

## 4. Digestions

### 4.1 Microwave Digestions

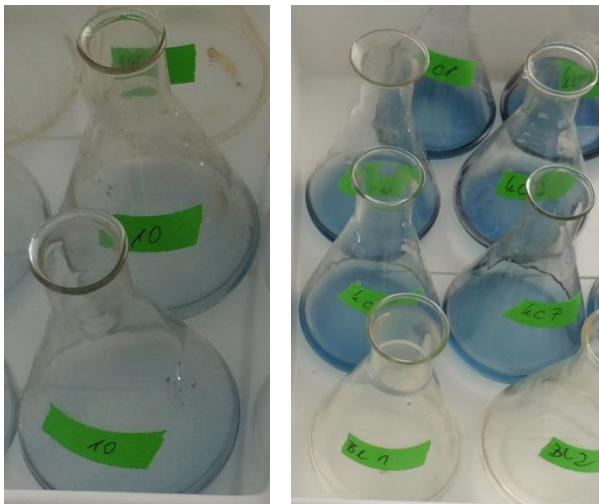
#### 4.1.2 Aqua regia: soil

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#### Suitability

The *aqua regia* digestion is suited for mineral soils, sediments, muds and ashes (e.g. Fe, Mn, Al, Na, Ca, K, Mg, P). Soils or sediments with high amounts of iron should not be ashed (chapter 3.3). Vessels for digestion must be cleaned by acids if trace element analytics (e.g. Cd, Cu, Pb, Zn) is planned as well.

Aqua regia cannot be used if it is planned to determine phosphorus photometrically (with molybdate in the reagent; Hansen & Koroleff 1999, chapter 5.2.3). Storage of the very acidic extracts in PE-tubes can cause further problems: too high P concentrations would be determined photometrically. (Fig. 4.1.2-1). Such extremely false-positive results were also found for other acidic extracts stored in PE-tubes (Fig. 4.1.2-2). The cause of the problem could not be clarified. Therefore, acidic extracts have to be neutralised before storage. It is assumed that this problem is caused by plasticisers.



**Fig. 4.1.2-1** Samples of aqua regia-digested bone char (BC) in the concentration range 6-9  $\mu\text{M}$  (diluted 1:10) with too dark blue colouring. These extracts were not neutralised and stored frozenly in PE-tubes. Below blanks, left 10  $\mu\text{M}$  phosphate standards without digestion.



**Fig. 4.1.2-2** Non-neutralised blanks (digestion in neutral persulfate solution), stored overnight in centrifuge tubes with extremely deep blue colouring. KW: Kraftwerkswasser (very clean, P-free water from "Kraftwerk Rostock")

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Silicates are not destroyed during *aqua regia* digestion. Therefore, element concentrations are so-called pseudo-total element concentrations of soils. (DIN 16174; 70-90% of element concentrations compared to methods with silicate destruction). Nevertheless, *aqua regia* digestions are handled as total element digestions in soil science (e.g. BBoSchutzV). For complete silicate digestions hydrofluoric acid and perchloric acid are necessary (DIN 14869-1). These digestions can only be processed in a few laboratories because special fumes and safety precautions are necessary!

Besides P, elements, which affect P availability and binding, are interesting in soil samples: Fe, Al, also Ca (chapter 5.1). Common quantification of P with Al, K, Mg, Mn, Zn is usual as well. For trace element analytics concentrations of Cd, Cu, Ni and Pb are often determined.

For example, Cu and P cannot be detected simultaneously by ICP-OES, because their wavelengths for detection are too similar. Some other heavy metals can cause problems in ICP-OES analytics and therefore an adjustment of it might be necessary: e.g. As and Hg. Other elements are measurable by ICP-OES but can pollute the nebulizer in higher concentrations: Na and S.

### **Concentration range**

The concentration range and limit of detection for P strongly depends on selection of the detection method. Generally, the ICP-OES is the method with the highest (that means worst) limit of detection and quantification (chapter 5.1). However, it is possible to increase material weigh-in and amount of extraction agent to adjust the concentration in the measurement solution to achieve the measurement range of the instrument.

Generally, the ICP-OES can detect all P compounds in the measurement solution and not only "free" phosphate. However, this might not cause any differences because strong digestion conditions converted almost all P compounds to phosphate. An advantage of the ICP-OES is the wider measurement range than those of photometrical methods (chapter 9), which can decrease potential errors by dilution.

Detection of P in nitric acid containing solutions is possible by vanadomolybdate-yellow (chapter 5.2.5). However, the sample weigh-in has to be relatively high to exceed the limit of quantification ( $0.3 \text{ mg P l}^{-1}$  or  $9.7 \text{ } \mu\text{mol l}^{-1}$ ) in the extract.

## Protocol

### Day 1: Preparation

- ▶ put on your protective clothing (gloves, coat, glasses)
- ▶ weigh in ca. 0.5 g air-dried fine soil (if necessary mortared, soil < 1 % carbonate) in Teflon vessels of microwave (note precise mass)
- ▶ add 6 ml conc. HCl under the fume hood (clean inner vessel wall thereby from sample material) and subsequently add 2 ml conc. HNO<sub>3</sub> to the soil sample (both acid with dispensers made from acid-resistant ceramic)
- ▶ Place standards (chapter 6.6) and 2 blanks (6 ml conc. HCl and 2 ml conc. HNO<sub>3</sub>) per run in the microwave.
- ▶ Set vessels with soil samples with acids open under the running fume hood overnight.

### Day 2: Digestion

- ▶ Close vessels, mark blanks and dissolved standards as "empty place" (if possible, in the microwave), operate microwave according to the instructions (see below), cool down for around 1 h.
- ▶ Transfer extraction solution via (plastic) funnel in 50 or 100 ml (plastic) volumetric flask (Fig. 4.1.2-3).
- ▶ Rinse microwave vessel and funnel with ultra-pure water into the volumetric flask and fill flask with ultra-pure water to 10, 25, 50 or 100 ml. This volume has to be exact because the element concentration is calculated from this volume.
- ▶ Silicates (pieces of sand and suchlike) are not destroyed in the *aqua regia* digestion, but the solution has to be clear. Otherwise it has to be assumed that the digestion was not complete and has to be repeated.
- ▶ Filter (e.g. Macherey-Nagel™ folded filter papers MN 612 retention 5-8 µm or phosphorus-poor MN 616 G retention 4-12 µm) the extraction solution into (acid-rinsed) polyethylene bottles (reference sample).
- ▶ Fill around 20 ml of solution into "ICP-vessels" or for photometric determination.
- ▶ Neutralise solution before storage for photometric P-detection (chapter 4.2).



**Figure 4.1.2-3** Volumetric flasks with funnels for filtration of soils, vessels of microwave in burst protection covers (MarsXpress)

**Table 4.1.2-1** Digestion program for microwave MarsXpress for *aqua regia* digestion of soils

Level	Max. Power (W)	Power (%)	Temperature (°C)	Holding (min)
1	1200	100*	160	15:00

\* Settings for "Power" depend on numbers of sample-filled vessels: 8-12 vessels (50 %), 13-20 vessels (75 %) and > 20 vessels (100 %).

### Day 3: Measurement

- ▶ Determination of P at the ICP-OES (wavelengths for P 214,914 or 213,617 nm, chapter 5.1)
- ▶ or with vanado-molybdate-yellow at the photometer (chapter 5.2.5).

### References

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