4. Digestions

4.5 Methods for the determination of P fractions or binding forms in soil samples

4.5.3 Estimation of P binding to pedogenic oxides in soil by wet chemical methods

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In soil, phosphorus is bound to various soil components and only a small proportion is dissolved in the soil solution. This means that P can be mobilized and bioavailable differently in different soils. Especially at **acidic pH values**, P in the soil is strongly bound to **pedogenic Fe and Al (hydr)oxides** (abbreviated as oxides in the following; partly Mn oxides). Since well and poorly crystalline Fe oxides in particular differ in their **ability to bind P**, extracts are used to estimate the Fe crystallinity in order to estimate the binding of P to these Fe oxides. As with all extracts, it should be noted that they are operationally defined extracts and extract not only the target substances, but in some cases also other binding forms or the extraction of the target substance is incomplete (Rennert 2019 and references therein). If these extracts are carried out in the successive horizons of a soil profile, they can, to a limited extent, **provide indications of transformation processes in the soil**. This is especially true for soils with Fe displacement processes such as podzols.

In general, **P is more strongly adsorbed** and **less desorbed** on **poorly crystalline**, especially **Fe oxides** (e.g. ferrihydrite) than on **better crystalline Fe** and **Al oxides** (e.g. gibbsite) (Gypser et al. 2018). The **crystallinity** of the pedogenic oxides can be **affected by** the **sampling and drying** of the samples (see also chapter 2.4) and can thus also have an effect on the results of the extractions. A drying temperature of 60 °C causes poorly crystalline Fe oxides to age, i.e. their crystallinity increases (Landa and Gast 1973). Ferrihydrite is transformed into more crystalline goethite and hematite at temperatures starting at 50 °C (Das et al. 2011), which can consequently influence P binding and P extractability. Soil samples should therefore be dried at lower temperatures, especially for these extractions.

It is assumed that, **in the dark, the oxalate extract** (Schwertmann 1964, Landa and Gast 1973, Miller et al. 1986) extracts mainly **poorly crystalline Fe** (and P bound to it) and the **dithionite extract** (according to Mehra and Jackson 1960; DCB) also **extracts better crystalline Fe oxides**. The dithionite extract according to Mehra and Jackson (1960) is used in various forms, but has been criticized for poor hematite extraction. Deb (1950) found that the oxalate extract in sunlight extracted Fe concentrations comparable to those of the DCB extract. Reyes and Torrent (1997) suggest an extract of 0.05 M ascorbic acid with 0.2 M citrate (pH 6, 16 h) to extract Fe from poorly crystalline oxides.

Based on the historical development, there are different names for poorly crystalline pedogenic oxides, e.g. active or reactive oxides, amorphous oxides, non-crystalline oxides (Rennert 2019 and references therein). Since there is no order in amorphous or non-crystalline material, even in the immediate atomic environment, Rennert (2019) therefore proposes to use the term "short-range ordered" as equivalent to "poorly crystalline" pedogenic oxides; however, this is not equivalent to "non-crystalline" or "amorphous". It should be noted that there is no sharp distinction between good and bad crystalline oxides in the soil, but rather a continuum. In this chapter, the terms bad(er) and good (better) crystalline are used to differentiate between them.

Note: If the extracts are carried out, the total element concentrations (Al, Fe, Mn and P) in the soil sample must also be determined. When calculating the P sorption capacity and P saturation, please note that the concentrations must be calculated in mol instead of g! When interpreting the results, it should again be noted that the extracts not only extract the target compounds, but also extract them incompletely or extract non-target compounds (Rennert 2019) and thus the target phases can be under- or overestimated.

The following parameters can be calculated from the oxalate extract, the dithionite extract and the total element concentration:

P sorption capacity = PSC in mmol kg^{-1}

$$PSC = 0{,}5\ \cdot (Al_{Ox} + Fe_{Ox})$$

Degree of P saturation of the pedogenic oxides in % (degree of P saturation = DPS)

$$DPS = \frac{P_{Ox} \cdot 100\ \%}{PSC}$$

Note: In some publications, Mn_{ox} is also added to Al_{ox} and Fe_{ox}! This should be taken into consideration, particularly in the case of elevated Mn concentrations in the soil.

