ChE-309 TP-3
Crystallization

instructions for use, spring 2025

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Your employer wants to design a method for purifying Disodium phosphate (Na_2HPO_4), which is a product used in various industrial and pharmaceutical applications. The company can continuously supply a water-based solution with a Na_2HPO_4 mass fraction of 0.07 at a temperature of 60 °C. Based on the planned Na_2HPO_4 orders, the company would like to produce 100 kg/h of pure and dry crystalline Na_2HPO_4. Your job in this hands-on session is to study the Na_2HPO_4 crystallization process in a demonstration reactor and, based on your results, design a reactor to scale up the production for your company.

1. Theoretical part

Crystallization is a unit operation of chemical engineering that consists in isolating a product in the form of solid crystals. It is one of the oldest physical operations practiced (e.g. NaCl isolation by evaporation of seawater).

The yield and purity of crystals are not the only important factors in modern and commercial crystallization. Indeed, the size and shape of the crystals are also taken into account. In general, it is wished to have crystals of similar size. This uniformity makes it possible to achieve the best compactness during packaging, to facilitate pouring, to facilitate washing and filtration, and to have a homogeneous behavior when using the crystalline product in subsequent processing steps. Sometimes large crystals can be requested by the buyer, although small ones are just as useful. Also, crystals of defined shape are sometimes required, such as needles rather than cubes.

Overall, crystallization is a complex phenomenon that involves three stages: nucleation, mass transfer from the solute to the crystallization surface, and incorporation of the solute within the lattice of the cristalline structure. It is commonly accepted that these phenomena refer to the kinetics of crystallization. Experimental data show that the driving force behind these three stages is supersaturation.

The chemical condition of supersaturation of a solution is achieved when it contains more solute than it can normally dissolve at thermodynamic equilibrium. In general, solubility increases with temperature and to produce these solutions, it is a change in the temperature of a saturated solution that will cause supersaturation. It is a metastable state and the solute in supersaturation precipitates at the slightest disturbance giving crystals in a liquid.

We consider a solution at a temperature, T_1, represented by the vertical line in Figure 1. If the concentration is given by point *a*, the solution is undersaturated and crystals of all sizes are dissolved. At point *b*, the balance exists between a saturated solution and crystals that cannot be seen with the naked eye. In the metastable region at point *c*, crystals can grow, but cannot nucleate. If no solid crystal is present, none can spontaneously form. At this concentration, the difference between the temperature at point *e* on the solubility curve and point *c* in the metastable zone is the difference in supersaturation temperature, ΔT_S which is typically about 1 °C. The supersaturation concentration, $\Delta c_S = c - c_S$, is the difference in concentration between points *c* and *b*. At point *d*, spontaneous nucleation of very small crystals occurs. These crystals are invisible to the naked eye. The temperature difference between points *d* and *f* is the limit of the supersaturation temperature difference.

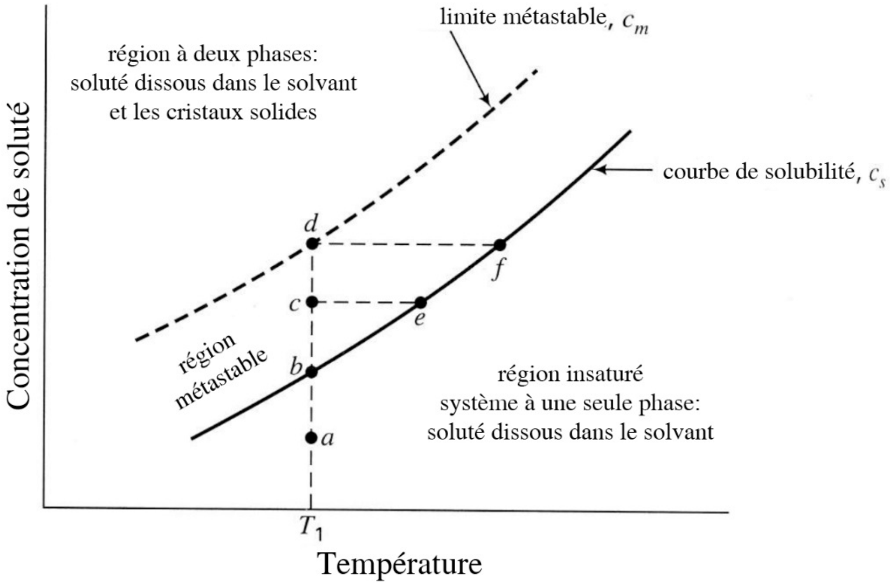


Figure 1. Typical solubility-oversolubility diagram.

