

Theory of Sample Preparation Using Acid Digestion, Pressure Digestion and Microwave Digestion (Microwave Decomposition)

■ Introduction

Purpose: Quantitative determination of elements in solids generally through the employment of the following spectroscopic technologies.

As a rule, acid digestion procedures are employed for the determination of elements in solids subsequent to sampling and mechanical sample preparation in order to completely transfer the analytes into solution so that they can be introduced into the determination step (e.g., ICP-AES, ICP-MS, AAS or polarography) in liquid form. The goal of every digestion process is therefore the complete solution of the analytes and the complete decomposition of the solid (matrix) while avoiding loss or contamination of the analyte.

Goals:

- Complete solution of the elements;
- Complete decomposition of the matrix;
- Avoiding losses and contamination;
- Reduction of handling and process times.

For technicians, there is an additional need to ensure that the digestion is safe, reproducible and simple, that is, that it can be performed without excessive manual effort. Since sample preparation typically also consumes the largest share of task time, this process also has economic significance.

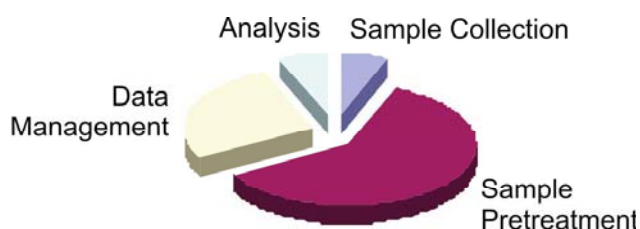


Figure 1: Distribution of task times to various task steps as a percentage

In this context, wet chemical digestions utilizing various mineral acids (e.g., HCl, HNO₃, HF, H₂SO₄, etc.), hydrogen peroxide and other liquid reagents is carried out in either an open system, that is, under atmospheric pressure, or in closed vessels. Further, the samples may be heated in convection or microwave ovens. Accordingly, these processes are described in the relevant literature more-or-less synonymously as acid digestion and pressure digestion or microwave digestion (microwave decomposition) and microwave pressure digestion.

The advantage of the closed procedure in comparison with open digestion in a recycling device or with the traditional "hot plate", lies in the significantly higher working temperatures which can be achieved.

While operating temperatures in open systems are limited by the boiling point of the acid solution, closed digestion vessels typically allow temperatures in the range of 200-260 °C to be reached. This results in a dramatic increase in the reaction kinetics, allowing digestions to be carried out in a matter of hours (pressure digestion with Tölg bombs [1]). However, this also makes it clear that the temperature represents what is actually the most significant reaction parameter. It is the ultimate determinant of the digestion quality, but also results in a pressure increase in the vessel and therefore in a potential safety hazard. Therefore, the pressure must ultimately also be considered.

In recent years, heating digestion solutions with microwaves has become increasingly popular. In this process the digestions are carried out in closed containers made of chemically inert materials which are transparent to microwaves.

Aside from the previously mentioned acceleration of the reaction kinetics resulting from the employment of a closed vessel, directly heating the sample solution leads to a further decrease in digestion times.

