

3. Preparation of Samples

3.4 Removal of Carbonate

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If carbonate concentrations – especially in soil and sediment samples – exceed 1 to 2 %, this carbonate has to be removed before digestion with *aqua regia*. Otherwise, carbonate reacts to CO₂ after addition of HCl and the sample bubbles outside the vessel and some of the HCl is consumed as well. Carbonate-containing samples have to be tested before adding concentrated HCl; slight bubbling in vessels could be acceptable.

If several grams of material are necessary, carbonate removal such as for grain size analysis is applicable (DIN ISO 11277). For small amounts of samples (mg) carbonate removal according to Harris et al. (2001) is more suitable. However, this method has not been tested so far in the labs of the working groups Soil Science or Applied Ecology and Phycology. The necessary sample mass has to be estimated from carbonate concentrations in samples, since carbonate is lost as CO₂ and sample material has to be sufficient for digestion. For soil samples with more than 50 % carbonate, which were prepared for grain size analysis, the procedure according to DIN ISO 11277 did not work. Even after several days with repeated HCl addition, large quantities of CO₂ bubbles build up. Therefore, the test for carbonate removal was aborted. For sediment samples with high concentrations of organic matter (OM) and carbonate, which would be ashed anyway, it could be considered to decompose carbonate by temperatures between 900 and 1000 °C. The three described methods below for carbonate removal have not been tested before in the labs. Therefore, it might be necessary to adjust the methods.

Decomposition of carbonate by acid washing according to DIN ISO 11277 for larger amounts of samples (up to ~50 g)

▶ **Procedure:**

- ▶ Weigh in airdried and ground soil (< 2 mm) in a beaker, note weigh-in mass
- ▶ put on protective clothing (lab coat, gloves, glasses)
- ▶ put the beaker with the soil sample under the fume cupboard and add ~10 % HCl (around 3 parts of water + 1 part conc. HCl, around 3 M HCl) in excess, to create a suspension
- ▶ mix with a glass rod from time to time until no CO₂ bubbles develop (normally ca. 30 to 60 minutes)
- ▶ add again some ml of HCl, mix carefully and observe
- ▶ repeat procedure as long until no visible bubbles build up
- ▶ weigh filter paper, if filter cake shall be dried in it (see below)
- ▶ build up a filtration aid under the fume cupboard: place funnels + filter over a big beaker
- ▶ transfer soil sample quantitatively into the filter, wash the beaker with ultrapure water into the filter as long until no soil is in the beaker
- ▶ take care, that the underlying beaker is not overflowed when catching the filtrate
- ▶ add some ml of HCl to the sample
- ▶ after filtration of part of the sample suspension, catch some drops of the filtrate with a test tube. Attention, acid!
- ▶ Add some drops of saturated NH₄-oxalate into the test tube
- ▶ Observe if Ca-oxalate precipitates as white turbidity (white streaks), *if yes,*
- ▶ Ad some new HCl to the filter cake after complete filtration and repeat test with NH₄-oxalat until no turbidity can be observed
- ▶ Wash filter cake at least 2 times with ultrapure water, until the filtrate is clear
- ▶ Either dry filter cake in the filter paper (60 °C in drying oven) and weigh out, notice the mass of filter paper,
or
- ▶ Wash filter cake from the filter with water into a weight beaker, dry the sample, (60 °C in drying oven) and weigh out
- ▶ Difference between mass before carbonate decomposition and after carbonate decomposition is the mass of carbonate removed as CO₂
- ▶ This mass difference has to be considered for calculation of elemental concentrations after sample digestion

It is unknown, which amounts of P are washed out with HCl. Therefore, HCl volume should be measured and P should be determined in the filtrate. Alternatively, HCl could be evaporated to a smaller defined volume.

According to DIN ISO 11277, four ml of 1 M HCl (around 3 % HCl) are necessary for each % of carbonate, plus an acid excess of 25 %. Around 250 ml ultrapure water are added to the soil; after that the HCl is added. The suspension is mixed up to 15 min or until the end of reaction (no bubble development) at 80 °C on a sand bath or heating plate and mixed from time to time.

Alternatively, the method of Harris et al. (2001) can be used for small samples amounts. In this method carbonate is decomposed by HCl vapours.