The following fractions can be calculated to estimate the different crystalline proportions and thus the binding capacity of the Fe oxides:

$$\text{Proportion of poorly crystalline Fe oxides in total Fe} = \frac{Fe_{ox}}{Fe_t}$$

$$\text{Proportion of poorly crystalline Fe oxides in pedogenic Fe oxides} = \frac{Fe_{ox}}{Fe_d}$$

$$\text{Proportion of pedogenic Fe oxides in total Fe} = \frac{Fe_d}{Fe_t}$$

$$\text{Proportion of well-crystalline Fe oxides in total Fe} = \frac{(Fe_d - Fe_{ox})}{Fe_t}$$

Abbreviations:

ox = Element concentration in the oxalate extract
d = Element concentration in the dithionite extract
t = Total element concentration (total)

Similarly, the P concentrations in the corresponding fractions can be calculated from the P concentrations of the extracts. The extracts can be carried out in the working group Soil Science (Faculty of Agricultural and Environmental Sciences, University of Rostock).

4.5.3.1 Oxalate extract for extracting the poorly crystalline Fe and Al oxides and the P

Principle and suitability of the extract

It is assumed that the oxalate extract (Schwertmann 1964, Landa and Gast 1973, Schwertmann 1973, Miller et al. 1986) mainly extracts poorly crystalline Fe (and P bound to it) in the dark. In the oxalate extract, oxalic acid and ammonium oxalate form a buffer at pH 3. At pH values <3.5, oxide surfaces are initially protonated before oxalate is subsequently adsorbed and complexed Al^{3+} and Fe^{3+} ions are released (Rennert 2019). Moreover, organically bound Fe, Al and Mn are also extracted. Depending on the crystallinity, Fe in the extract can thus come from dissolved Fe, organically bound Fe compounds and the poorly crystalline ferrihydrite, but also from less crystalline goethite and hematite as well as lepidocrocite; Al in the extract can come from e.g. hydroxy interlayers, less crystalline Al oxides and aluminosilicates as well as from allophanes (Rennert 2019).

According to Parfitt and Childs (1988), the oxalate extract is one of the best methods for estimating the proportion of poorly crystalline Fe oxides, especially ferryhydrite, even if Fe is also extracted from some Al layered silicates (allophanes, imogolites). In sunlight, the oxalate extract extracts Fe concentrations comparable to those of the DCB extract (Deb 1950). Extraction times between 1 and 5 hours were tested for the oxalate extract according to Schwertmann; the setting of 2 hours shaking time is arbitrary (Schwertmann 1964). If the concentrations of Fe are still considerably too high for measurement on the ICP despite 12-fold dilution (e.g. in the presence of turf iron ore, see DIN 19684-6), the sample weight can be reduced (e.g. 0.5 g) or the extracts must be diluted more for the measurement.

Interpretation of the results

The oxalate extract should not be considered on its own, but at least in relation to the total element concentration. P can also be calculated in the same way as Fe (e.g. proportion of oxalate-extracted P in dithionite or total P, see equations above for Fe). The results for P can be used to calculate the P sorption capacity (PSC) and the proportion of P saturation of the pedogenic oxides (DPS) (see equations above).

Comparative values for orientation: DPS values determined in humus-rich topsoil in soil profiles in the state of Mecklenburg-Western Pomerania for the DBG conference 2013 (Ahl & Leinweber 2013).

- in the forest: DPS by 10 %
- “Normal” arable topsoil DPS 20...30 %
- DPS values >30 % were found with heavy manure fertilization or massive input of other P-rich biomass; in the case of soils, this could also be an indication of anthropogenic influence in the past
- DPS values of >90 % or even >100 % were found on former gravel mining sites, which were massively fertilized with liquid manure for recultivation in GDR times and then used as cattle pasture after reseeding, as well as in the fEx horizon of a (former) hortisol in the monastery garden in Rostock! It is assumed here that parts of the P bound to the OBS were also extracted with oxalate.

