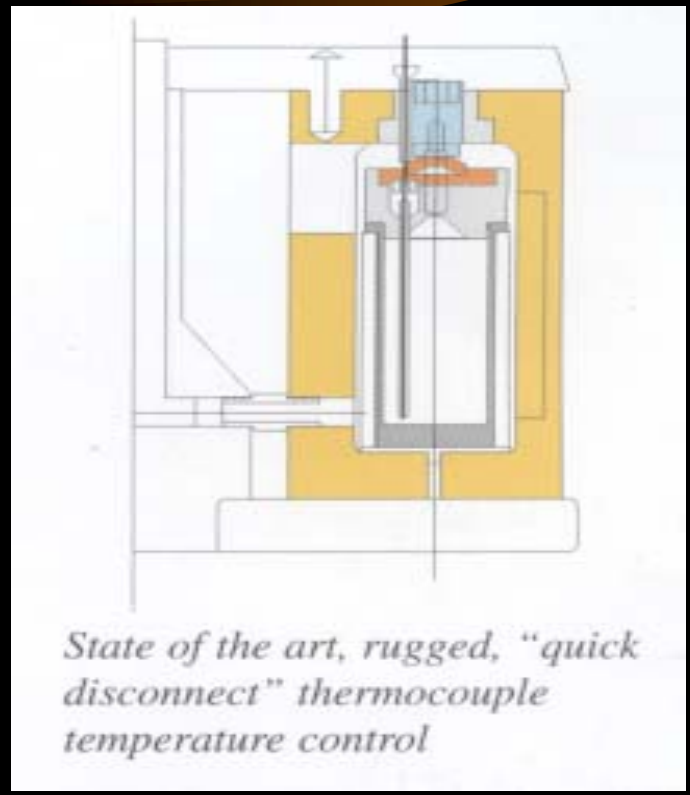
Maxidigest MX350
Prolabo

Star 2
CEM

UniClever BM-1o
Plazmatronika

High pressure MW systems

Ethos plus
from Milestone



digestion vessel
Ethos

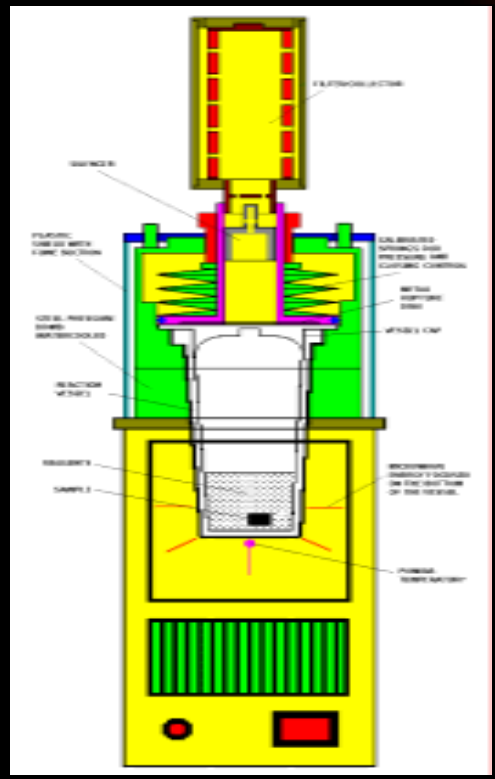
High pressure system

Plazmatronika-
Nano 2000