The growth and nucleation rates of crystals are complicated functions taking into account many factors. However, classical nucleation theory describes the nucleation rate as the form of Arrhenius' equation. The driving force is the supersaturation ratio, *S*, which is defined as the ratio of the actual activity in solution of the compound to be crystallized to the activity at equilibrium. In the case of reasonably diluted solutions for which the concentration and activity are equal, we can write $S = c/c_s$.

Qualitatively the nucleation and growth rates increase with an increase in *S* but, according to the Arrhenius equation, if crystallization occurs due to a cooling, the nucleation and growth rates will surely decrease because they are dependent on temperature. Figure 2 shows a characteristic situation for these rates as a function of temperature.

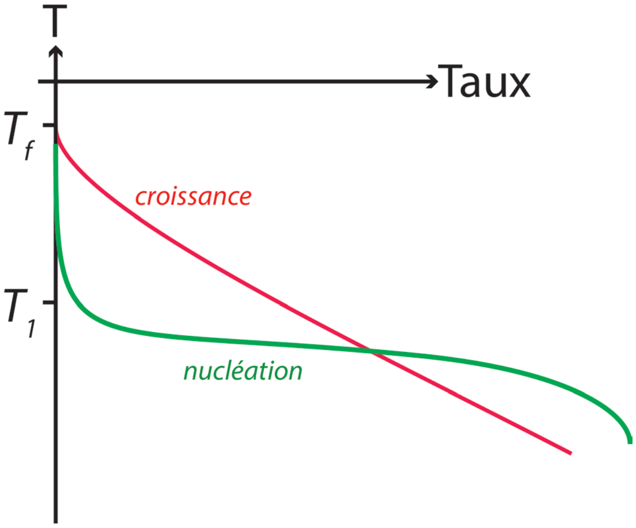


Figure 2. Relative rates of growth and nucleation of a cooling crystallization (f-d points in Figure 1).

2.1. Yields and material balances in crystallization

In most industrial crystallization processes, the stock solution and solid crystals are in contact for a sufficiently long time to reach equilibrium. Therefore, the stock solution is saturated at the final temperature of the transformation and the final concentration of the solute in the solution can be obtained from the solubility curve. The crystal yield from a crystallization can then be calculated using the initial solute concentration, the final temperature and the solubility at that temperature.

In some cases of industrial crystallizations, the crystal growth rate can be quite slow, due to a very viscous solution or a small area of crystals exposed to the solution. Thus, some oversaturations may remain leading to lower yields than expected. In material balances, calculations are simple when solute crystals are anhydrous. Simple material balances between water and solute can be carried out.

2.3 Particle size distribution of crystals

An important factor in the design of crystallization materials is the distribution of particle sizes of the resulting crystals. Usually, dry crystals are sorted to determine particle sizes. The percentage retained on the different sizes selected is recorded. Standard sized sieves (tamis) or screens are then used. The data are represented in the form of a graph giving the diameter of the particles (sieve with mesh opening) in mm compared to the cumulative percentage retained at this size. See example in Figure 3.

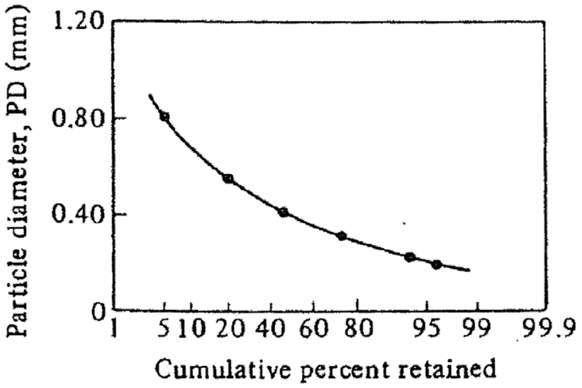


Figure 3. Example of crystal size distribution.

