4. Digestions

Dana Zimmer, Rhena Schumann

Materials with dominantly mineral matrix, such as soils, can be digested by aqua regia without previous ashing. If material with more than 30 % of organic matter (OM) is not ashed before digestion, this material should be extracted with HNO_3 plus H_2O_2 instead of digestion with just HNO_3, since digestion only with HNO_3 might be incomplete. This is especially the case, if hardly decomposable material such as wood or potato tubers have to be digested. Herbaceous subsurface plant biomass can be digested well by HNO_3. However, the extract often has a green to yellow colour, which does not allow photometric determination of P. Dried peat, digestates and suchlike should be digested with H_2O_2 plus HNO_3 as well to guarantee complete decomposition. Currently, few experiences exist for microwave extractions of (dried) animal material and organic-rich muds. According to information from CEM, fish and suchlike can be digested in wet as well as in dry state in a microwave with concentrated HNO_3. Water samples (seston, rainwater) are mostly digested by peroxide sulphate. P concentrations in water samples are mostly low. Therefore, P is analysed photometrically, because of the lower detection limit compared to the ICP-OES.

4.1 Microwave Digestions

For aqua regia and nitric acid digestions, samples have to react with the acids overnight under a fume hood to avoid too high pressure in the vessels due to the development of gases by decomposition of organic matter. This precautionary measure is not necessary, if ashes are processed. It is also not usual for water samples.

Samples with high OM concentrations such as bone char have to be monitored during digestion in the microwave for temperature and pressure. Vessels from older microwave systems have to be tested if they resist the potential pressure (check manufacturer specifications). Microwave vessels have to be renewed if necessary. Plant and animal tissues have high P concentrations and therefore the weigh-ins must be very low (mg range). Least material losses, for example during transfer to digestion vessel or subsequent dilution, can affect precision and accuracy.

If samples with > 1 % carbonate (e.g. carbonate containing soil, calcareous muds, mussel shells) have to be digested with aqua regia or HCl, the

carbonate has to be decomposed with HCl previously (note weigh-in and out before and after carbonate decomposition). Otherwise, carbonate reacts to CO_2 after addition of HCl und the sample bubbles outside the vessel and some of the HCl is consumed as well. The mixing ratio of HCl and HNO_3 has to be maintained.

Dry material should be weighed in for microwave digestion. If complete drying is not possible, wet or sticky material must not maintain at the vessels wall. Sample material has to be at the bottom of the vessel and has to be covered with extracting agent. Otherwise sample material can burn in the vessel wall and damage the vessel. Such damaged vessels must not be used for further digestions!

During one microwave process only very similar samples may be digested with the same extracting agent, to guarantee homogeneous development of temperature and pressure. Therefore, all microwave places should be filled. If this is not possible, it has to be considered that not more than two places are empty side by side (better only one empty place). Blanks count as empty places. The minimum number of samples per digestion run can be found in the manual of the microwave (e.g. Mars 5 Xpress, Fa. CEM)

Even modern microwaves, which can control energy input according to temperature or pressure in digestion vessels, can only give the same energy input to all vessels. Very new control units such as Mars 6 Xpress, Fa. CEM have the possibility to remove empty places from energy control/ temperature measurement. This possibility can also be used for vessels with blank samples. In this way the blank vessels get the same energy such as the samples. Standards, which are not standard soils or similar materials, but organic P-containing compounds such as diphenyl- or glucose-6-phosphate need less energy compared to blanks. Therefore, they should be handled like blanks.

After digestion and time for cooling down, microwave vessels have to be opened slowly and carefully under the fume hood, because a high pressure is possible in the vessels. This is especially important for organic-rich samples and unknown matrices. As soon as the vessels have been emptied, they have to be placed in cold water and rinsed (removal of residues of acids and mineral particles). Subsequently, vessels have to be placed overnight in an alkaline, phosphate-free purification bath. On the next day, vessels have to be cleaned by a soft brush and rinsed with ultra-pure water. The inner wall of the vessels has to be controlled for scratches. Vessels with scratched or melted inner wall must not be used again, they have to be disposed. This may cause high costs.