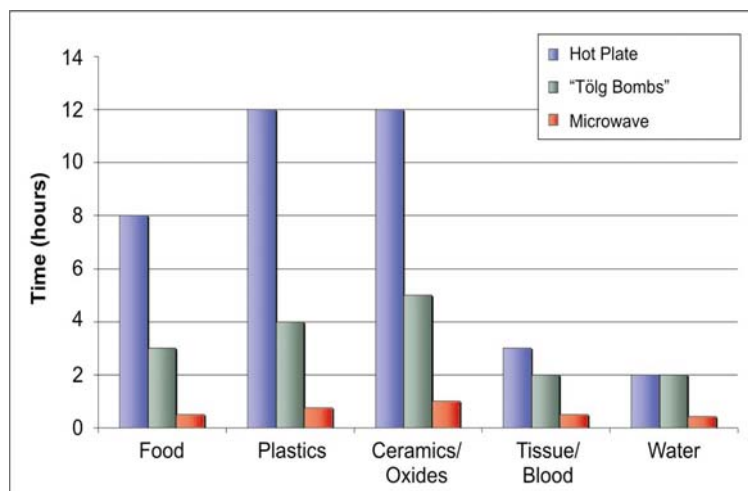


Figure 2: Times typically required for digestions

On the other hand, the special physical and chemical features of microwave heating do give rise to several problems which must be carefully considered during the design or selection of a microwave digestion or microwave decomposition system.

The actual heating in the microwave field is dependent on the type of sample, the sample quantity, etc. Only in rare instances will two samples exhibit exactly the same behavior. Therefore, for reasons of safety and in order to ensure optimum reproducibility, this unequal heating of samples in the microwave field must always be taken into consideration. The speed with which the samples are heated can result in exothermic reactions being induced during the digestion process, which is why a variety of sensor systems have been developed to monitor the pressure and temperature reaction parameters as well as to allow the microwave power to be controlled on the basis of readings returned by these systems.

Only materials which are totally chemically inert with respect to the employed mineral acids and reagents may be used in the design and construction of the pressure vessels. Particularly hard plastics (e.g., PEEK) are only transparent to microwaves and resistant to acids to a limited degree and are thus unsuitable.

■ The Chemistry of Acid Digestion

Acid digestions – whether open or closed pressure digestions – are carried out with the aid of a wide variety of reagents. Aside from the various mineral acids, other reagents such as hydrogen peroxide, potassium peroxide sulfate, boric acid, and many more are also employed. Naturally, the selection of the specific reagents or the preparation of a reagent mixture depends on the sample to be digested.

Organic sample materials are generally decomposed into carbon dioxide with the aid of oxidizing acids primarily nitric acid and reagents (primarily hydrogen peroxide) and completely mineralized. Before the oxidative attack, plastics are frequently dehydrated *in situ* by the addition of sulfuric acid. Caution is required during this procedure, particularly when dealing with reactive samples, that is, with materials (fats, oils, etc.) whose decomposition process under these conditions is exothermic. These types of samples can, however, be safely decomposed by slow heating rates or by heating to different temperature levels.

In contrast, the spectrum of inorganic sample materials is significantly broader. Even conditions during sample pretreatment, e.g., if a ceramic was fired at a low or higher temperature, can have an influence on whether a sample is easy or difficult to digest. In general, however, inorganic samples are also to be completely mineralized and dissolved. To do this, primarily acid mixtures of hydrochloric acid and/or hydrofluoric acid components are employed. However, the solubility of the resulting salts must be considered so that the solutions remain stable of longer periods of time.