Protocol for oxalate extraction

Sample preparation:

- Drying soil samples (see chapters 2.4, 3.1)
- Sieve soil samples <2 mm and use this <2 mm fraction (fine soil)
- Determine total element concentrations in a subsample (e.g. using aqua regia extract, see chapter 4.1.2)

Reagents:

Either both solutions can be prepared separately and then combined or the oxalate buffer can be prepared in one step. To save chemicals (DIN 19684-6), the second option is preferable.

(1) Weighing for 1 liter oxalate buffer (according to DIN) (separate preparation)

- Solution 1: Weigh 28.42 g Di-ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 * H_2O$)) into a 1-liter flask and fill up with ultrapure water
- Solution 2: Weigh 25.21 g oxalic acid dihydrate $C_2H_2O_4 \cdot H_2O$ into a 1-liter flask and fill up with ultrapure water
- Mix 700 ml solution 1 (corresponds to 19.89 g ammonium oxalate) with 535 ml solution 2 (corresponds to 13.48 g oxalic acid) and check the pH value of the extraction solution, it should be between pH 3.0 (Schwertmann 1964) and 3.2 (DIN ISO 19684-6), adjust with ammonia solution if necessary

Note: The pH value is usually around 3.0 and around 100 ml of ammonia solution is required to adjust the pH to 3.2. The pH 3.0 should therefore be used.

(2) Preparation of 1 liter of oxalate buffer extraction solution in one batch

- Weigh 16.11 g di-ammonium oxalate monohydrate $(NH_4)_2C_2O_4 \cdot H_2O$ and 10.92 g oxalic acid dihydrate $C_2H_2O_4 \cdot H_2O$ in a 1-liter flask
- Fill the flask up to 700 to 800 ml with ultrapure water and stir on the magnetic stirrer until the salts have dissolved
- Fill up to approx. 900 ml with ultrapure water, check pH value see above and adjust to 3.0 if necessary (see note above), fill up to 1 liter with ultrapure water

Procedure:

- Prepare at least 3 replicates per soil sample and at least 1 blank per 10 extraction samples.
- Weigh 1.5 g fine soil (applies to 0.1 to 5 g Fe kg^{-1} soil) into 50 ml centrifuge tubes or 5.00 g fine soil into 200 to 250 ml plastic bottles (see DIN)
- Add 30 ml or 100 ml oxalate buffer, respectively
- Shake overhead in the dark for 2 hours
- Centrifuge at 1500 x *g* for 10 min
- Filter the extract through dry P-free filters
- Dilution: at least factor 12 (1 part sample plus 11 parts ultrapure water, dilution must be tested, at higher Fe concentrations Fe can flocculate)
- Transfer aliquot to ICP tubes and store in the refrigerator or freezer until measurement (if stored for >1 day)

- Determination of elements using ICP-OES (Al_{ox} 396.153 nm, Fe_{ox} 238.204 nm, Mn_{ox} 257.610 nm and P_{ox} 214.914 or 213.617 nm)

The oxalate extracts can be carried out in the working groups Soil Science and Agronomy (both Faculty of Agricultural and Environmental Sciences, University of Rostock).

Alternative extraction to the oxalate extract for the estimation of poorly crystalline Fe and Al oxides **according to Reyes and Torrent (1997):**

According to Reyes and Torrent (1997), the oxalate extract also extracts Fe and Al from the two Al silicates allophane ($Al_2O_3 \cdot (SiO_2)_{1.3-2} \cdot (H_2O)_{2.5-3}$ [1]) and imogolite ($Al_2SiO_3(OH)_4$ [2]), while a **solution of citrate + ascorbate (C-A extract)** does not extract this Al and Fe. This means that an oxalate extract overestimates the proportion of pedogenic, poorly crystalline Al and Fe oxides if higher proportions of these phyllosilicates are present in the soil (Reyes and Torrent 1997). It is not possible to distinguish whether the additional Fe extracted with oxalate (compared to the C-A extract) originates directly from the allophane Fe or from the Fe oxides included in the allophanes (Reyes and Torrent 1997). The C-A extract can therefore be used to extract the poorly crystalline Al and Fe oxides in a more targeted manner. However, according to Reyes and Torrent (1997), if organic soil matter is present, a **citrate extract is recommended in addition to the C-A extract**, as the C-A extract also extracts parts of the Al and Fe bound to the organic soil matter, while the citrate extract preferentially extracts Al and Fe bound to the organic soil matter. **The difference between the element concentrations (Al, Fe, P) from the C-A extract (poorly crystalline + organically bound) and the citrate extract (organically bound) then gives the element content from the poorly crystalline oxides.**