3. Practical Laboratory Exercises

3.1 Objectives

The objective is to study the crystallization of Na_2HPO_4 *in water. The variations in concentration as a function of time will be described, and the effectiveness of the crystallization will be quantified by performing a material balance. In addition, supersaturation* *will be calculated. Finally, the crystal size distribution will be evaluated and a methodology to control the crystal size distribution will be developed.*

3.2 Experimental procedure

3.2.1 Description of the installation

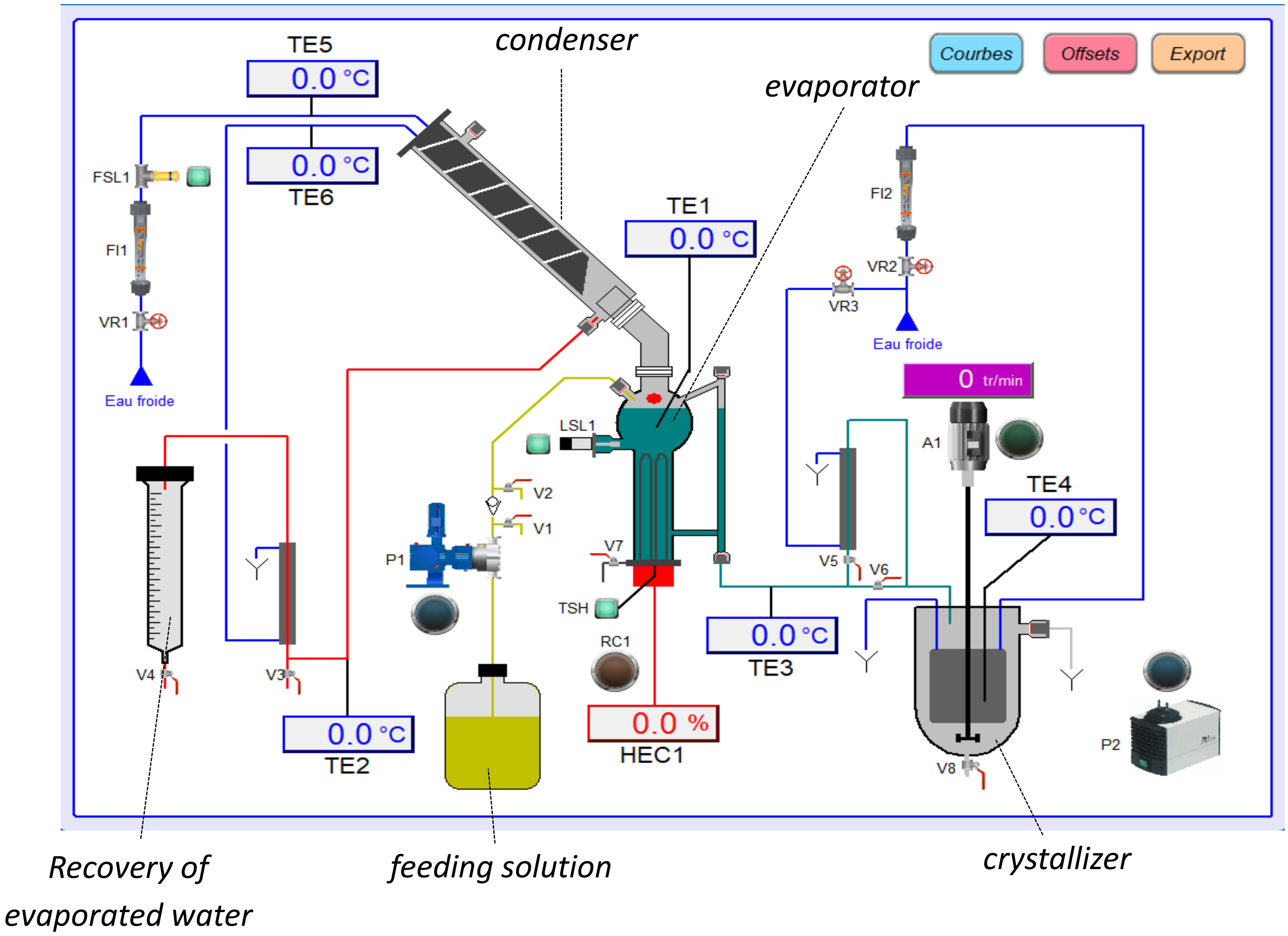


Figure 4: Diagram of the installation

As this is a new piece of equipment in the company, many different parameters need to be tested. Thus, each group will follow a protocol with parameters proposed by a previous group. As such, there is not a general operation procedure, but the following provides a typical example:

3.2.2 Preparation of solution for crystallization

- In a Beaker with a volume of 4L, dissolve about 280 g of Na_2HPO_4 in 4L demineralized H_2O.
- Place a magnetic stirring bar in the flask and heat/stir on the hot plate until the solution appears homogeneous (do not boil).
- Measure the refractive index of the solution and dry 10mL of it to weight the remaining Na_2HPO_4 mass.

3.2.3 Crystallization

- Fill the evaporator with 2.5L of solution close to saturation and the crystallizer with ~1.2L of the same solution.
- Prepare 4L of feeding solution at concentration.
- Switch on the cooling system and start to heat the evaporator at 80% (HEC1) till the solution is boiling and then set (HEC1) to 55%.
- Record the time to evaporate the solution every 100mL evaporated.
- After 1L of solution has been evaporated in the evaporator, start the pump (P1) and manually set the pump at 60%.
- Switch on the stirring in the crystallizer at 100rpm (A1).
- Record the time every 500mL of feeding solution pumped.
- Record the temperature in the crystallizer.
- When the volume in the crystallizer is 2.5L again the solution will start to flow to the crystallizer, write down the time and collect few mL of the solution(V7) to measure its refractive index.
- After feeding the 4L of solution, stop heating and pump demineralized water to rinse the machine.
- Open crystallizer valve V8 to recover the solution+ crystals. Filtrate the solution and dry the crystals obtained with a vacuum system under the hood. Then let the crystals dry for some time.

3.2.4 Crystal recovery and Crystal size distribution measurement

- To measure the size distribution, place the dry crystals in the top sieve. Shake the battery on the agitator for 5 min. Weigh the crystals by staying in each sieve and also those passed through.
- Heat the solution filtrate from the crystallizer to 20°C and measure its refractive index.

- Saved your data following the method in the appendix.
- Wash the set up.

4. Report

4.1.Mass balance and flow rate:

a. Report the volume evaporated and volume pumped in the evaporator as a function of time and estimate the evaporation flow rate and input rate flow in mL/min and calculate the flow rate of solution going to the crystallizer.

b. Calculate the concentration in the evaporator when the solution starts to flow in the crystallizer and compare to the one measured using the refractive index value and the graph in the appendix.

c. Write the expression of concentration as a function of time in the evaporator from when the solution starts to flow in the crystallizer. (Hint start to write dc/dt in function of Qvap and Qin and resolve the differential equation). Plot the evolution of concentration in the evaporator as a function of time.

d. Calculate the saturation ratio in the crystallizer when the 1.2L of solution was cooled down from room temperature to the final temperature in the crystallizer. Plot the evolution of concentration in the crystallizer in function of time.

e. Using the expression of concentration flowing in the crystallizer calculate the mass of Na_2HPO_4 send to the crystallizer at the end of the process and calculate the yield of the process after weighting the crystals.

4.2 Crystal size distribution.

a. Make a graph of the crystal size distributions.

The crystals you used to measure the size distribution were made during the last TP using the following parameters: given by the assistant.

Do you expect the crystals formed during your TP to be smaller or bigger? Comment your answer.

b. Describe a protocol that could be used to obtain bigger/smaller crystals (to be discuss with the assistant) and one to increase the yield.