Nitric acid	
	Oxidizing acid $(CH_2)_n + 2HNO_3 \rightarrow CO_2 + 2NO + 2H_2O$ Frequently mixed with H_2O_2 or HCl, HF, H_2SO_4 Boiling point: 122 °C (HNO_3 65%) Vapor pressure: ~25 bar (at ~225 °C) Forms soluble nitrates with all elements except: Au, Pt, Al, B, Cr, Ti, Zr
Nitric acid / hydrogen peroxide	
	Increased oxidation potential $2H_2O_2 \rightarrow 2H_2O + O_2$ Reoxidizes NO_x into NO_3^- and thus suppresses the formation of the yellow nitrous oxides typical of nitric acid. Typical HNO_3 mixture: $H_2O_2 = 4:1$
Hydrochloric acid	
	Non-oxidizing acid Boiling point: 84°C (HCl 32%) Vapor pressure: ~25 bar (at ~205 °C) Forms soluble chlorides with all elements except: Ag, Hg, Ti Dissolves the salts of weaker acids (carbonates, phosphates, borates) Digestion of iron alloys The following oxides are insoluble: Al, Be, Cr, Sb, Sn, Si, Ti, Zr
Nitro hydrochloric acid	
	$HCl : HNO_3 = 3:1$ Forms $NOCl$ and releases chlorine as the active component: $2NOCl \rightarrow 2NO + Cl_2$ Vapor pressure: ~25 bar (at ~200 °C) Digestion of precious metals, sulfides Fresh batches always prepared when required
Hydrofluoric acid	
	Non-oxidizing acid Decomposition of silicates $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$ Excess required otherwise there will be a loss of BF_3, SiF_4, GeF_4, SeF_4 Boiling point: 108 °C (HF 40%) Vapor pressure: ~25 bar (at ~240 °C) Usually employed in a mixture with other acids Digestion of minerals, ores, soil, stone and plants Complexing required to mask fluorides prior to further use: $H_3BO_3 + 4HF \rightarrow HBF_4 + 3H_2O$
Sulfuric acid	
	Non-oxidizing acid Dehydration of organic materials, particularly plastics Boiling point: 340 °C (H_2SO_4 98 %) Vapor pressure: negligible Usually employed in a mixture with other acids Digestion of plastics, ores, minerals Insoluble sulfates with Ba, Pb, Sr

■ Reagent Purity – Acid Purification by Means of Acid distillation or Subboiling

Basically, liquid reagents are commercially available in various suitable purity grades. Naturally, their price increases exponentially with the degree of purity. Alternatively, acids can also be purified for trace analysis by means of subboiling. BERGHOF offers special acid cleaning equipment for this purpose. The equipment is made entirely of plastic and can therefore also be employed for hydrofluoric acid.

Heating is contactless by means of an infrared lamp whose power is adjusted so that a maximum temperature approx. 10°C below the boiling point of the specific acid is maintained without the need for additional temperature regulation. Starting with commercial grade (analytic grade) acid, a simple acid distillation is already sufficient to achieve purity levels in the sub-ppb range. Multiple distillations will purify the acid still further.

Advantages:

- Can be used for HNO₃, HCl, HF and H₂O;
- Reduces costs for higher purity chemicals;
- Required purity levels always available fresh;
- Contaminated acid batches can be cleaned.

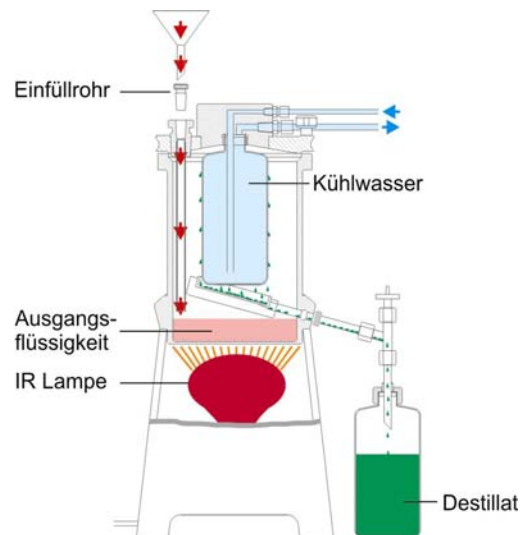


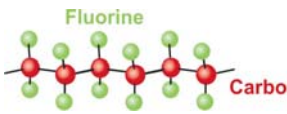
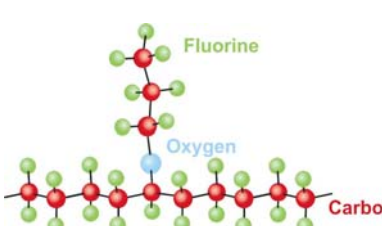
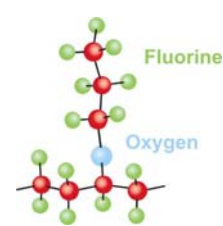
Figure 3: Cross-section BERGHOF subboiling BSB-939-IR

■ Vessel Materials

Naturally the employed vessels must be resistant to the acids and reagents being used. Glass (except for solutions containing HF), PP, PE and Teflon materials (primarily PFA) are therefore all suitable for vessels in which digestion solutions are to be stored.