There are some new microwaves, which can digest samples one after the other and without pressure (e.g. CEM Discover SP-D). These microwaves have an automatic sampler for 24, 48 or 72 places. Each vessel is separately closed and temperature- and pressure-controlled irradiated after the other. In this way, different samples can be processed after the other. The digestion time is 10 minutes for each sample. Therefore, the total time is not much longer than for a common microwave.

For heavy metal analytics in the trace level vessels have to be cleaned with diluted nitric acid for some hours or overnight. Finally, they have to be rinsed with ultra-pure water (0.05 µS cm^{-1}). After digestion of a sample series microwave vessels should be cleaned with nitric acid by a cleaning program in the microwave.

Water samples (seston and free dissolved nutrients) can be digested in microwaves as well. The very low concentrations of OM enabling digestion with "soft" extracting agents in low concentrations. Especially for this reason, the energy input has to be secured, that means that all closures have to be completely tight, not to impede pressure development (Fig. 4.1-1, 3 very low results). Natural material fatigue can impede pressure development within a few years for some products. Under these circumstances the vessels have to be renewed. Sample volumes are 10 to 50 ml. Samples with low element concentrations (< 1 µm L^{-1}) need ultra-clean vessels (Fig. 4.1-1, 1 very high result).

The described procedure applies for phosphorus and metals, but it is the same for usage of vessels for nitrogen as well. Therefore, it can be an advantage to use separate vessels for phosphorus, metals and nitrogen. This may be a cost factor, because one vessel costs around 100 €. Samples in fig. 4.1-2 were digested in the same microwave (without temperature and pressure control) such as the TP-samples but in new vessels. The reproducibility is much better in new vessels (lower interquartile range).

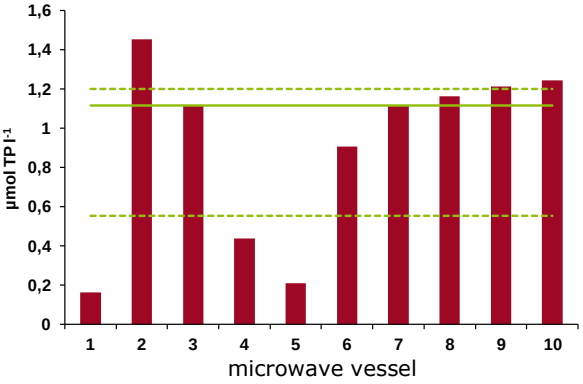

Figure 4.1-1 10 replicates of a sample from Vitter Bodden, date: 05.07.2013 for TP (µmol L^{-1}) in digestions with incomplete yield

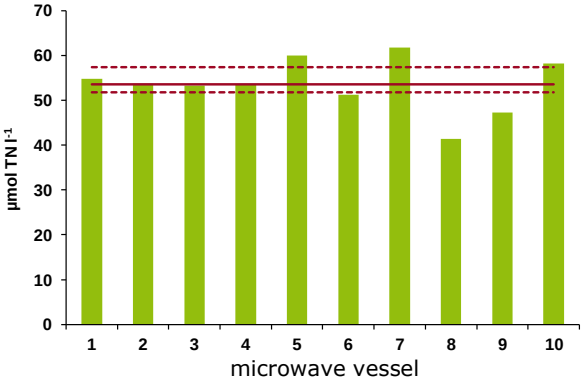

Figure 4.1-2 10 replicates for TN same samples like in Fig. 4.1-1. The vessels for TN were new. Bars: single values, Line: Median, dotted lines interquartile range

For citation: Zimmer D, Baumann K, Berthold M, Schumann R (*insert year of download*): Handbook on the Selection of Methods for Digestion and Determination of Total Phosphorus in Environmental Samples. Version 1.0. DOI: 10.12754/misc-2020-0001