Procedure for the extraction of poorly crystalline Al and Fe oxides according to Reyes and Torrent (1997):

There is no indication of the sample weight. As a comparison was made with the oxalate extract in the publication, a similar sample weight (0.5 g to 1.5 g soil) is assumed. Reyes and Torrent (1997) recommend that no more than 0.25 mmol (=15 mg) Fe per liter should be extracted with the C-A extract, i.e. the sample weight may have to be adjusted for the respective soil.

Protocol Citrate-ascorbate extract (C-A solution)

Reagents for the **citrate-ascorbate solution = C-A solution (1 liter)**

tri-sodium citrate dihydrate $C_6H_5Na_3O_7 \cdot 2H_2O$ molar mass: 294.10 g mol^{-1}

- Weigh 58.82 g tri-sodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) into a 1 liter wide-necked volumetric flask
- Add approx. 800 ml ultrapure water and stir on the magnetic stirrer and attach the pH meter
- Add solid ascorbic acid (approx. 7.6...8.4 g for 1 L) while stirring until a pH value of 6 is reached (between 0.38 and 0.42 g ascorbic acid is required per 50 mL solution)
- The solution then has an ascorbic acid concentration of between 0.043 and 0.048 M, up to a molarity of 0.05 M this has no effect on the extraction
- Fill up to 1 liter with ultrapure water

Extraction procedure

- Shake the sample in 50 mL of a 0.2 M Na-citrate-0.05 M Na-ascorbate solution (C-A solution; pH 6) in a maximum 60 mL centrifuge tube for 16 hours
- Centrifuge (1500 x *g*), filter through P-free filters
- Measurement of Al, Fe, (Mn) and P on ICP-OES

Notes on C-A extract (Reyes and Torrent 1997)**:**

- The air space in the centrifuge tube should not be larger than 15 ml to prevent oxidation of the extraction agent.
- The extraction solution is well buffered and only small pH changes were observed in the extract.
- Up to 50 mg $CaCO_3$ equivalent per 50 ml solution had no effect on the amount of extracted Fe. For samples with higher carbonate concentrations, 1 mmol citric acid per mmol $CaCO_3$ should be added so that the final pH value is 6 ±0,1.
- For deviations of <0.1 pH units, no effects of carbonate on the amount of extracted Fe were detected.

Protocol citrate extract

Reagents for the **0.2 M citrate solution (1 liter)**

- Weigh 58.82 g tri-sodium citrate dihydrate $C_6H_5Na_3O_7 \cdot 2H_2O$ into a 1 liter wide-necked volumetric flask
- Add approx. 800 ml ultrapure water and stir on the magnetic stirrer and attach the pH meter
- Adjust to a pH value of 6 with 1 M KOH
- Fill up to the calibration mark with ultrapure water

Preparation 1 liter 1 M KOH

Molar mass KOH 56.1056 g mol^{-1}

- Pour approx. 800 to 900 ml ultrapure water into a volumetric flask
- Carefully add 56.11 g KOH (solid). Be careful, the solution will heat up!
- After cooling down to room temperature, fill the volumetric flask with ultrapure water to 1 liter

Extraction procedure

- Shake the sample in 50 mL of a 0.2 M Na-citrate solution (pH 6) in a maximum 60 mL centrifuge tube for 16 h (the sample weight must be identical to that in the C-A extract)
- Centrifuge at 100 x *g*, filter through P-free filters
- Measurement of Al, Fe and P concentrations on the ICP-OES.

Notes:

- It is essential to clarify in advance for both extracts whether the solutions can be measured on the ICP-OES at the given Na concentrations or whether dilution is necessary!
- When preparing the reagents, always work under the fume hood and wear protective clothing, as you are working with acids and alkalis.