The digestion vessels themselves, however, must be made of a Teflon material or quartz glass in order to ensure both chemical as well as temperature stability. In addition, optimized surface characteristics and reduced absorption and adsorption effects are also significant. TFMTM-PTFE has proven to be the material of choice for digestion vessels and is the only material used by BERGHOF. Of course, the use of quartz glass vessels always brings with it the risk of the glass breaking. Flaws caused by pressure stress over time and finally resulting in the glass breaking are frequently difficult if not impossible to detect. For this reason BERGHOF only offers quartz vessels as an optional insert to be used inside the actual digestion vessels themselves.

Compared to fluoropolymers, all other plastic materials exhibit a reduced chemical resistance so that their employment in digestion vessels must be viewed critically. Particularly PEEK (PolyEtherEtherKetone) is attacked by nitric acid and, under unfavorable conditions, can also absorb microwave radiation. This can result in vessel overheating up to the point of melting.

PTFE (polytetrafluoroethylene)  $-\text{[CH}_2\text{-CF}_2\text{]}_n-$ • Perfluorated plastic • Melting temperature, approx. 330°C • Can be used at temperatures up to + 260°C • Nearly universal chemical resistance • High purity
TFM™ – PTFE  $\left[\begin{array}{c} \text{CF}_3 \\ \\ (\text{CF}_2)_2 \\ \\ \text{O} \\ \\ (\text{CF}_2)_4\text{-CF-}(\text{CF}_2)_5 \end{array} \right]_n$ • Perfluorated plastic with perfluoroalkoxy side chain (<1 % by weight) • Melting temperature, approx. 330°C • Can be used at temperatures up to + 260°C • Nearly universal chemical resistance • High purity • Improved surface structure compared with PTFE
PFA  $\left[\begin{array}{c} \text{CF}_3 \\ \\ (\text{CF}_2)_2 \\ \\ \text{O} \\ \\ (\text{CF}_2)_2\text{-CF-CF}_2 \end{array} \right]_n$ • Perfluorated plastic with perfluoroalkoxy side chain (4-10 by weight) • Melting temperature, approx. 290°C • Can be used at temperatures up to + 220°C • Nearly universal chemical resistance • High purity • Improved surface structure compared with PTFE • Less resistant than PTFE and TFM™-PTFE
Quartz • Melting temperature > 1100°C • Can be used at temperatures up to + 300°C for digestion • Attacked by hydrofluoric acid • High purity

■ Open versus Closed Acid Digestion

Open acid digestions are performed either with a reflux system or in a beaker on a laboratory hot plate (hence the name, “Hot Plate Method”). Common to both methods is the temperature limitation as a consequence of the solution’s boiling point and the risk of contaminants from the air. Volatile elements such as mercury may be lost during the digestion process, leading to false results. The quality of the digestion is frequently unsatisfactory despite long digestion times of, typically, 2-15 hours.

The temperature limitation can be overcome by working with a closed pressure vessel. This results in a dramatic increase in the reaction kinetics, allowing acid digestions to be carried out in a matter of hours (pressure digestion with Tölg bombs [1]) or, if microwave heating is employed, in 20-40 minutes. However, this also makes it clear that the temperature represents what is actually the most significant reaction parameter. It is the ultimate determinant of the digestion quality, but also results in a pressure increase in the vessel and therefore in a potential safety hazard. Therefore, the pressure must ultimately also be considered.

