

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 America Book Series 5, Madison, Wisconsin, USA. PDF available upon request!

Method

To carry out mineralogical analyses by laser diffraction, the samples must undergo 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**. 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 (in grey box under water bath lab 1440)
- 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*

- 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 and sandy soil
- Wet the samples with 2 ml of demineralized water.
- For the next steps of the procedure, work with series of 8 samples to be able to centrifuge and neutralize the samples at the right timing.
- For the first series of 8 samples, add 10ml of HCl 10% drop by drop, be careful the reaction can be very strong if the sample is very carbonated.
- Close the vials. After shaking them energetically reopen them. (The CO₂ produced by the dissolution of CaCO₃ may cause the cap to pop if it remains closed too long!)
- Place the 8 samples in the ultrasonic bath without lid, previously heated to 70°C, set the timer for 10 minutes of ultrasound (check that the vials are well in the water).
- After 10 minutes, remove the 8 samples from the ultrasonic bath immediately and check the reaction status.
- If the reaction still strong, extend the attack for another 5 minutes and recheck
- 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.

- 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!

- 2nd attack **if necessary**: repeat the steps described above. 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.
- 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'.
- Repeat the rinsing operation described below two to three times:
 - i) Check that each of the 8 tubes is filled to the same height.
 - ii) Centrifuge the 8 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 remove 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 8 samples has been neutralized, move to the next 8 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 H₂O₂ 35%
- Technical H₂O₂ 10%
- NaOH 0.1N or NaOH 0.5N
- Demineralized water
- Ethanol

c) *Removal of organic matter*

- 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 and sandy soil
- Wet the samples with 2 ml of demineralized water.
- Under the fume hood, add 2ml of 10% hydrogen peroxide and agitate by gently stirring the tubes without closing them.
- The humidification and destruction of organic matter by H₂O₂ releases sometimes a significant amount of acidity. To preserve the soluble minerals at acid pH (CaCO₃) 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).

- Cover the vials with their caps but don't close them tightly.

- Leave them for 12 hours (one night) under the fume hood.
- 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!).
- Two hours later, check the reaction of your samples and add 1 ml of H₂O₂ 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 H₂O₂, shake, check the pH and return the samples to the oven.
- 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 H₂O₂, 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 H₂O₂, so we have to add more.

- With a disposable pipette add drop by drop 2-4 ml of H₂O₂ 35% in the morning and add 2-4 ml of H₂O₂ 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 H₂O₂ and NaOH, the water level increases in the tube, diluting the added H₂O₂ each time more. If the level reaches 30-40 ml, it's better to centrifuge the tubes and discard the supernatant to bring the level back to a reasonable amount. For clayey samples it's preferable to evaporate to not lose the fine particles.

- After one week or two at most, the reaction is stopped. There is no more foam production but only bubbles from the degassing of H₂O₂.
- The water level in the tubes must now be reduced to <10 ml. This can be done by letting the samples evaporate in the oven at 45°C or by centrifuging them and discarding the supernatant (except for clay samples).

3. DISPERSION

a) Equipment

- Agitation plate

b) Reagents

- Sodium hexametaphosphate 40g/L (Calgon)

c) Process

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

4. DIAGRAM OF EXPERIENCE

4.1 Safety Equipment



4.2 Decarbonation

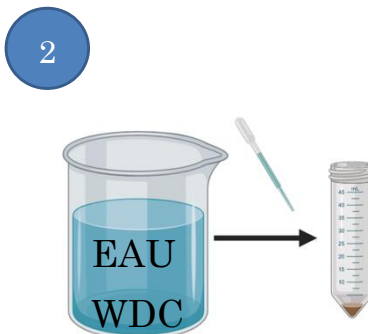
Decarbonation is usually not necessary. However, if it's necessary, it must be carried out before the destruction of the organic matter.