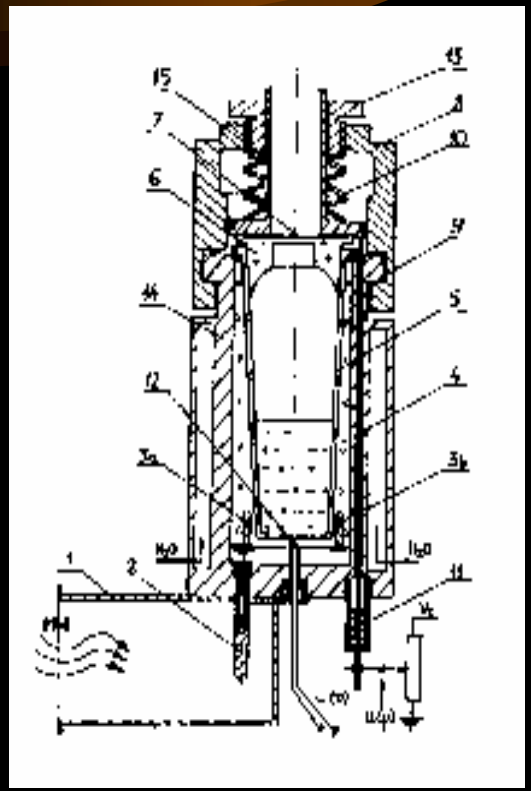
Reactor/mineralizer Ertec

Concept of a novel closed system with self-matching feature

Ertec system Magnum

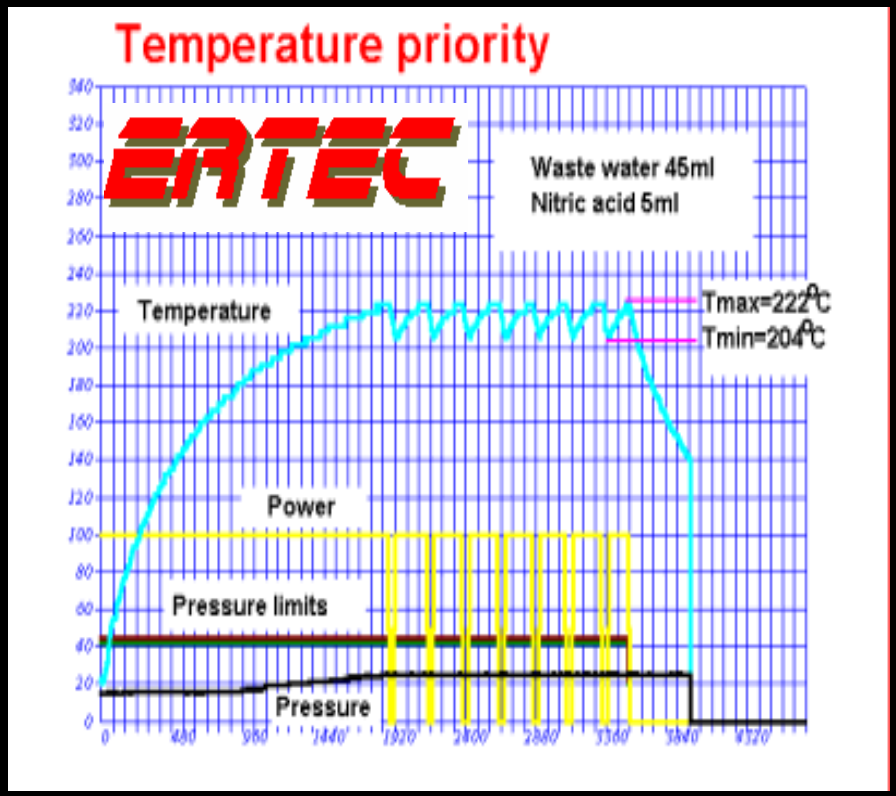


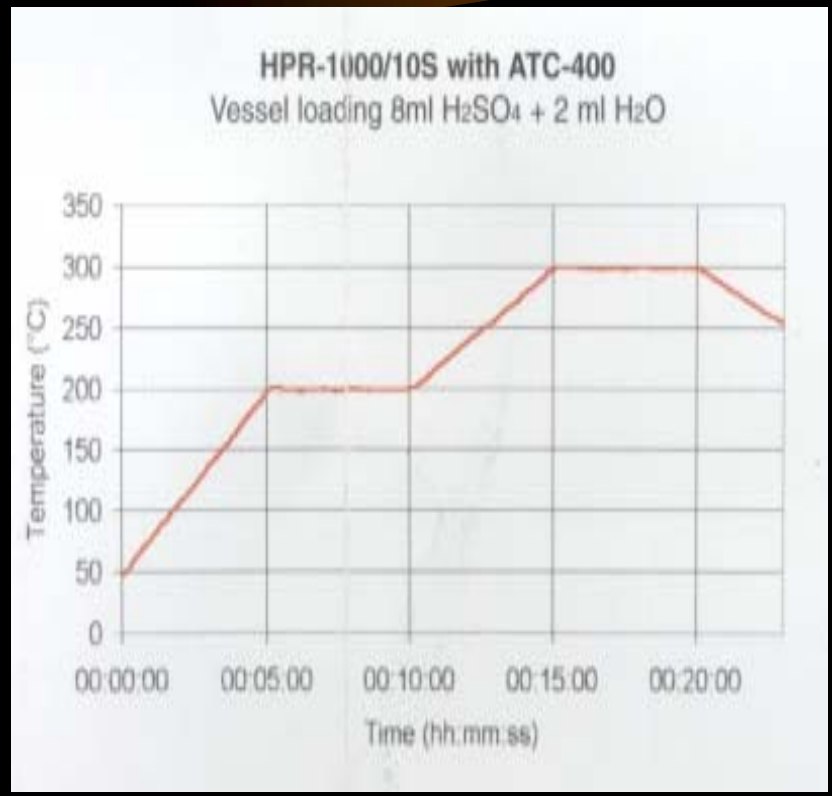
Construction of ERTEC mineralizer/reactor