Open acid digestion	Closed acid digestion
Max. temperature limited by the solution's boiling point	Max. temperature: 260-300°C
Permits large sample weigh-ins	
High acid consumption	Reduced acid consumption resulting in reduced blank values
Digestion quality frequently unsatisfactory	High digestion quality
Loss of volatile elements (e.g., Hg, Pb salts)	No loss of volatile elements
Contamination risk	
Digestion duration: 2-15 hours	20 to 60 min. (microwave digestion) 2 to 5 hours (Tölg bombs)

Regardless of the heating process used (conventional or microwave), the pressure development during closed acid digestion is a product of the acid mixture's vapor pressure at the employed temperature and the possible formation of gaseous substances (generally carbon dioxide during the digestion of organic samples). While tables provide the vapor pressure of acids, the partial pressure of the carbon dioxide can be estimated using the ideal gas equation and the sample weigh-in.

Example:

Digestion of 500 mg of carbon in HNO ₃ at 200°C; vessel capacity: 60 ml.
$p(\text{CO}_2) = 6.9 \cdot m_c [\text{g}] \cdot T/V [\text{K/ml}]$ $V = 60 \text{ ml}, 0.5 \text{ g carbon}, 200^\circ \text{ C} \rightarrow p(\text{CO}_2) = 26 \text{ bar}$ Total pressure: = $p(\text{CO}_2) + p(\text{acid}) = 26 + 10 \text{ bar} = \text{approx. } 36 \text{ bar}$

■ Practical Pressure Digestion Procedures

A) Pressure Digestion in “Tölg Bombs” [1]

It has been more than 30 years since BERGHOF introduced a series product based on the pressure digestion method developed by Prof. Tölg [1]. Since this time, BERGHOF has sold these stainless steel pressure digestion vessels with a TFM™ PTFE liner under the trade name, **digestec**. The vessels are available in a variety of capacities ranging from 25 to 250 ml, a max. operating temperature of 260 °C, and a max. operating pressure of 200 bar. In any case, safety is assured by an appropriately dimensioned pressure relief device. For safety reasons, heating takes place in special heater blocks and not in a laboratory oven. Therefore, digestion is generally carried out at a specific external temperature. This leads due to the thermal isolating effect of TFM™-PTFE liners to a slow, gentle and therefore safe heating of the samples. Final operating temperatures are typically reached after 45-60 min.

Due to the high max. operating pressure of 200 bar and the max. operating temperature of 260 °C, these systems are capable of completely digesting nearly any sample and transferring them into solution. A decisive advantage of this methodology lies in the ability of extending the digestion period nearly indefinitely. This allows even the hardest samples (e.g., SiC, $\alpha\text{-Al}_2\text{O}_3$) to be completely dissolved.

The **digestec** digestion system therefore offers the highest possible level of flexibility and represents an economical alternative to microwave digestions or microwave decomposition, particularly for laboratories which only process a limited number of samples.



Figure 4: BERGHOF Stainless steel pressure digestion system with a 12-sample heating block and temperature regulator

Application examples for pressure digestion in stainless steel pressure digestion systems

Matrix	Sample weight [mg]	Acid	Temperature [°C]	Time [h]
Cellulose / starches	1,000	HNO ₃	140-160	1-2
Leaves / grain	1,000	HNO ₃ / HF	150-180	2-3
Tissue / liver	1,000	HNO ₃	170-190	2-4
Fats / oils	500	HNO ₃ (H ₂ O ₂)	180-200	3-4
Plastics	1,000	HNO ₃ / H ₂ SO ₄	180-200	3-4
Coal / resins	500	HNO ₃	200-240	3-8
Stone	1,000	HF / HCl / HNO ₃	180-200	2-3
Ceramics / oxides	500	HF or HCl	180-250	2-16
SiC	250	HNO ₃ , HF, H ₂ SO ₄	250	12-72

B) Pressure Digestion with Microwave Heating - Microwave Digestion or Microwave Decomposition

In contrast to the pressure digestion systems described above, samples in digestion equipment heated by microwaves are heated directly by the absorption of microwave radiation. This allows for an extremely rapid, simultaneous heating of, typically, 8-12 sample solutions which represents the actual "microwave effect" or advantage of microwave heating. Once the setpoint temperature is reached, the decomposition reactions proceed at the same rate as in conventionally heated stainless steel pressure digestion vessels. Thus, typical microwave digestions take merely 20-40 minutes. The strength of microwave digestion lies in its significantly higher sample throughput resulting from the decrease in the duration of digestion.