- What is the input flow rate and how much solution do you evaporate before feeding the solution in the evaporator?
- What is the initial concentration?
- What is the feeding speed (pump %power)

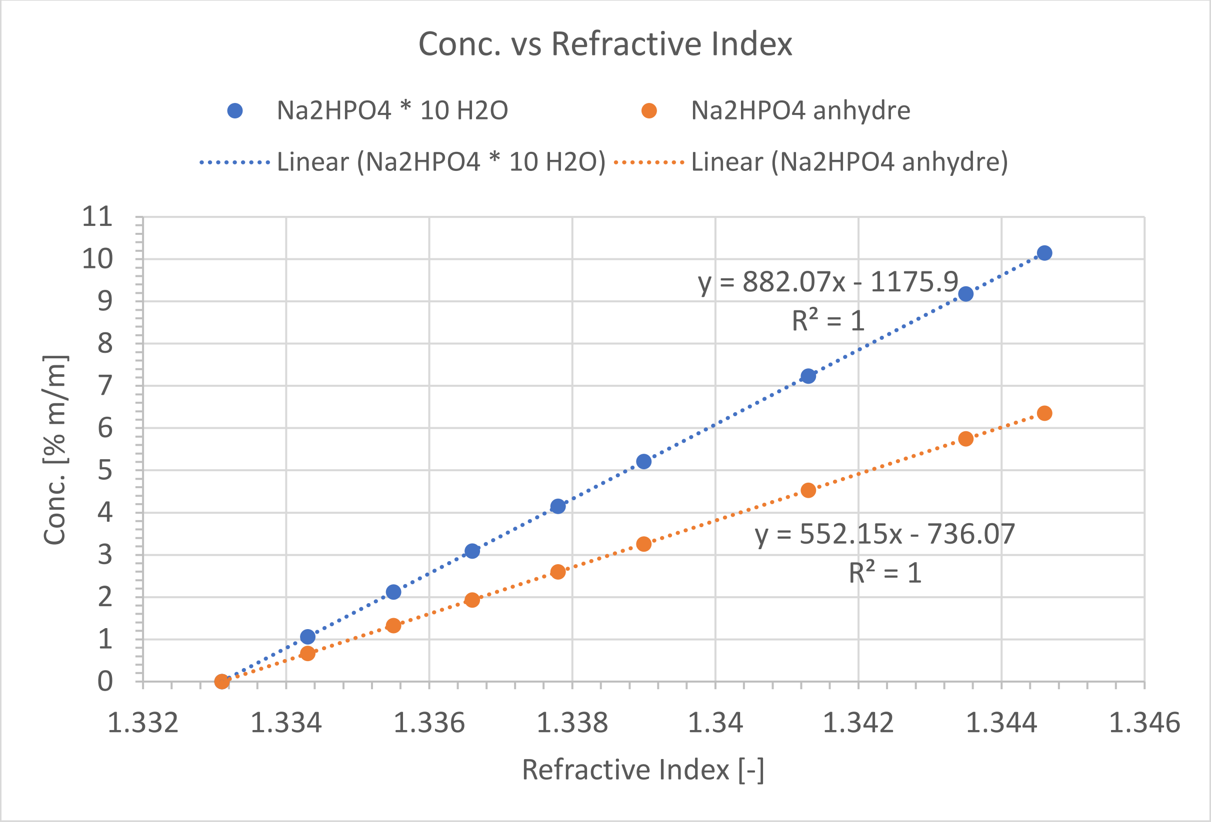
4.3 Design problem (From introduction section):.

Using the enthalpy of crystallization found and the solubility curve given in the appendix, design a stirred crystallization tank that would give a yield of 100 kg / hour of crystals. An initial solution with a mass fraction of Na_2HPO_4 of 0.07 and a temperature of 60 °C is assumed.

- What is the input flow rate and evaporation rate?
- What is the volume of the reactor?
- How could the process be improved?

5. Appendix

Concentration vs Refractive index at 20°C



Save your data :

Pour récupérer les données de l'étude réalisée, brancher une clé USB sur le connecteur situé sous l'écran, (ne pas tenir compte de la fenêtre qui s'ouvre, soit attendre la fin du décompte qui s'y affiche, soit appuyer sur annuler) appuyer ensuite sur le bouton Export.

Il apparait alors au milieu de l'écran le message « Backup in process!! » vous indiquant que le transfert des données sur la clé USB est en cours.

L'export crée un fichier par jour et sera placé dans un répertoire nommé « MP1004 ».