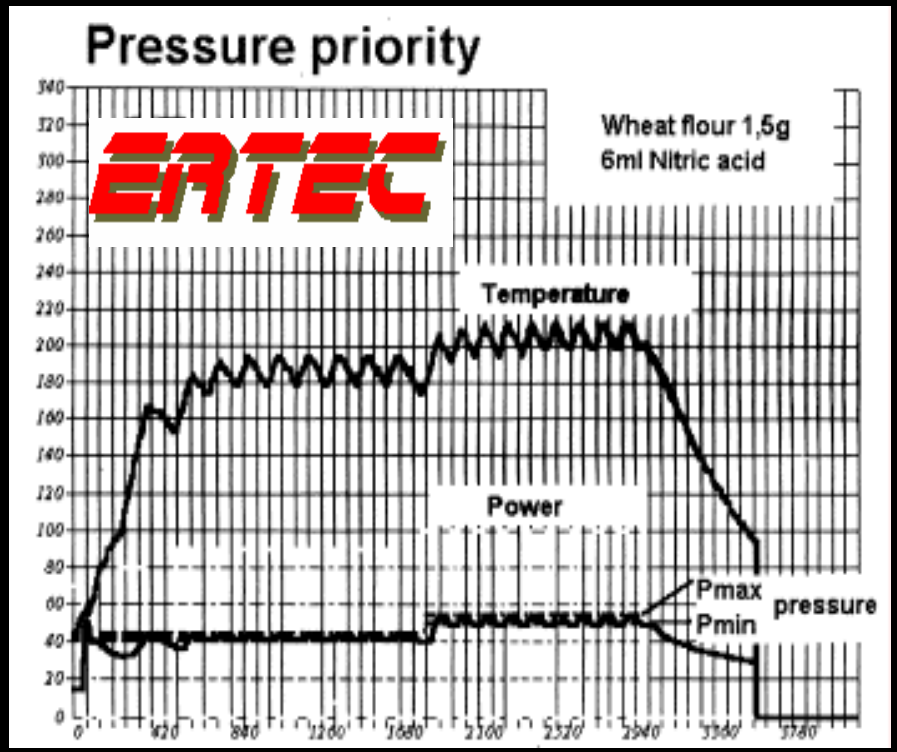
Magnum cross section

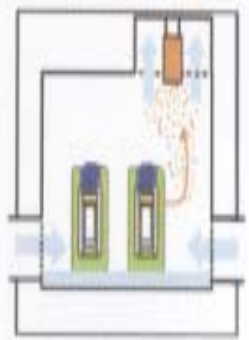
Temperature measurements





Measurement and control of pressure

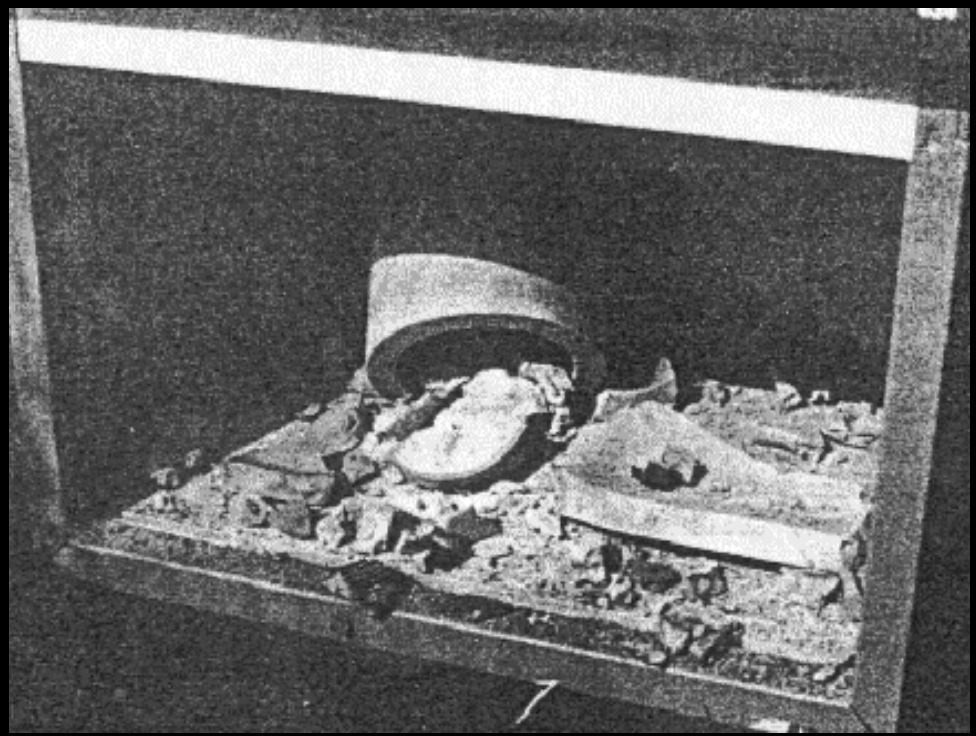


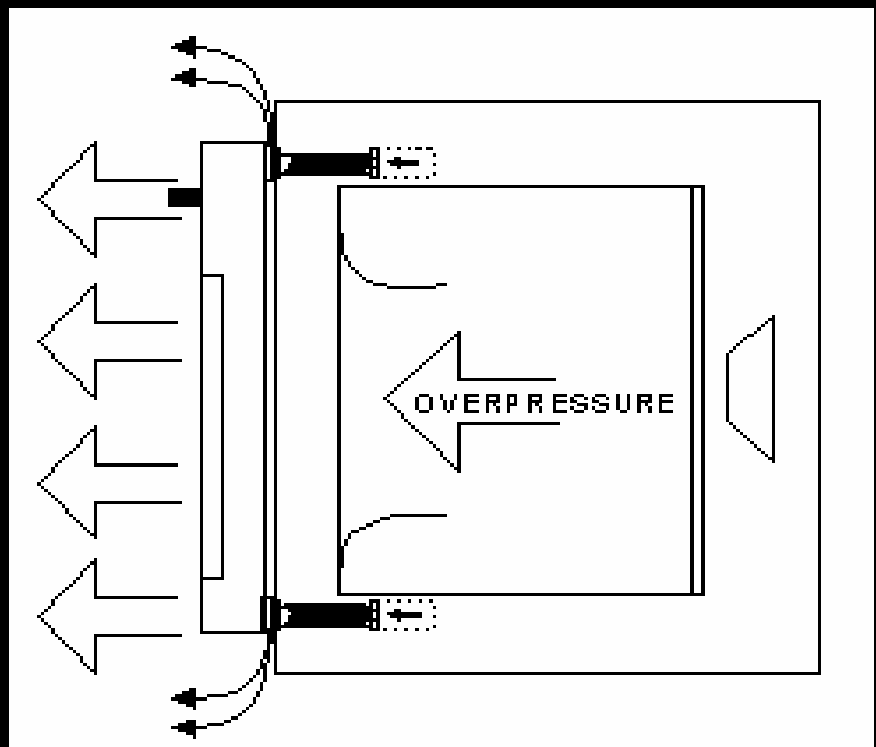


QP for pressure limit control
Another first from Milestone's R&D Department. This unique sensor continuously monitors the level of acid vapors in the microwave cavity.

Once over a preset level, the sensor automatically responds by adjusting the microwave power.
All vessels in the cavity are monitored simultaneously and independently to effectively limit the pressure in each vessel, thereby preventing overpressure and venting.

Bezpieczne konstrukcje





Rozpuszczanie materiałów nieorganicznych

Table7. Dissolution speed of „conventional" and microwave closed approaches

	Conventional Teflon bomb		Microwave digestor
Matrix	**(h)**	**(min)**	**(min)**
Al_2O_3	24	1440	20
AlN	2	120	15
BN	5	300	15
Si_3N_4	6	360	15

Digestion efficiency

Table 5 Effective of destruction of the organic matrix in the study systems decomposition