However, since this rapid heating is accompanied by an equally rapid pressure increase and, possibly, spontaneously induced exothermic reactions, the temperature progression of each sample must be continuously recorded and the microwave power must be regulated accordingly. From a safety aspect, it is therefore most practical that the pressure progression be re-corded in parallel with the temperature and that this measurement also be employed to influence power regulation. In this way, an optimal process control can be achieved, particularly from the point of view of safety.

It is on the basis of these underlying considerations that BERGHOF designed its **speedwave MWS-3+** microwave digestion system. Technologies specifically developed and patented to measure both temperature and pressure were implemented for this application. With the aid of a mid-IR thermometer, the temperatures of all samples solutions are measured directly, that is, without time delay and without contact, by measuring the development of the vessel wall temperature.

The decisive advantage of this sensor lies in the fact that the heat radiated by the sample is directly measured through a window in the vessel while conventional IR sensors merely measure the heat radiated by the vessel itself. The optional optical pressure monitoring permits the acquisition of the internal pressure of all vessels (also contact-free). Neither technique requires the measurement of a reference vessel. Combined, temperature and pressure monitoring offer optimal process control, particularly from the point of view of safety.

Beyond this, thanks to the unique top-loading design, together with vessels consisting of only a few components, handling is as simple as possible. The digestion vessels themselves have been designed to provide a long service life.



Figure 5: BERGHOF speedwave MWS-3+ microwave digestion systems

Application examples for pressure digestion in microwave pressure digestion systems

Matrix	Sample weight [mg]	Acid	Temperature [°C]	Time [min]
Cellulose / starches	500	HNO ₃	160	25
Leaves / grain	500	HNO ₃ / HF	190	30
Tissue / hair / blood	50-250	HNO ₃	170-190	25
Fats / oils	700	HNO ₃ (H ₂ O ₂)	180-210	30-40
Plastics	700	HNO ₃ / H ₂ SO ₄	180-210	45-60
Coal / coke	250	HNO ₃ , HF, H ₂ SO ₄	200-240	45-60
Stone	1,000	HF / HCl / HNO ₃	180-200	30
Ceramics / oxides	500	HNO ₃ / HF / HCl	180-250	45-90

■ Temperature Measurement

The non-contact method for temperature measurement in microwave heated pressure vessels patented and perfected by BERGHOF proved over the last years to be the fastest, easiest and cleanest method for temperature measurement in microwave digestion.

Infrared temperature measurement is based on the physical fact, that each solid body emits heat radiation which depends only on his temperature and emission coefficient. At temperatures above 500°C the maximum of this irradiation is in the infrared frequency range. The exact formula for this phenomena was developed by 'Boltzmann':

$$S = \alpha T^4$$

As most bodies absorb also infrared irradiation it is generally only possible to detect the temperature by this principle of bodies on which surface the view is unhindered. This means that there is no other infrared-absorbing object between the sensor and the body. This is why, by the conventional broadband measuring sensors only the vessel surface temperature can be detected and not the sample temperature itself.

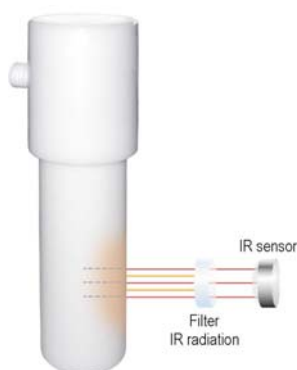


Figure 6: BERGHOF mid-IR measuring principle to determine the sample temperature

Therefore the only useful method could only be based on a detection of the heat radiation in a frequency range where the vessel material is transparent. By this the real sample temperature is determined easily and directly in real time.