Decarbonation takes place under the fume hood of lab1440

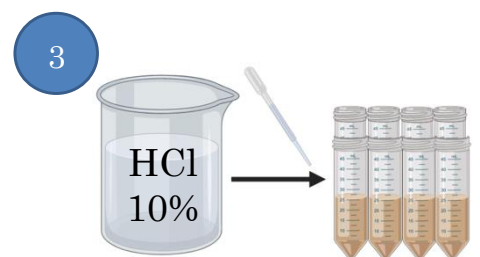


Weigh :

- 0.6 g sample for fine clay soils
- 1.0 g sample for loamy and sandy soils



Add 2mL of demineralized water

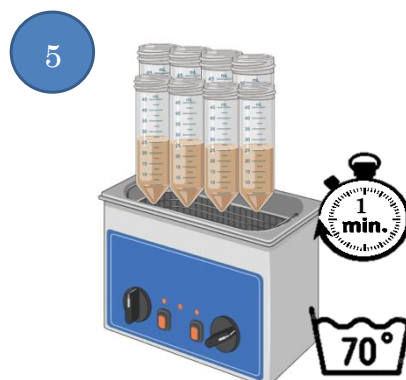


Under fume hood add drop by drop 10mL 10% HCl (make a series of 8 samples)
⚠ Strong reaction if the sample is very carbonated. (do not foam)



Close the 8 tubes and shake vigorously or with the vortex.

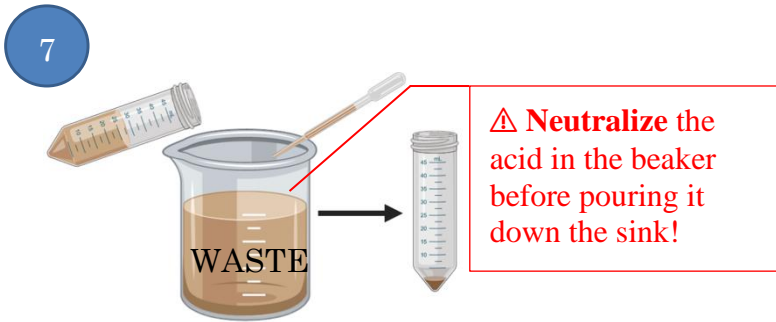
Degas by opening the cap.



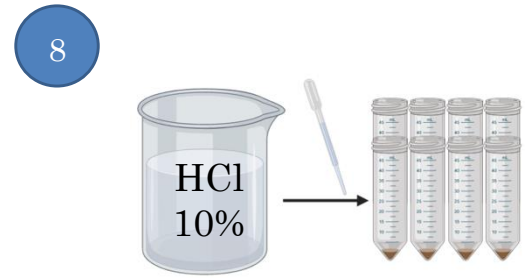
Immerse the tubes in the ultrasonic bath. Check the reaction after 10 min. If it reacts, extend the attack for 5 min and recheck. Close the tubes when finished.



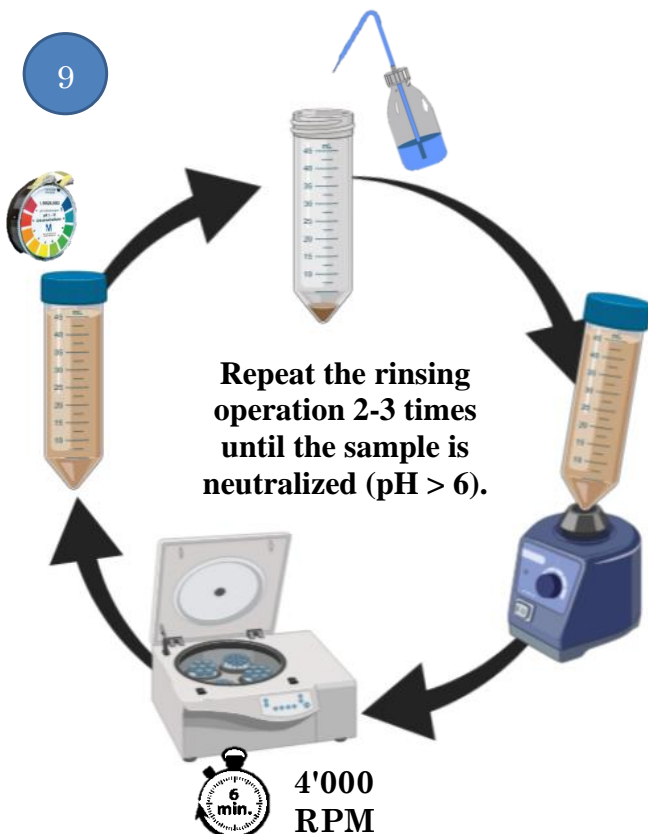
Balance the 8 tubes by making up to 50mL with demineralised water. Increase the times to 10-15 min for samples that do not sediment well.