Cert.Ref Material	Microwave System	CRM-total C [%]	Degree of C removed C [%]	RSD of RCC [%]
Pig Kidney	Paar Physica	48,96	99.25	35.9
186	MLS MEGA		97.54	39,7
	Prolabo T		98.93	21.4
	Prolabo S		94.25	40.8
Dogfish	Paar Physica	44,20	98.87	34.2
DORM 2	MLS MEGA		97.07	27.6
	Prolabo T		98.70	35.0
	Prolabo S		94.00	38.4
Mussel	Paar Physica	43,88	99.01	32.4
Tissue 278	MLS MEGA		97.70	42.6
	Prolabo T		99.21	10.0
	Prolabo S		95.26	39.3
Brown Bread	Paar Physica	45,60	99.08	28.9
BCR 191	MLS MEGA		97.14	31.8
	Prolabo T		98.94	11.4
	Prolabo S		95.21	35.5
Aquatic Plant	Paar Physica	37,82	98.92	30.9
BCR 60	MLS MEGA		97.65	34.1
	Prolabo T		98.87	22.6
	Prolabo S		95.11	38.7

RCC - residual carbon content

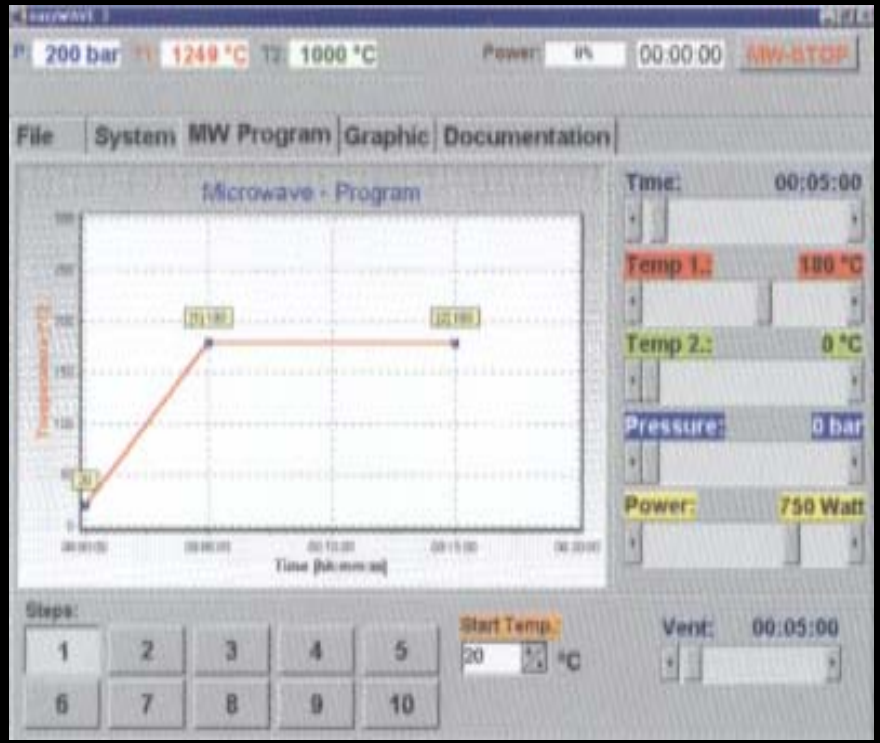
Digestion reagents

Solution of reagents	Matrix	Uwagi
HNO_3	Biological materials	incompletye digestion at atrmospheric pressure
$HNO_3 + H_2O_2$	Biological materials	Effective digestion of small samples
$HNO_3 + H2SO_4$	general use	Frequently used but promotes losses of easili volatile elements such as As, Ge, Hg, Se
$HNO_3 + HCl$	general use	aqua regia
$HNO_3 + HClO_3$	Biological materials	High oxidation potential, low loss of As, Hg, Se, In and so on .., safe
$HNO_3 + HClO_4$	Biological materials	Effective decomposition , low loss of Pb
$HNO_3 + HCl + HF$	general use	-
$HNO_3 + HF$	general use	-
$HNO_3 + HClO_4 + H2SO_4$	general use	Temperature regime must be controlled , loss of As, Hg, Fe Sb
HF	innorganic materials	-
$H2SO_4 + HClO_4$	general use	Small samples , denger of explosion
$H2SO_4 + H_2O_2$	general use	Losses of As, Hg, Ge, Ru, Se and many other volatile elements
$HClO_4$	Biological materials	Strong oxidizer, denger of explosion
$H_2O_2 + Fe^{3+}$	Biological materials except oils, fats and grees	Decomposition with OH^* radicals, low temperature of decomposition, good for large samples, no loss of elements