The accuracy of this measurement is further improved by filtering out the irradiation emitted by the surface of the digestion vessels. From the detected infrared-radiation and the 'Boltzmann' equation, modified for this frequency range, the sample temperature is calculated in real-time.

It is possible with this technology to detect the sample temperature in Teflon-vessels and their quartz inserts inside a microwave oven in a measurement range from 100 to 300 °C. The precision is relative high (+/- 1 °C at 200 °C). Only through the precise knowledge of all sample temperatures inside the microwave oven the microwave power could be regulated in an optimal way.

■ Pressure Measurement

The latest development from the house of BERGHOF is a non-contact, optical pressure measurement in all digestion vessels specifically developed for microwave digestion systems.

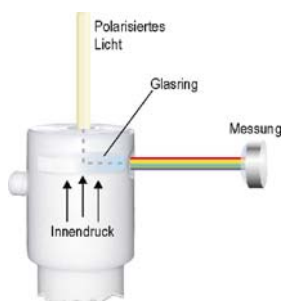


Figure 7: BERGHOF Principle of measurement for monitoring pressure

The method is based on the measurement of the change of the optical properties of a glass ring, which is permanently integrated in the pressure vessel lid as sensor element.

If illuminated by polarized light this ring causes a change in color of the transmitted light, which is proportional to the internal pressure of the vessel. The internal pressure is transferred directly to the glass ring by the TFM lid with its sliding lip seal.

The glass ring in each lid is mounted in such a way that it does not need to be reinstalled for every new digestion and therefore the ring has absolutely no effect on vessel handling. No additional time and labor is necessary for the connection of sensors.

At every full rotation of the turntable, i.e. every ten seconds each digestion vessel passes through an optical system comprising a polarized light emitter and a light receiver. During this time the pressure of all vessels in the microwave is determined simultaneously to the above de-scribed temperature measurement. The pressure curve is displayed in real-time on the controller and memorized for all vessels. The precision of this method is ± 5 bar (± 72 psi) over the complete operating range from 0 to 120 bar (0 – 1740 psi) and therefore more than sufficient for the safe control of digestion processes.

The **speedwave MWS-3+** is continuously controlled by both measured temperature and pressure data. The microwave is controlled solely by the temperature as long as the internal pressure of the vessel is far less than the pre-set maximum pressure. For this pressure limit any values from '0' to the maximum pressure of the vessel type are allowed and could be defined by the operator.

If the internal pressure of the vessel approaches the maximum pressure limit of the vessel the microwave power is adjusted accordingly and thereby the burst of rupture discs prevented effectively.

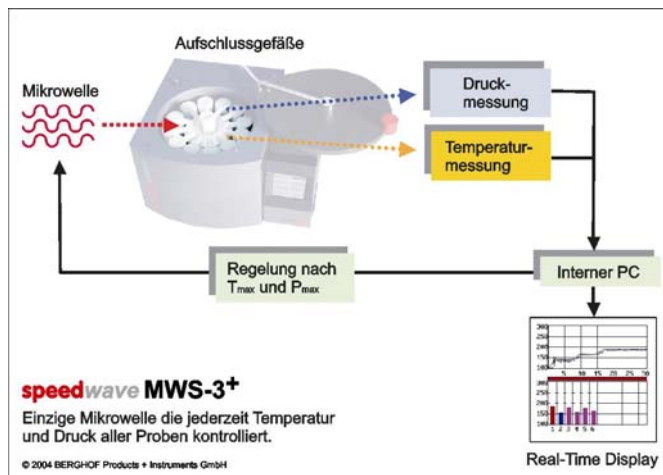


Figure 8: Principle of the microwave control mechanism

■ Special Characteristics of Microwave Digestion or Microwave Decomposition

Certain microwave effects such as the unequal heating of samples and blank solutions can only be indicated with the aid of mid-IR sensor technology.