The extracts according to Reyes and Torrent (1997) have not yet been carried out in the working groups Soil Science and Agronomy (University of Rostock) but could be requested.

4.5.3.2 Dithionite extract for the extraction of the more crystalline Al and Fe oxides and the P

Principle and suitability of the extract

The dithionite extract, which is used to extract poorly and well crystalline iron oxides, dates back to **Mehra and Jackson (1960)**. The dithionite extraction according to Mehra and Jackson (1960) was converted into a DIN: **DIN ISO 12782-2**. In this DIN the principle is explained as follows (gray font): The extraction principle is mainly based on the reduction of Fe(III) phases to more soluble Fe(II) phases and on the tendency of the chemicals to form complexes for the extraction of iron from crystalline materials (Dijkstra et al. 2005). The amount of *crystalline* Fe-(hydr)oxides is determined by extraction with dithionite *minus* the amount of amorphous Fe-(hydr)oxides determined by extraction with ascorbate according to ISO 12782-1 and other possible reactive iron phases determined by extraction with dithionite which are important in certain materials, such as volatile sulphides (AVS) and silicate under acidic conditions.

The extract according to Mehra and Jackson (1960) is also known as **dithionite citrate bicarbonate extract**, **DCB** for short. According to **Varadachari et al. (2006)**, however, the extraction is incomplete for hematites, for example, and contains some further contradictions. According to Varadachari et al. (2006), the modified dithionite extract is therefore a **dithionite carbonate oxalate extract**, in short **DCO**. The extract according to Varadachari et al. (2006) has a greater quantitative efficiency than the original DCB extract (Rennert 2019). According to Rennert (2019), an extract of ascorbic acid, due to the ability of ascorbic acid to reduce Fe(III) well crystalline oxides such as hematite and goethite, alone or in combination with oxalate, could also serve as a substitute for the DCB extract according to Mehra and Jackson (1960).

<u>Sample preparation for all variants of the dithionite extract:</u>

- Dry soil samples (see chapter 2.4, 3.1)
- Sieve soil samples <2 mm and use this <2 mm fraction (fine soil)
- Determine total element concentrations in a subsample (e.g. using aqua regia extract, see chapter 4.1.2)

Protocol for the dithionite extract (DCB) according to Mehra and Jackson (1960)

Preparation of chemicals:

0.3 M Na-citrate solution ($C_6H_5Na_3O_4$ 2 H_2O):

- Weigh 88 g of Na citrate into a 1-liter volumetric flask
- Fill up to the calibration mark with ultrapure water

1 M $NaHCO_3$ solution:

- Weigh 84 g $NaHCO_3$ into a 1-liter volumetric flask
- Fill up to the calibration mark with ultrapure water

For a saturated NaCl solution:

- Add NaCl to water until it precipitates

Extraction procedure:

- Weigh 1 g of lutro fine soil into 50 ml centrifuge tubes or glass tubes (for heating block)
- Add 20 ml of 0.3 M Na citrate and 5 ml of 1 M $NaHCO_3$
- Heat to 75 to <80 °C in a water bath under the fume cupboard, eye protection!
- Add 1 g solid $Na_2S_2O_4$ (Na-dithionit) (Na-dithionite) while stirring vigorously (glass rod) and heat for a further 5 min, stirring frequently
- Add 1 g of solid $Na_2S_2O_4$ (Na-dithionite) again and heat for a further 10 min, stirring frequently
- The sample should now be gray (not red, yellow or brown), otherwise add Na-dithionite again!
- Remove samples from the water bath and allow to cool slightly (sample begins to precipitate)
- Centrifuge samples for 10 min at approx. 1100 x *g* (try out)
- If the sample does not flocculate after centrifugation, add 1 ml of saturated NaCl and centrifuge again
- Decant the supernatant using a P-free filter
- Dilution 1 : 10 for ICP-OES measurement

Protocol for the dithionite extract (DCO extract) according to Varadachari et al. (2006)

Note on dithionite extract (DCO) according to Varadachari et al. (2006):

The extraction has not yet been carried out in the laboratories of the working group Soil Science (Faculty of Agricultural and Environmental Sciences, University of Rostock), but, generally, could be tested there. Extraction must be carried out under the fume cupboard! Depending on the size of the water bath, up to 5 samples can probably be extracted at once. Due to the centrifuge, an even number of samples must be selected, or empty samples must be weighed with water in advance and placed in the centrifuge!