Material of digestion vessels, memory effects

Material	Melting point	Maximal . T[°C]	tg x10^4
Teflon PFA	302	260	2,1
Teflon FEP	252-262	204	2,1
Halon PTFE	320	260	2,1
Polymetylpentane	240	175	2,1
Polyethylene	120-135	71-93	2,2-2,3
High press.polyethylene	146	121	2,25
Polypropylene	168-171	100-105	2,24-2,4
Polystyrene	242	82-91	2,7-3,1
Polycarbonate	241	121	2,9
NYLON 6	216	102	3,4
Quartz glass	1665		3,8-4,1
Borosilicat.glass	1080		6,3-6,8
Phenol resin	rozkladaju sa	120-190	4,1-5,0

Software and data aquisition



Digestion of difficult organic samples with dry mass over 1g

ERTEC

Sample	Mass [g]	Reagents [ml]	Digestion procedure power [%] pressure set. [at]	Pressure reached (oscillation) [at]	Total digestion time [min]
Green coffee	1,5	6 HNO_3	5'/60% 20-17at; 5'/100% 45-42at 10'/0%	45 (45-42)	20
Tea fix	1,5	6 HNO_3, 2 H_2O	5'/60% 20-17at; 5'/80% 45-42at; 10'/100%	45 (45-42)	20
Rice	2,5	8 HNO_3, 4 H_2O	10'/60% 20-17at; 10'/0% 45-42at; 10'/0%	105 (45-42)	30
Goulash soup	1,5	8 HNO_3, 4 H_2O	10'/60% 20-17at; 10'/100% 45-42at; 10'/0%	74 (45-42)	30
Dry mushrooms	2	8 HNO_3, 4 H_2O	10'/60% 20-17at; 10'/100% 45-42at; 10'/0%	45 (45-42)	30
Peanut	1,5	8 HNO_3, 4 H_2O	10'/60% 20-17at; 10'/100% 45-42at; 10'/0%	45 (45-42)	30
Poppy seed	2	8 HNO_3, 4 H_2O	10'/60%; 10'/100%; 10'/0%	82 (45-42)	30

Efficiency of digestion systems

Dzienna zdolność przerobowa różnych systemów do mineralizacji			
Rodzaj próbek	Masa próbki (sucha)	Wysokociśnieniowy system modułowy (2 moduły)	Systemy mikrofalowe z wnęką wielomodową (6 stanowisk)
Organiczne	do 0,5 g	64 próbek dziennie	48 próbek dziennie
	do 1 g	48 próbek dziennie	zwykle niemożliwe
	do 2 g	24 próbek dziennie	niemożliwe
	do 5 g	12 próbek dziennie	niemożliwe
Nieorganiczne	do 0,5 g	32 próbek dziennie	30 próbek dziennie
	do 1 g	24 próbek dziennie	18 próbek dziennie
	do 2 g	12 próbek dziennie	czasem niemożliwe
	do 5 g	6 próbek dziennie	niemożliwe
Mieszane	do 0,5 g	48 próbek dziennie	36 próbek dziennie
	do 1 g	36 próbek dziennie	24 próbek dziennie
	do 2 g	18 próbek dziennie	zwykle niemożliwe
	do 5 g	10 próbek dziennie	niemożliwe

MW vs Conventionally driven reactions

Kind of reaction:	MW reactor		Conventional	
	yeld	time	yeld	time
Dielsa-Alder Condensation (antracen with dimethyl ester of fumarine acid)	87%	10min	67%	4h
Cyclocondensation reaction - synthesis of pirymidobenzimidazolics - synthesis of derivatives of cumarine	38-86% 75-90%	15-30min 1-10min	brak 60-90%	48h 6h
Reformation of Claisen aromathical alkilic ethers	100%	90s	100%	12min
Alkilation of salts of carboxylic acids - production of octyl acetat - production of hexadecyl acetat	99% 96%	2min 2min	2% brak	2min 20h
Reakcje o-alkilation with alkilic dihalogens	80-90%	5min	90%	30min
Cation Reformation , pinakolin reformation after adsorption of pinakol onto montmorylonit	99%	15min	99%	15h
Oxidation reactions - oxidation of I- and II-order alcohols leading to aldehydes and ketons in the presence of MnO_2 - oxidation of I- and II-order alcohols to acids and ketons against H_2O_2 - epoxidation of double bonds against H_2O_2	50-80% 60-97% 91-98%	3-7min 10-20min 100min	25-40% 83-96% 54-65%	11h 4h 100min
One-step precipitation of magnetite	100%	10 min	100%	60 min
Precipitation of zirconia powders	100%	20 min	100%	240 min
Precipitation of zink oxides	100%	3 min	90%	40 min