Ions in the sample inevitably increase the absorption of microwave radiation by the solution which results in blank solutions only being able to be heated to temperatures approx. 20-30 °C lower. This effect is illustrated on the right.

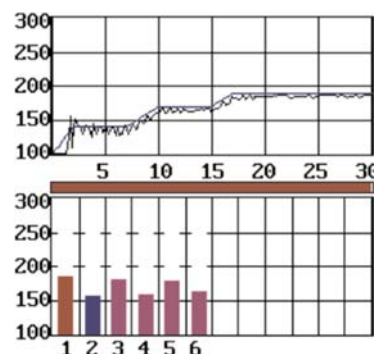


Figure 9: Digestion of samples (vessel 1,3 and 5) blank solutions (vessel 2,4 and 6)

Only through the precise knowledge of all sample temperatures can the microwave power optimally regulated. The speed of mid-IR temperature sensor is illustrated below. Here a typical, fast and exothermic reaction was detected in the heating-up period and corrected by the control mechanism. As the short temperature peak indicates, an exothermic reaction was induced during the heating-up phase. This resulted in an extremely rapid heating of the sample by reducing the microwave power the temperature of the sample was rapidly regulated to the setpoint temperature.

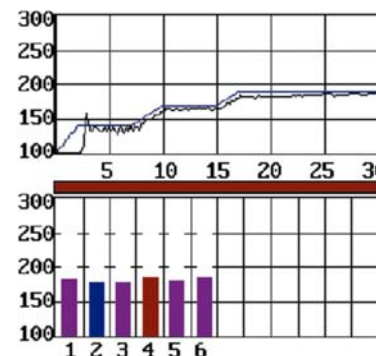


Figure 10: Control of fast exothermic reactions

Thanks to the added information gained from the precise knowledge of the pressure and temperature progression, method development and optimization times for a process can be shortened. The example on the right illustrates the maximization of the sample weigh-in.

Powdered coffee was digested in 6 vessels with weigh-ins ranging from 50 to 300 mg. It is quite apparent that the pressure (right-hand bar) increases with sample weight. This information gain aids in optimizing method development and thus helps save time.

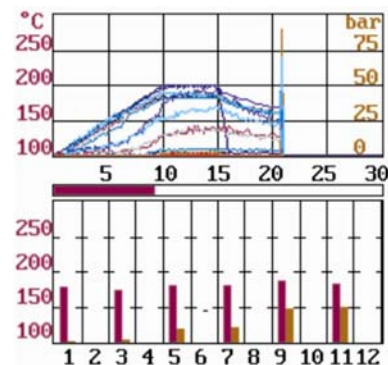


Figure 11:
Gain on information due to pressure monitoring

■ Summary

The described technologies for monitoring temperature and pressure enable for the first time to detect both parameters in real-time simultaneously during microwave digestion. All sample pressure and temperature curves are memorized.

The advantages for the user are:

- The system offers optimal safety through continuous monitoring of all critical reaction parameters, e.g. temperature and pressure.
- The measurement interval depends on the rotational speed of the turntable. For method development of new, unknown samples the turntable is stopped and a single sample is positioned directly in front of the sensor thus reducing the measurement interval to <1 sec.
- All electronic components are outside of the pressure vessels and the microwave field. By this contamination of the samples or damage of sensors are impossible, thereby reducing costs of ownership.
- Both sensor systems are maintenance free and therefore very economic.
- Pressure vessels require no additional connections for sensors and are therefore optimally manufactured with smooth surfaces and without "dead" volumes. There is no additional labor needed for vessels handling as no sensors inside the pressure vessel have to be mounted, removed and cleaned for each digestion.

Literature:

[1] L. Kotz, G. Kaiser, P. Tschöpel und G. Tölg Z. Anal. Chem. 260, 207-209 (1972).