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



Test if there are still carbonates: add 2-3 drops of 10% HCl to the sediment base.
If reagent: carry out a **2nd** attack (step 2 to 7) otherwise go to the next step (9).



Rinsing operation* :

- Fill the tubes with demineralized water to the 50mL mark.
- Close the tube and disperse the sediment by shaking vigorously or use the Vortex
- Centrifuge the 8 samples (6min; 4'000 RPM)
- Measure the pH of the supernatant (pH paper 1-10)
- Spill or use a pasteur pipette to remove the supernatant.
- 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).*

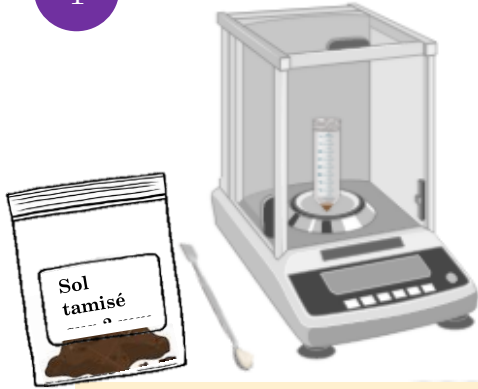
Once the first set of 8 samples has been neutralized, proceed to the next 8 samples.
The important thing is to limit the reaction time of the samples with 10% HCl to 10 minutes to avoid clay transformation.

4.3 Destruction of organic matter

Start at step 3 if decarbonation has been done before.

Work under the fume hood of lab 1440

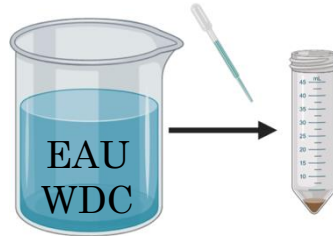
1



Weigh :

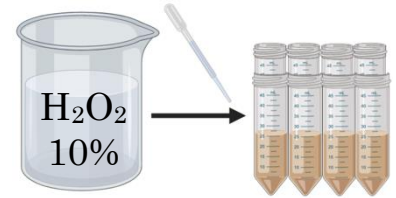
- 0.6g sample for fine clay soils
- 1.0g sample for loamy and sandy soils

2



Add 2mL of demineralized water

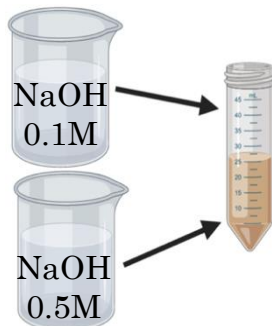
3



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 0.1M NaOH (or 0.5M NaOH) dropwise.

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.

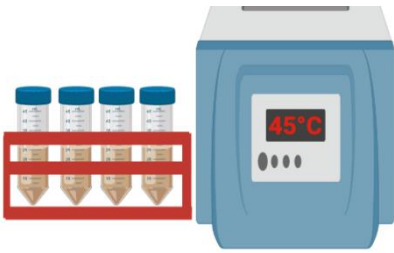
5



Cover the Falcons with their cap but do not seal them tightly.

Leave them 12 hours (one night) under the fume hood.

6



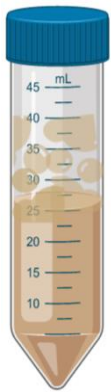
The next day place the samples in the oven at 45°C to accelerate the reaction.

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 H₂O₂ 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 H₂O₂ 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).

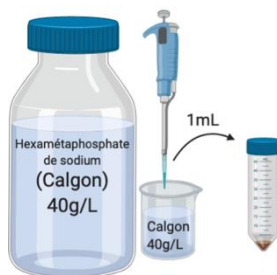
**If the liquid level reaches 30-40 ml, centrifuge the tubes (6min; 4'000 RPM) and discard the supernatant before the next attack. For samples containing a lot of clay it is better to let the sample evaporate in the oven .*

Reduce the volume to <10mL by evaporating in the oven or centrifuging to remove some of the supernatant.

4.4 Dispersion

Carry out the dispersion **the day before** the analysis date on the instrument.

1



Add 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.

Contacts

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Références

Pansu, M. et Gautheyrou, J. (2003). *L'analyse du sol : minéralogique, organique et minéral*. Springer-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 America Book Series 5, Madison, Wisconsin, USA. *PDF disponible sur demande!*