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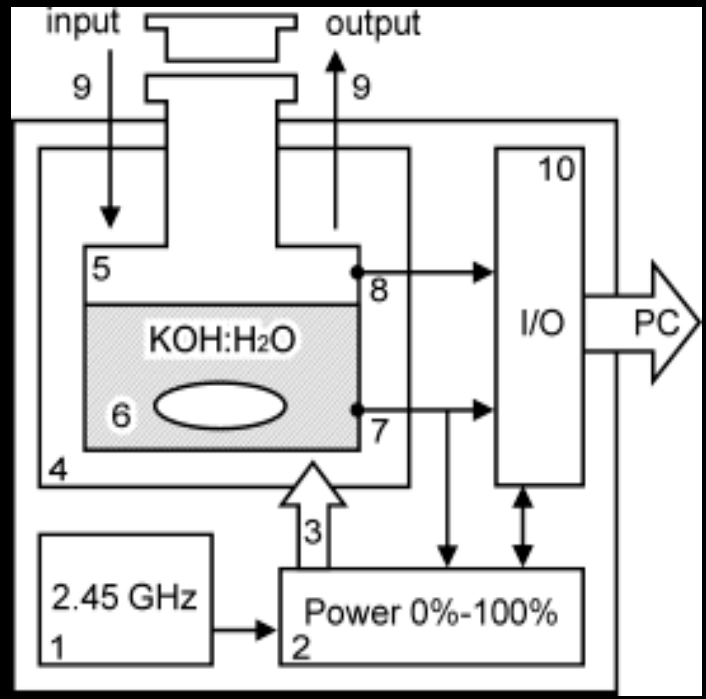
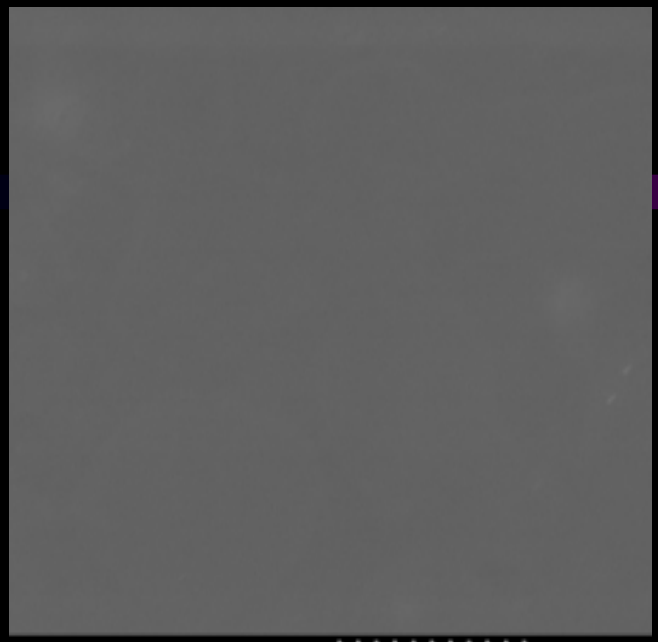
Novel method, named EMSi (Etching Microwave Silicon) a Teflon® reaction vessel containing silicon substrates immersed in the 3 - 5 M KOH solution is positioned inside the microwave resonator and irradiated by 2.45 GHz microwaves. Etching rates for (100) planes: V_{100} equal to 5 ÷ 10 μm/min, in almost cold (60°C ÷ 70°C) solutions have been obtained. New, microwave enhanced etching of silicon enabled fast fabrication of the 3D silicon micromechanical structures.

