Granulometry: particle size distribution

Background

1. Principle of Laser Particle Sizing

There are several methods for measuring the size distribution of mineral particles in a sample. For diffraction particle size distribution, the sample, suspended in a solution, is passed through a laser beam. The beam is diffracted according to the number and size of the particles passing through it. After passing through the sample, the angle and intensity of the laser diffraction is measured by a series of detectors. From these data, the program calculates the particle size and expresses the relative volume percentage for each defined particle size class (Pansu and Gautheyrou, 2003).

2. Comparison of methods

The comparison of the results from various methods is generally quite surprising and sometimes the results differ completely. Firstly, in the sieving/pipetting method, the results are calculated according to the respective weight of the fractions, whereas in the laser diffraction method, the calculation is made according to the volume of the analyzed particles. Secondly, the shape of the grains plays a role. It is easy to imagine that an elongated particle can pass through the mesh of a sieve corresponding to its smallest diameter. In this case, it will be considered "smaller" than it is. Conversely, the laser particle size analyzer program calculates the size of the particles assuming that they are all spherical and extrapolates the volume of these spheres from the largest measured diameters. This time, the same elongated particle will appear "larger" than it is. But at the end, what is the size of a particle? What size should be considered and how should it be measured?

3. Interest of the mineral granulometry

Particle size distribution is one of the characteristics of the mineral fraction of soils or sediments. The study of different curves obtained can be a useful clue to understanding the distribution of surface formations in the landscape. In the carbonate domain, for example, the alteration residue of rocks and marls (after decarbonation) can be used as a "signature" of the geological material in place. By comparing this signal with that of the overlying soils, it’s possible to determine whether there have been further deposits over the rock (this is referred to as a lithological discontinuity and the rock is the substrate material), or if the soil has developed from the alteration of the underlying geological material (which in this case is the parent material).
N.B. We encourage you to read the following reference: Gee, G. W. & Bauder J. W. (1986) Particle-size analysis. In Klute, A. (Ed.) Methods of Soils Analysis, Part. 1. Soil Science Society of Amercia Book Series 5, Madison, Wisconsin, USA. PDF available upon request!

Method

To carry out mineralogical analyses by laser diffraction, the samples have to follow three successive treatments to release and dissociate the mineral particles:

1. Decarbonation
2. Destruction of organic matter
3. Dispersion

1. DECARBONATATION

Decarbonation **is generally not necessary**. However if, it's really required for the study, it must be done before the destruction of the organic matter.

!! Decarbonation is done under the chemical hood of lab 1440!!

a) Equipment

- 50mL centrifuge tubes 50 ml
- Ultrasonic bath (filled with demineralized water)
- Centrifuge
- 10 ml disposable pipette
- 10 ml micropipettes and 10 ml tips

b) Reagents

- Technical HCl 10%.
- Demineralized water

c) Removal of carbonates

1. Weigh for each samples the soil previously sieved at 2 mm, according to its characteristics in a 50mL centrifuge tube (tubes with blue caps in the grey box in lab 1440):
   - 0.6 g of fine clay soil
   - 1.0g of loamy soil
   - 1.2-1.5g of sandy soil
2. Wet the samples with 2 ml of demineralized water.
3. For the next steps of the procedure, work with series of 12 samples to be able to centrifuge and neutralize the samples at the right timing.
4. For the first series of 12 samples, add 10ml of HCl 10% drop by drop, be careful the reaction can be very strong if the sample is very carbonated.
5. Close the vials. After shaking them energetically reopen them. (The CO_2 produced by the dissolution of $CaCO_3$ may cause the cap to pop if it remains closed too long!)
6. Place the 12 samples in the ultrasonic bath without lid, previously heated to 70°C, set the timer for 10 minutes of ultrasound (check that the tubes are well in the water).
7. After 10 minutes, remove immediately the 12 samples from the ultrasonic bath and check the reaction.
   – If the reaction still strong, extend the attack for another 5 minutes and check again.

– If the reaction is stopped (which is usually the case), close the tubes and centrifuge for 6 minutes at 4'000 RPM (for samples that do not sediment well, increase the centrifugation time to 10 to 15 minutes). Make sure that the tubes are well-balanced, e.g. by adding demineralized water up to the 50 ml mark.

8. Under fume hood, carefully open the lids and dispose of the supernatant in a large plastic beaker. There are two options for doing this:

   A. Carefully spill the supernatant, being sure that you don't lose even the tiniest fraction of the sample.

   B. Using a 10 ml disposable pipette, pump the supernatant carefully, taking care to not recover even the tiniest fraction of the sample

   N.B. Small particles can be floating in the supernatant. Usually this is organic matter (roots, leaves, wood, etc.). This is a good thing, if these particles are discarded along with the supernatant.

