PRE TREATMENT OF SEDIMENT FOR GRAIN SIZE ANALYSIS WHITH A LASER MICROGRANULOMETER
(carbonates, organic matter, biogenic silica)

MATERIAL

1. Glassware:
   Porcelain crucible, 50 ml Falcon® tube, glass slide, glass stick, wash bottle 100 ml. (volumetric flask for chemical preparations)
2. Equipment:
   Laboratory weighing scale, centrifuge, bain-marie, vortex, microscope, laboratory oven, magnetic agitator.
3. Purified water: **H_2Od**
4. Chemical:
   - Hydrochloric acid 37% [7647-01-0] : **HCl_A** 4% solution, **HCl_B** 20% solution
   - Hydrogen peroxyde 35% p/p (133vol.) [7722-84-1] : **H_2O_2** at 35% p/p (can be diluted if too brutal reaction)
   - Sodium carbonate [497-19-8] : **Na_2CO_3** 2M solution
   - Sodium hydroxyde [1310-73-2] : **NaOH** 1M solution
   - Sodium hexametaphosphate (calgon) [6891-31-1] : **calgon** 1g/L solution
   - * Ethanol [64-17-5] : used if the carbonate removal or organic matter destruction are too brutal (one pressure of wash bottle will stop or mitigate the reaction)

Caution: All chemical reactions should be performed under the fume hood and following all security requirement (lab coat, glasses and gloves). Used specific bin for reaction supernatants.

METHOD

1. Sample preparation:

   - Dry the sample in the laboratory oven at maximum 40°C for 24 hours. Let it longer if the sample is not completely dried.
   - Take between 1 and 2 g of sediment. Residue of the different destructions need to be sufficient for the micro-granulometry analysis (40 mg for fine sediment, 150 mg for large sediment)

2. Carbonate removal:

   - Put the withdraw in the porcelain crucible. Flood with **HCl_A** (*). Should observed an effervescence corresponding to CO_2 emission.
   - Mix using the glass stick. Let the reaction continue for 15 min.
   - Add between 1 and 2 ml of **HCl_A**. Wait a few seconds. Repeat the action until the reaction is over (no emission).
   - To control the efficiency of the reaction, add between 1 and 2mL of **HCl_B**. If not, repeat the action.
   - When the reaction is completed, put the sample into a Flacon® tube. Add 50 mL of **H_2Od**. Vortex to unsettle the sediment.

- Centrifuge 7 min at 3000 rpm. Remove the supernatant and resuspend the pellet in **H_2Od**. Repeat this step 2 to 3 times.
- Dry in the oven at 40°C and weight when dry. *Comparison with weight before treatment will indicate the percentage of carbonate within the sample.*

3. Organic matter removal

- Realise the treatment directly in the tube with open lid (emission).
- Caution, the reaction can be really brutal. Add a few drops of **H_2O_2** to evaluate the reaction intensity beforehand (*).
- Add 20 mL of **H_2O_2**. Carefully mix to resuspend the sediment.
- Put the tube in the bain-marie at 65°C for 6 hours. Mix occasionally to resuspend the sediment. Add 1 to 2 ml of **H_2O_2** if needed.
- After 6 hours, take the tube out. Resuspend the sediment and add 1 to 2 mL of **H_2O_2**. Let the reaction occur at room temperature. Mix occasionally and add **H_2O_2** if needed. *It can take several days before the reaction is completed.*
- Once the reaction is completed, add 50ml of **H_2Od**. Vortex to resuspend the sediment.
- Centrifuge 7 min at 3000 rpm. Remove the supernatant and resuspend the sediment in **H_2Od**. Repeat this step 4 to 5 times.
- Dry in the oven at 40°C and weight when dry. *Comparison with weight before treatment will indicate the percentage of organic matter within the sample.*

4. Biogenic silica removal, 2 ways:

A. Sediment with low silica content

a. Reaction within the seal tube using sodium carbonate.
b. Add 40 ml of **Na_2CO_3** (2M). Mix and put the tube in the bain-marie at 90°C for 6 hours. Mix every 2 hours.
c. After 6 hours, add 50 ml of **H_2Od**. Vortex and resuspend the sediment.
d. Centrifuge 7 min at 3000 rpm. Remove the supernatant and resuspend in **H_2Od**. Repeat this step 5 to 6 times. *Caution, ample formation of salt. Rinse abundantly.*
e. Check on a smear slide at x500.
    1. If absence of diatom, dry in the oven at 40°C and weight when dry. *Comparison with weight before treatment will indicate the percentage of biogenic silica within the sample.*
    2. If diatoms, repeat previous step **b** to **e** with only 2 hours bain-marie. Dry in the oven at 40°C and weight when dry. *Comparison with weight before treatment will indicate the percentage of biogenic silica within the sample.*

B. Sediment with high silica content

a. Reaction within a seal tube using sodium hydroxide 1M.
b. Add 20 ml of **NaOH** (1M). Mix and put in the bain-marie at 70°C for 8 hours. Mix every 2 hours.
c. After 8hours, add some **NaOH** and put back in the bain-marie at 70°C for again 8 hours. This step can be done several times.
d. Once the reaction is completed, add 50 ml of H2Od. Vortex and resuspend the sediment.
e. Centrifuge 7 min at 3000 rpm. Remove the supernatant and resuspend in **H_2Od**. Repeat this step 5 to 6 times.
f. Check on a smear slide at x500. No diatoms should be observed.
g. Dry in the oven at 40°C and weight when dry. *Comparison with weight before treatment will indicate the percentage of biogenic silica within the sample.*

5. If the sediment is agglomerate, add 1 ml of **calgon** (1 g/L solution). Mix and let the reaction for 1 to 24 hours depending on the sample nature. It should be fully dissociated.

6. The sample is ready for grain size analysis with a laser microgranulometer.
MALVERN: MASTERSIZER hydro2000G with automatic sampler (0,020 to 2000µm).
Measurement according to Mie's theory with Fraunhofer's approximation. Results in percentages.

Literature :

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