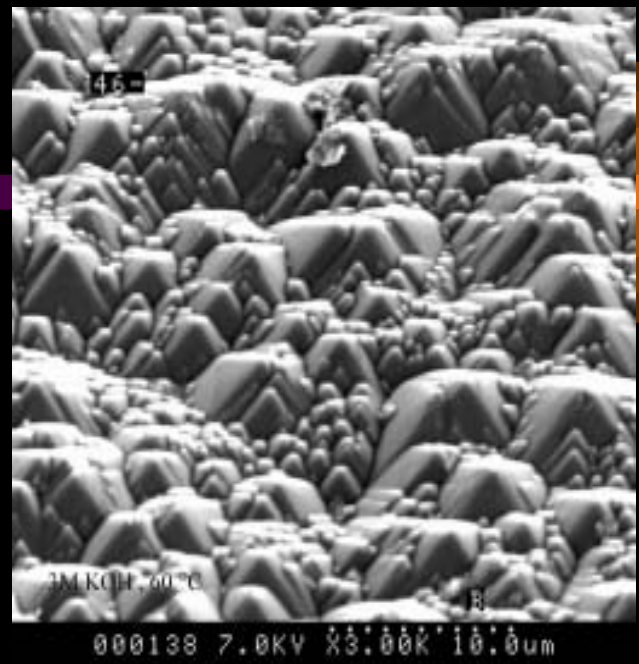


EMSi etching: a) scheme of the stand: 1-microwave generator, 2-power supply unit, 3-connector, 4-single or multimode resonator, 5-reaction chamber, 6-silicon substrate, 7-temperature sensor, 8-pressure sensor, 9-cooling water, 10-I/O, b) process characteristics: pressure, microwave power and temperature versus time.

All stainless steel reactor for etching experiments

Standard procedures	Microwaves enhanced
low etching rates $V_{(100)} \approx 1$ μm/min at 80°C	high etching rates $V_{(100)} \leq 10$ μm/min at 80°C
etching rates depend on etchant's temperature	etching rates depend on microwave power "pumped" into the solutions
hillocks formed in low concentration KOH or (and) low temperature	no hillocks
good anisotropy (10 M KOH ~ 40÷50) higher for stronger solutions	sufficient anisotropy 30÷20 higher for weaker solutions
batch process	single wafer process, batch process possible
long (hours)	short (< 60 minutes)
etching rates at 60°C negligible	etching rates at 60°C high (~ 5 μm/min)
etching rates in 3 M KOH negligible	etching rates in 3 M KOH high (~ 5 μm/min)
SiO_2 , Si_3N_4 mask	Si_3N_4 mask only; selectivity 1:10000
60°C process impossible	60°C process good





) new etchiung EMSi, open system, $V_{(100)}$=5,1 μm/min,

b) conventional etching, $V_{(100)}$=0,4 μm/min, Photography SEM x5000, x3000

Bezpieczenstwo użytkowania urządzeń mikrofalowych

1. Dyrektywa niskonapięciowa
2. Dyrektywa ciśnieniowa dot. Prostych zbiorników ciśnieniowych pV<10.000 bar cm3
3. Dyrektyw kompatybilnosci EM (Pr < 5 mW/cm2)
4. Dokumentacja techniczna
5. Dokumentacja pomiarów i prób technicznych
6. Certyfikat CE producenta (lub/i -jednostki akredytowanej)

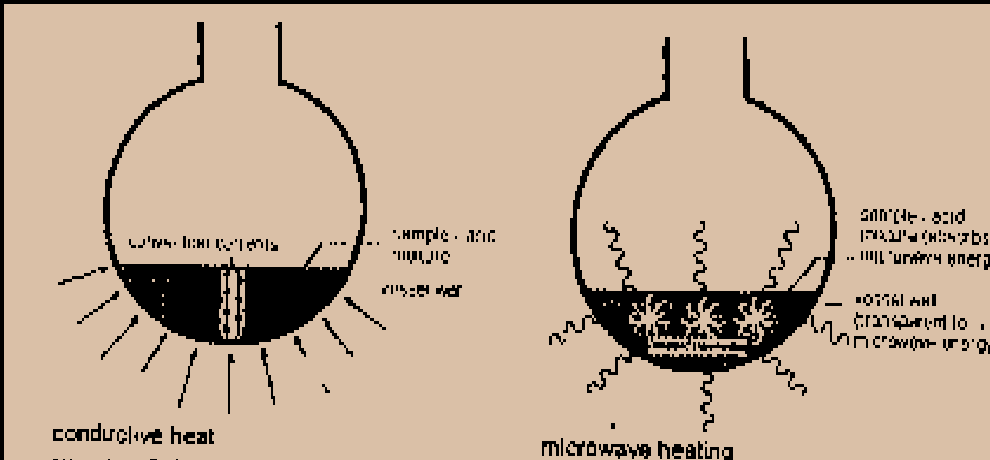


Fig. 1. Schematic of sample heating by conduction and microwave energy

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