Caution: The acid residues collected must be neutralized before being poured into the sink!

9. Do a second attack **if necessary**: repeat the steps described above (§2-§8).

   To determine if there are carbonates, a few drops of HCl 10% can be put on the sediment. If there is a reaction, then a second attack must be carried out.

10. Immediately after pouring out the supernatant, fill the centrifuge tube with demineralized water to the 50 ml mark, close the tube and disperse the sediment by shaking energetically or using the 'Vortex'.

11. Repeat the rinsing operation described below two to three times:

    i) Check that each of the 12 tubes are filled to the same height.

    ii) Centrifuge the 12 samples for 6 minutes at 4,000 RPM (increase to 10 to 15 minutes for a more stable pellet).

    (iii) Pour the supernatant into the sink either by pouring directly into the sink or by pipetting with a 10 ml disposable pipette.

    (iv) Fill the tube with demineralized water to the 50 ml mark. Don't do this step for the last rinse!

Usually, 3 rinses are sufficient to rince the HCl 10% and neutralize the sample. The pH of the solution can be checked with pH 1-10 paper. Check that the pH is >6.

Once the first set of 12 samples has been neutralized, move to the next 12 samples. The most important is to keep the reaction time as short as possible of the samples with HCl 10% to 10 minutes to avoid clay transformation at low pH values.

2. DESTRUCTION OF ORGANIC MATTER

!! The destruction of the organic matter is done under the chemical fume hood of lab 1440!!!

a) Equipment

- Centrifuge tubes 50 ml (in grey box under water bath lab 1440)
- Oven set at 45°C
- pH paper
- 10 ml disposable pipette
- 10 ml micropipettes and 10 ml tips

b) Reagents

- Technical H_2O_2 35%
- Technical H_2O_2 10%
- NaOH 0.1N or NaOH 0.5N
- Demineralized water
- Ethanol

c) Removal of organic matter

1. Weigh for each samples the soil previously sieved at 2 mm, according to its characteristics in a 50mL centrifuge tube (tubes with blue caps in the grey box in lab 1440):
   - 0.6 g of fine clay soil
   - 1.0g of loamy
   - 1.2-1.5 g of sandy soil
2. Wet the samples with 2 ml of demineralized water.
3. Under the fume hood, add 2ml of 10% hydrogen peroxide and agitate by gently stirring the tubes without closing them.
4. The humidification and destruction of organic matter by H_2O_2 releases sometimes a significant amount of acidity. To preserve the soluble minerals at acid pH ($CaCO_3$) and to avoid the degradation of clays, it's necessary to buffer the solution at neutral pH (between 6.5 and 7.5). To do this:
   i) Use pH 1-10 and pH 1-6 papers to check pH.
   ii) Add dop by drop. using a disposable pipette 0.1 M NaOH (or 0.5 M NaOH if necessary). Then check the pH using a small piece of pH paper held with plastic tweezers. It should be around pH 7. Discard the pieces of pH paper in the 'fume hood bin' provided for this purpose.
   iii) During the first few days of the attack, check if the pH is neutral using pH paper. Sometimes a fair amount of acidity is released during the first few days; afterwards the pH generally remains more stable.

!! Beware of foam formation (reaction of organic matter)!! If necessary, add a little bit of ethanol (if ethanol flows along the vials, check the notation of the sample names).

5. Cover the vials with their caps but don't close them tightly.
6. Leave them for 12 hours (one night) under the fume hood.
7. The next day, place the vials in the oven set at 45°C to accelerate the reaction (use the oven to the left of the fume hoods in lab 1440. DON'T CHANGE THE TEMPERATURE SETTINGS!).
8. Two hours later, check the reaction of your samples and add 1 ml of H_2O_2 35% (with a 1 ml disposable pipette) if the foam doesn't exceed the 30-40 ml mark. Otherwise, wait a little longer for the reaction to decrease and the foam to decrease as well. After the addition of H_2O_2, shake, check the pH and return the samples to the oven.
9. A few hours later, check again your samples and add about 2-3 ml of H2O2 35% (with a 10 ml disposable pipette) if the foam doesn't exceed the 30-40 ml mark. If your samples foam strongly, wait a little longer. After adding H_2O_2, shake, check the pH and return the samples to the oven.

!! As long as there's foam formation, there's destruction of organic matter. If there is no more foam, it means that there is not enough H_2O_2, so we have to add more.

10. With a disposable pipette add drop by drop 2-4 ml of H_2O_2 35% in the morning and add 2-4 ml of H_2O_2 35% in the evening for one week or two. Remember to check the pH, stir the samples after each addition of hydrogen peroxide.

!! By adding more H_2O_2 and NaOH, the water level increases in the tube, diluting the added H_2O_2 each time more. If the level reaches 30-40 ml, it's necessary to let samples evaporate the oven (45°C) to bring it back to reasonable quantities before the next addition.