Sample weighing: The sample quantity depends on the Fe_2O_3 content. The specified extraction agent quantities apply to a maximum of 50 mg Fe_2O_3. 50 mg Fe_2O_3 corresponds to 35 mg Fe, which may be present in the weighed sample. In Cambisols (according to IUSS Working Group WRB (2022); Braunerde according to Ad-hoc-AG Boden (2005) and similar soil types on glacial till the Fe concentrations range between 6 and 21 g kg^{-1} (Zimmer und Leinweber 2013). In podzols on sand, Fe concentrations varied between <1 g and 2.5 g Fe kg $^{-1}$ (Baum et al. 2013). The unit g per kg is equivalent to unit mg per g. At 21 mg Fe g^{-1}, 1.5 g of soil could therefore be weighed in without exceeding the 35 mg per extraction. At lower total Fe concentrations, e.g. 6 mg g^{-1}, the sample weight could theoretically be increased to 5 g. At higher Fe concentrations in the soil samples, the sample weight must be reduced.

Varadachari et al. (2006) list among others the following **weaknesses of the DCB extract** according to Mehra and Jackson (1960) and Aguilera and Jackson (1953):

- Several studies by other authors show that better crystalline Fe oxides, especially hematite, are only incompletely removed with the DCB extract; in some cases, even more Fe is extracted by the oxalate extract than by the DCB extract.
- There is no evidence that the propagated pH value of 7.3 and the reaction temperature of 80-90 °C are reasonable.
- The authors do not state that dithionite solutions are unstable and must be prepared fresh daily.

- The statements on the pH values for the precipitation of FeS contradict each other.
- The post-extraction washes were repeated too infrequently to ensure that the reduced Fe was actually completely present in the centrifuged supernatant/extract.
- The published X-ray diffractograms before and after the reaction cannot prove complete hematite extraction, as typical lines for hematite also appear in the diffractograms after DCB extraction.

The following points were investigated by Varadachari et al. (2006) for the dithionite extract from theoretical considerations and experiments:

- The mechanisms of reduction by Na-dithionite
- The specific structure of the dithionite ion means that it is stable in the dry state but not in the dissolved state and therefore decomposes to elemental S at acidic pH values; it is stable at neutral to alkaline pH values and S is hardly/not precipitates
- Dithionite is a stronger reducing agent under alkaline conditions than under acidic conditions (standard potential in alkaline: E^0 = 1.12 V; in acidic E^0 = 0.056 V);
- While dithionite decomposes in aqueous phase, especially under acidic conditions, H_2S and S are formed, which can precipitate with Fe to form largely insoluble FeS
- Metal oxides in the oxidized state such as Fe(III) are largely stable and are only dissolved by changing the oxidation state, e.g. to Fe(II), which requires a strong reducing agent
- In the decomposition of dithionite, the SO_2^- radical is the strongest reducing agent

From this, Varadachari et al. (2006) derive, among other things, the following conditions for reactions with dithionite:

- The reactions must take place at alkaline pH values, as the reducing power of the dithionite is strongest here and the formation of H_2S is largely avoided.
- The precipitation of FeS by the FeS formed in side reactions, even under alkaline conditions, must be avoided by adding complexing agents.

The following reaction conditions were therefore optimized by Varadachari et al. (2006) (the optimum combination is shown in brackets):

Effects of the complexing agent (oxalate), the temperature (100 °C), the pH value (8), the amount of complexing agent (30 ml for 2 g Na-dithionite), the reaction time (30 min), the amount of dithionite (2 g) and the method of dithionite addition (portion wise).

DCO extraction protocol; an attempt was made to adapt the process to the existing equipment in the working group Soil Science; however, the process has not yet been tested.

