

Sample preparation using pressure digestion

by Dr Dieter Gutwerk

Today practically any sample material can be digested with an appropriate pressure digestion system. In the majority of cases, microwave-heated systems are the more economical solution due to their higher sample throughput over a given period of time. However, the "classical" stainless steel pressure digestion vessels continue to be the systems of choice when samples are particularly difficult to digest, when high sample throughput is not required, or when the highest possible degree of flexibility is desired.

All analysts long for a universal method that can process all samples prior to subsequent analysis. Pressure digestion of samples is one such universal procedure and is therefore one of the standard sample preparation procedures currently employed in analytical chemistry for element quantification. In brief, in pressure digestion the sample material is placed in a sealed chamber with an acid mixture and heated to a temperature, typically between 200 and 260°C, at which point it is completely decomposed and is solubilised.

Compared to open digestion under reflux or with the traditional "hot plate", the advantage of the pressure digestion method is that significantly higher working temperatures can be achieved. Whereas in open systems the temperatures are limited by the boiling point of the acid solution, temperatures in the 200-260°C range can be typically achieved in sealed digestion vessels. This results in a dramatic acceleration of the reaction kinetics, allowing digestion reactions to be carried out in a matter of hours in the case of pressure digestion using Tölg bombs or in less than an hour in the case of microwave digestion. In both these methods it is clear that the temperature itself is actually the most significant reaction parameter. Although it is the ultimate determinant of the digestion quality, it also results in a pressure increase in the vessel and therefore in a potential safety hazard. As a consequence, pressure aspects, which are independent of the heating method, must always be considered as well. The following article is intended to offer a more detailed discussion of the differences between these two possible practical procedures, their relative advantages and suitable application areas.



Figure 1. Stainless steel pressure digestion system with a 12-sample heating block and temperature regulator.

Pressure digestion in "Tölg Bombs"

It has now been more than 30 years since Berghof introduced a range of products based on the pressure digestion method originally developed by Prof. Tölg [1]. Since then, Berghof has sold these stainless steel pressure digestion vessels with a chemically modified PTFE liner, namely TFM PTFE, under the trade name "Digestec" [Figure 1]. The vessels are available in a variety of capacities ranging from 25 to 250 mL, a maximum operating pressure of 200 bar, and a maximum operating temperature of 260°C. For safety reasons, the heating takes place in special heater blocks and not in a laboratory oven. The digestion is therefore generally carried out at a specific external temperature. Internal pressure development is practically irrelevant both because of the high pressure loads which the stainless steel containers are capable of withstanding, and because of the slow heating rate. In any case, safety is assured by an appropriately dimensioned pressure relief device.

Due to the high maximum operating pressure of 200 bar



Figure 2. MWS-3+ microwave digestion system.

Matrix	Sample weight	Acid	Temperature	Time
Cellulose / starches	1000 mg	HNO ₃	140-160°C	1-2 hr.
Leaves / grain	1000 mg	HNO ₃ / HF	150-180°C	2-3 hr.
Tissue / liver	1000 mg	HNO ₃	170-190°C	2-4 hr.
Fats / oils	500 mg	HNO ₃ (H ₂ O ₂)	180-200°C	3-4 hr.
Plastics	1000 mg	HNO ₃ / H ₂ SO ₄	180-200°C	3-4 hr.
Coal / resins	500 mg	HNO ₃	200-240°C	3-8 hr.
Stone	1000 mg	HF / HCl / HNO ₃	180-200°C	2-3 hr.
Ceramics / oxides	500 mg	HF or HCl	180-250°C	2-16 hr.
SiC	250 mg	HNO ₃ , HF, H ₂ SO ₄	250°C	12-72 hr.

Table 1. Examples of applications of pressure digestion in stainless steel pressure digestion systems.

Matrix	Sample weight	Acid	Temperature	Time
Cellulose / starches	500 mg	HNO ₃	160°C	25 min.
Leaves / grain	500 mg	HNO ₃ / HF	190°C	30 min.
Tissue / hair / blood	50-250 mg	HNO ₃	170-190°C	25 min.
Fats / oils	700 mg	HNO ₃ (H ₂ O ₂)	180-210°C	30-40 min.
Plastics	700 mg	HNO ₃ / H ₂ SO ₄	180-210°C	45-60 min.
Coal / coke	250 mg	HNO ₃ , HF, H ₂ SO ₄	200-240°C	45-60 min.
Stone	1000 mg	HF / HCl / HNO ₃	180-200°C	30 min.
Ceramics / oxides	500 mg	HNO ₃ / HF / HCl	180-250°C	45-90 min.

Table 2. Examples of applications of pressure digestion in microwave-heated pressure digestion systems.

and the maximum operating temperature of 260°C, these systems are capable of completely digesting nearly any sample and rendering it soluble. A clear advantage of this methodology lies in the ability to extend the digestion period nearly indefinitely. This allows even the hardest samples (e.g., SiC, alpha Al₂O₃) to be completely dissolved [Table 1]. The digestec system thus offers the highest possible level of flexibility and is a cost-effective alternative to microwave digestion, particularly for laboratories which only process a limited number of samples.

Pressure digestion with microwave heating

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 extremely rapid, simultaneous heating of typically 8-12 sample solutions. Once the previously set temperature point is reached, the decomposition reactions proceed at the same rate as in conventionally heated stainless steel pressure digestion vessels. Thus, typical microwave digestions overall take only 20-40 minutes. As illustrated in Table 2, microwave digestions are currently employed for a huge range of sample types and have therefore replaced stainless steel pressure digestion vessels in all applications other than the specialised niche applications cited above. The success of the microwave digestion technique lies in

its significantly higher sample throughput which is a result of the decrease in the digestion time.

However, since this rapid heating is accompanied by an equally rapid pressure increase, and possibly by spontaneously induced exothermic reactions, the development of the temperature of each sample must be continuously monitored and the microwave power should be adjusted accordingly. From a safety point of view, it is therefore desirable that the pressure development be recorded in parallel with the temperature and that this is used to regulate the power. In this way, an optimal process control can be achieved, particularly from the point of view of safety.

With these basic design considerations in mind, Berghof has developed the speedwave MWS-3+ microwave digestion system [Figure 2]. Proprietary methods for the dual measurement of temperature and pressure were specifically developed and incorporated in the new system. A mid-IR thermometer is used to measure the development of the temperature of the vessel wall, so that the temperatures of all sample solutions can be assessed directly, that is, without any time delay and without contact with the sample. An optional optical pressure monitoring system that also does not require direct contact with the sample enables the determination of the internal pressure on all vessels. Neither measurement technique requires the use of a reference vessel. Taken together, the temperature and pressure monitoring systems offer optimal process control, particularly from the point of view of safety.

In addition to this, practical sample handling is extremely easy and simple, thanks to the unique top-loading design and the fact that the vessels only consist of a few components. The digestion vessels themselves have been designed to provide a long service life.

References

1. Kotz L, Kaiser G, Tschöpel P and Tölg GZ. Anal Chem 1972; 260: 207.

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