After one week or two at most, the reaction is stopped. There is no more foam production but only bubbles from the degassing of H_2O_2.

11. Bring the level in the tubes <10mL by allowing the samples to evaporate in the oven (45°C). It's necessary to reduce the sample volume so you can transfer it to the analytical tubes of the granulometer.

3. DISPERSION

a. Equipment

- Agitation plate

b. Reagents

- Sodium hexametaphosphate 40g/L (Calgon)

c. Process

The day before the particle size analysis:

1. Add 1 ml of 40 g/l Na hexametaphosphate solution to each sample.
2. Close the vials and place them on the stirring plate (speed approx. 100/min) overnight.
3. The samples are ready.

Contacts

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Références

Pansu, M. et Gautheyrou. J. (2003). *L'analyse du sol : minéralogique, organique et minéral*. Springler-Verlag France, p.993.
Gee, G. W. & Bauder J. W. (1986) Particle-size analysis. In Klute, A. (Ed.) Methods of Soils Analysis, Part. 1. Soil Science Society of Amercia Book Series 5, Madison, Wisconsin, USA. *PDF disponible sur demande!*

DIAGRAM OF THE EXPERIMENT

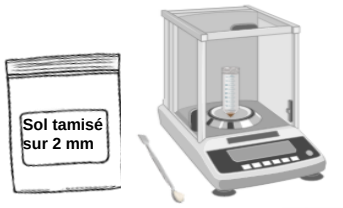
Safety/ Protective equipment

Decarbonation

Decarbonation **is usually not necessary**. However, if it's necessary, it must be carried out before the destruction of the organic matter.

Decarbonation takes place under the fume hood of lab1440

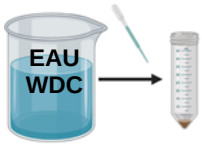
1



Weigh:

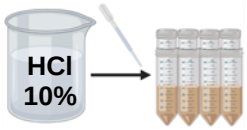
- 0.6 g sample of fine clay soil
- 1.0 g sample of loamy soil
- 1.2 – 1.5 g of sandy soil

2



Add 2.0 mL demineralized water

3



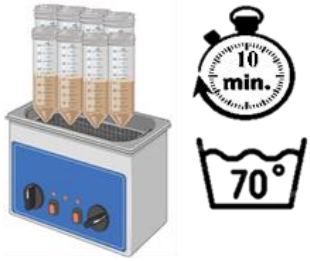
Under fume hood: Add drop by drop 10mL 10% HCl (make a series of 12 samples)

⚠ *Strong reaction if the sample is very carbonated (do not foam to overflow).*

4

Close the 12 tubes and shake vigorously or with the vortex.
Degas by opening the cap.

5



Immerse the tubes in the ultrasonic bath. Check the reaction after 10 min. If it reacts, extend the attack for 5 min and recheck. Close the tubes when finished.

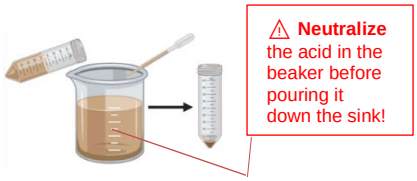
6

Equilibrate the 12 tubes by completing to 50mL with demineralized water.

Centrifuge 6 min at 4000 RPM.

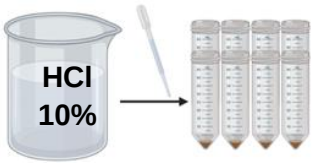
Increase time to 10-15 min for samples that do not sediment well.

7



Spill or use a pipette to remove the supernatant into a beaker (do not lose any fraction of the sample).

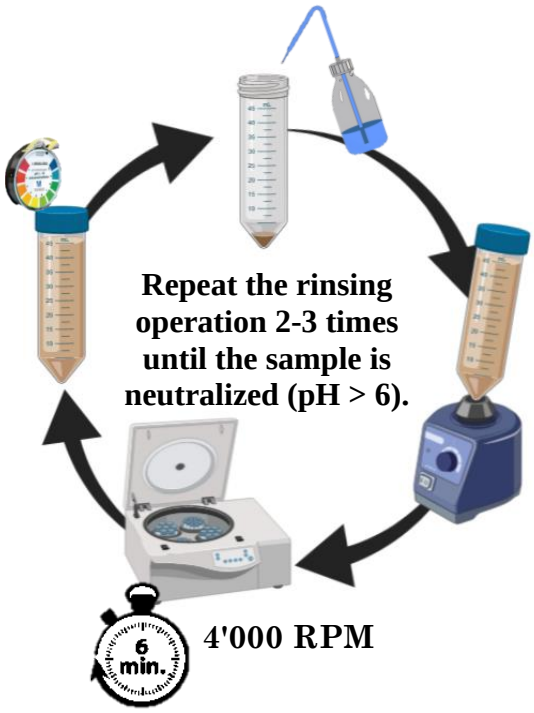
8



Test if there are still carbonates: add 2-3 drops of 10% HCl to the sediment base.