- Weigh-in: approx. 1 g soil <2 mm (depending on Fe content, see above)
- Add 30 ml of the oxalate-carbonate solution to a 250 ml Erlmeyer flask, add sample (the depth of the solution should be a maximum of 1.5 cm to ensure contact of the sample with the reductive zone (dithionite) occurring near the surface)
- Place Erlenmeyer flask with suspension in the hot water bath under the fume cupboard.
- As soon as the water bath has reached approximately 100 °C (at least 70 to 80 °C), add 0.4 g Na-dithionite ($Na_2S_2O_4$) while continuously stirring the sample with a glass rod (when adding the sample and the dithionite, remove the glass rod briefly so that nothing sticks).
- Continue to add Na-dithionite approx. every 5 min until a total of 2 g Na-dithionite (optimum) has been added (no more, otherwise the solution will become acidic)
- Approx. 30 min after the first and 10 min after the last addition of dithionite, remove the Erlenmeyer flask from the water bath and allow to cool to room temperature
- Transfer the suspension completely into 50 ml centrifuge tubes (funnel) (rinse with (try 10 ml at a time?) 1 M NaCl or KCl), centrifuge (3000 x *g* for 20 min?) and transfer the supernatant through a filter into a graduated flask (100 ml?)
- Wash the sample up to 5 times with 1 M NaCl or KCl (10 to 15 ml each time): shake up each time, centrifuge and decant the supernatant into the volumetric flask each time
- Fill the volumetric flask up to the calibration mark with 1 M NaCl or KCl
- Measurement of Fe, Mn, Al and P in the extract using ICP-OES, compare with oxalate extract (in the dark) to estimate well and poorly crystalline Fe (see formulas above)

Preparation of the reagents:

Oxalate-carbonate buffer solution:

- Weigh 33.3 g Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and 35.3 g anhydrous Na carbonate (Na2CO3) into a 1-liter volumetric flask
- Add ultrapure water and heat if necessary to dissolve the chemicals (oxalic acid reacts to form Na-oxalate),
- Check the pH value (it should be 8.05), add oxalic acid or carbonate, if necessary (pH should be >7 in any case),
- Allow the solution to cool and fill up to 1 L

1M NaCl solution:

- Weigh 58.44 g NaCl into a 1-liter flask
- Fill up to 1 liter with ultrapure water

Notes:

- Na-dithionite should be stored in a desiccator, as it easily absorbs water at normal humidity, which causes decomposition of the Na-dithonite and thus leads to a loss of extraction efficiency.
- Washing the reaction suspension: After completion of the reaction, the suspension transferred to a centrifuge tube must be washed at least 5 times and the respective supernatants must be combined after centrifugation. To this, 1 M KCl or NaCl is added repeatedly. Washing also appears to be necessary above all to prevent dispersion of the clay and the deposition of extraction agent residues in the clay residue, i.e. if the extraction residue is also to be collected as pure clay minerals.
- The success of extractions with oxalate or dithionite can be estimated by measuring the crystallinity by X-ray diffraction (XRD) of the Fe oxides before and after extraction in the soil sample (e.g. Pawluk 1972, Landa and Gast 1973, Rennert 2019). Since oxalate should only extract the poorly crystalline Fe oxides and poorly crystalline Fe oxides cannot be detected by XRD, the XRD spectra before and after extraction with oxalate should be identical. Since dithionite (or DCO) should also extract the well-crystalline Fe oxides, the corresponding peaks must be missing in the spectra after extraction compared to the non-extracted samples.
- The dithionite extracts are not part of the routine analysis of the working group Soil Science (Faculty of Agricultural and Environmental Sciences, University of Rostock), but could generally be carried out there on request.

- There were problems with both the KCl and NaCl solution in the ICP-OES during experiments. It is therefore essential to speak to the laboratory technician for the ICP-OES in advance!

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For citation: Zimmer D, Baumann K (*year of download*) Chapter 4.5.3 Estimation of P binding to pedogenic oxides in soil by wet chemical methods (Version 1.0) in Zimmer D, Baumann K, Berthold M, Schumann R: Handbook on the Selection of Methods for Digestion and Determination of Total Phosphorus in Environmental Samples. DOI: 10.12754/misc-2020-0001