Carbonate decomposition according to Harris et al. (2001) by HCl vaporisation for small sample amounts (~30 mg)

▶ **Procedure:**

- ▶ Weigh in 30 mg of oven-dried and grinded soil sample in Ag-foil-capsules (8-5 mm; sample scoop), take no Sn-capsules, since they will be damaged by HCl vapour
- ▶ Put the open capsules into microtiter plate and add around 50 µl ultrapure water, to moisture the soil to field capacity
- ▶ Place the microtiter plate(s) into a 5-liter-vacuum-desiccator
- ▶ Place the desiccator under the fume cupboard
- ▶ put on protective clothing (lab coat, gloves, glasses)
- ▶ place a 150 ml beaker with 100 ml conc. HCl (12 M) in the desiccator
- ▶ close the desiccator and fumigate the soil sample around 6 hours with HCl
- ▶ open the desiccator under the fume cupboard. Attention, acid vapour!
- ▶ Remove sample scoops with soil samples and dry them at 60 °C in a drying oven for around 4 hours
- ▶ Dhillon et al. (2015) recommended drying of soils samples at 105 °C for 16 hours, in order to remove all HCl residues and avoid corrosion on C-analyser. If samples are digested by aqua regia this is not necessary
- ▶ Weigh out samples and calculate mass difference for determination of element concentrations

Carbonate decomposition by heating to around 1000 °C

According to safety data sheets, the decomposition temperature of CaCO_3 is 825 °C. Peters and Wiedemann (1959) and Narsimhan (1961) report, that a stronger decomposition starts at around > 890 °C. At this temperature CaCO_3 reacts to CaO and CO_2 . During lime burning, temperatures of around 1200 °C are reached in order to produce CaO from CaCO_3 . The decomposition temperature for MgCO_3 is around 550 °C (Liu et al. 2011, Sawada et al. 1979); in safety data sheets it is > 350 °C.

CaCO_3 and MgCO_3 are the most common carbonates in soils. Heating of soil samples to > 900-1000 °C causes therefore also decomposition of carbonates, so that such samples can be analysed as carbonate-free samples.

In the labs of the Biological Station Zingst there is a muffle furnace for ashing of soil samples at 550 °C. This oven can be heated to temperatures of 1000 °C. Especially for samples with high amounts of organic substances and carbonate the usage of parallel decomposition of organic substances and carbonate at high temperatures can be considered. According to Wang et al. (2011), sediment samples could be heated stepwise (with exception of marine sediments): first to 500 °C (with weigh out) for 12 hours and after weighing a second heating to 800 °C for 12 h (with further weigh out), not only to ash the samples and remove the carbonate before digestion but also to determine percentage of organic matter and carbonate. For marine sediments 550 °C for 12 hours or 500 °C for 15 hours for determination of organic substances are recommended by Wang et al. (2011). According to Burlakovs et al. (2015), Heiri et al. (2001) and Santisteban et al. (2004), the following temperatures are recommended: 105 °C (12 to 24 hours) for gypsum concentration, 550 °C (for 4 hours) for organic substances and 900 °C (for 2 hours) for carbonates.

Sampling ash can be used to digest samples with acid persulfate or aqua regia and to determine P concentrations. If these methods are planned to be used for parallel determination of organic and carbonate C (not only for ashing and carbonate decomposition), the following points have to be considered:

- ▶ Crystal water from clay minerals is removed at around 500 °C (e.g. Dean 1974, Grim 1953, Santisteban et al. 2004)
- ▶ Gypsum, sulphide minerals and metal-oxyhydroxides can be oxidised and/or dehydrated (e.g. Ralska-Jasiewiczowa et al. 2003)
- ▶ at temperatures between 425 °C and 520 °C minerals such as siderite (FeCO_3), magnesite (MgCO_3), rhodochrosite (MnCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are decomposed (e.g. Duval 1963, Brauer and Negen-dank 1993, Ralska-Jasiewiczowa et al. 2003, Weliky et al. 1983)

- ▶ Goethite (FeOOH) is dehydrated at temperatures between 280 °C and 400 °C and converted to hematite (Derie et al. 1976, Prasad et al. 2006, Schwertmann 1959)
- ▶ Gibbsite (Al(OH)₃) loses water at temperatures of around 300 °C (Davies 1974)
- ▶ Generally, the mineralogy of the sample is changed significantly.

Depending on the mineralogy of the sample (e.g. clay-%, other carbonates, Fe-(hydr)oxides) the parallel determination of concentrations of organic substances and carbonate during ashing or carbonate decomposition can be affected by errors. For solely ashing and carbonate decomposition temperatures between 900 to 1000 °C for 4 hours are recommended. Samples are weighted in in porcelain crucibles (determine empty mass of crucible) and ashed in muffle furnace for 4 hours. Subsequently, ash-containing crucibles are weighted, and the mass of the empty crucible is subtracted. The difference between sample weigh-in and out is the mass loss, which must be considered for digestion and subsequent determination of P concentrations in the samples.

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