If there is a reaction: carry out a **2nd** attack (step 2 to 7) otherwise go to the next step (9).

9



Rinsing operation:

1. Fill the tubes with demineralized water to the 50mL mark.
2. Close the tube and disperse the sediment by shaking vigorously or use the Vortex
3. Centrifuge the 12 samples (6min; 4'000 RPM).
4. Measure the pH of the supernatant (pH paper 1-10).
5. Spill or use a Pasteur pipette to remove the supernatant.
6. Fill the Falcon with demineralized water to the 50mL mark. Do not perform this step during the last rinse!

Repeat 2-3 times until the sample is neutralized (pH >6).

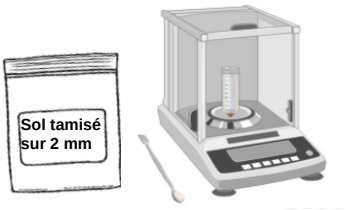
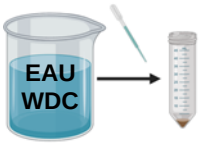
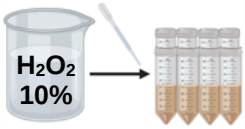
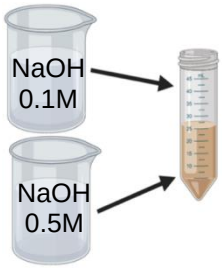
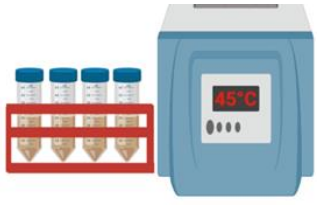
Once the first set of 12 samples has been neutralized, proceed to the next 12 samples.

The important thing is to limit the reaction time of the samples with 10% HCl to 10 minutes to avoid clay transformation.

Destruction of organic matter

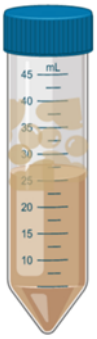
Start at step 2 if decarbonation has been done before.

Work under the fume hood of lab 1440

1		Weigh : - 0.6 g sample of fine clay soil - 1.0 g sample of loamy soil - 1.2 – 1.5 g of sandy soil
2		Add 2mL of demineralized water
3		**Under fume hood** add drop by drop 2mL of 10% hydrogen peroxide (H2O2) and stir the Falcon gently without closing it. ⚠ strong reaction if the sample contains a lot of organic matter (do not foam it to overflow.
4		The destruction of organic matter generates acid and causes the degradation of clays. Buffer the sample to a pH between 6.5 and 7.5 by adding dropwise 0.1M NaOH (or 0.5M NaOH). Check the pH using the pH paper (pH 1-10 and pH1-6). During the first days of the attack check that the pH is still neutral.
5		Cover the Falcons with their cap but do not seal them tightly. Leave them 12 hours (one night) under the fume hood.
6		The next day place the samples in the oven at 45°C to accelerate the reaction. Wait 2 hours and then check the reactivity of the samples: - If the foam does not exceed 30-40mL add drop by drop 1mL of H_2O_2 35%, shake, check the pH and return to the oven *If the day before the samples have strongly foamed, keep them for 2 hours under the chapel before returning to the oven.*

- Otherwise wait until the reaction and the foam decrease (leave in the oven).

7



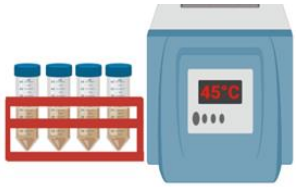
As long as the sample foams, there's organic matter.

In general, add* drop by drop 2-4mL H_2O_2 in the morning and at the end of the day until the samples no longer foam and only bubbles remain from the degassing process.

After each addition shake the sample and check the pH (adjust the pH with 0.1M NaOH if necessary).

**If the liquid level reaches 30-40 ml, let the sample evaporate to <10mL in the oven (45°C) before the next etching.*

8



Once the reaction is complete, reduce the sample volume to <10 ml by evaporating your samples in the oven at 45°C.

If there is too much volume you will not be able to transfer the entire sample to the analysis tube of the particle size analyzer.

Dispersion

Carry out the dispersion **<u>the day before</u>** the analysis on the instrument**.**

1

Add 1.0 mL of 40g/L Na Hexamethaphosphate solution (Calgon) to each sample.

2

Close the Falcons and put them on the stirring plate (speed approx. 100/min) overnight.