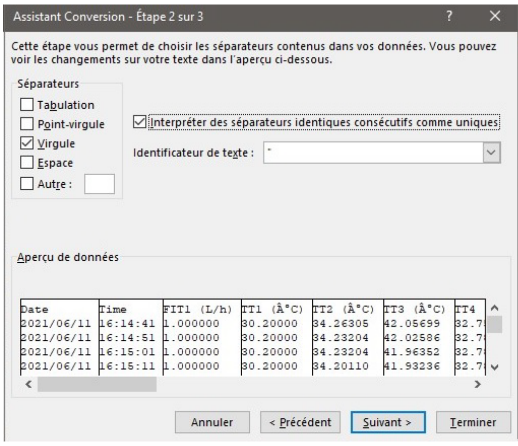
Procédure de traitement des données exportées sous Excel :

Lorsque vous ouvrez le fichier d'exportation des données sous Excel toutes les données sont condensées dans une unique colonne. Pour pouvoir exploiter ces données il faut dans un premier temps les convertir et ensuite remplacer les points des nombres par des virgules.

<u>Conversion des données</u>

- Ouvrir le fichier .csv.
- Sélectionner la première colonne
- Aller dans le menu « **Données** » puis « **convertir** ».

- Cocher « **Délimité** » puis « **suivant »**, cocher « **Virgules** » et « **interpréter…** » et sélectionner les guillemets puis « **Suivant** ».



Cette étape vous permet de choisir les séparateurs contenus dans vos données. Vous pouvez voir les changements sur votre texte dans l'aperçu ci-dessous.

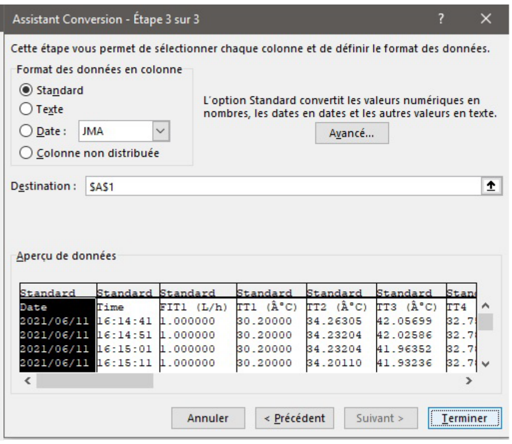
Séparateurs
☐ Tabulation
☐ Point-virgule
☑ Virgule
☐ Espace
☐ Autre :

☑ Interpréter des séparateurs identiques consécutifs comme uniques

Identificateur de texte : "

Aperçu de données

Date	Time	FIT1 (L/h)	TT1 (Â°C)	TT2 (Â°C)	TT3 (Â°C)	TT4
2021/06/11	16:14:41	1.000000	30.20000	34.26305	42.05699	32.7
2021/06/11	16:14:51	1.000000	30.20000	34.23204	42.02586	32.7
2021/06/11	16:15:01	1.000000	30.20000	34.23204	41.96352	32.7
2021/06/11	16:15:11	1.000000	30.20000	34.20110	41.93236	32.7



Cette étape vous permet de sélectionner chaque colonne et de définir le format des données.

Format des données en colonne
● Standard
○ Texte
○ Date : JMA
○ Colonne non distribuée

L'option Standard convertit les valeurs numériques en nombres, les dates en dates et les autres valeurs en texte.

Destination : A1

Aperçu de données

Standard	Standard	Standard	Standard	Standard	Standard	Stand
Date	Time	FIT1 (L/h)	TT1 (Â°C)	TT2 (Â°C)	TT3 (Â°C)	TT4
2021/06/11	16:14:41	1.000000	30.20000	34.26305	42.05699	32.7
2021/06/11	16:14:51	1.000000	30.20000	34.23204	42.02586	32.7
2021/06/11	16:15:01	1.000000	30.20000	34.23204	41.96352	32.7
2021/06/11	16:15:11	1.000000	30.20000	34.20110	41.93236	32.7

- « **Standard** » et « **Terminer** ».
- Les données sont maintenant présentés correctement, un relevé de mesure par colonne.

(Pour qu'Excel « considère » ces données comme des nombres il faut ensuite remplacer les points par des virgules)

Remplacement de symboles

- Sélectionner les colonnes contenant les nombres à décimale.
- Menu « **Accueil** » ➔ « **Rechercher et sélectionner** » puis « **Remplacer** »
- *Rechercher* les « **.** » et *Remplacer* par des « **,** » puis « **Remplacer tout** »
- Vous pouvez maintenant exploiter les données.