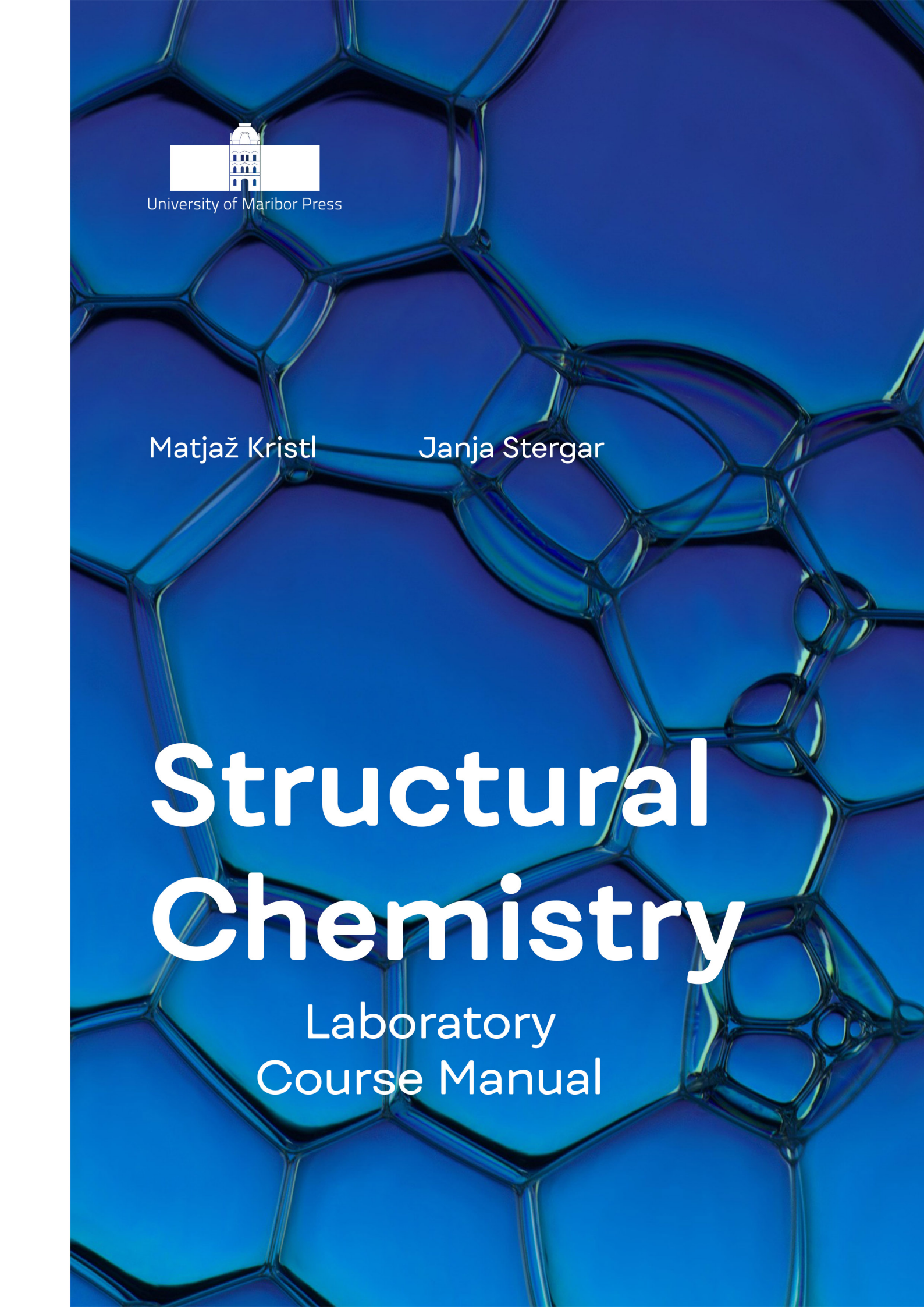

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Matjaž Kristl
Janja Stergar
Structural Chemistry
Laboratory Course Manual

University of Maribor
Faculty of Chemistry and Chemical Engineering

Structural Chemistry

Laboratory Course Manual

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EXPERIMENT 1

Supercooled liquids

Theoretical background

Liquids do not always freeze at their theoretical freezing point (e.g., water at 0 °C) if suitable crystallisation nuclei are not present. Water cooled below its freezing point is known as supercooled water. When the temperature of pure water is lowered, it may remain liquid for some time, even when cooled well below zero. If a small ice crystal is introduced into supercooled water, the water will instantly begin to freeze and turn into ice. This ice crystal provides a template for the water molecules, showing them how to arrange themselves so that ice can form. Other solid substances can also act as crystallisation nuclei and cause heterogeneous nucleation – the rapid freezing of supercooled water. Very pure water in a very clean container can be cooled to approximately −48 °C, at which point homogeneous nucleation occurs.



Figure 1: Freezing of supercooled water
Source: own.

Objective of the experiment

To investigate the supercooling of water, to determine the temperature to which water can be supercooled without freezing, to examine how different types of water (demineralised, tap, mineral) behave during supercooling, to assess how prior boiling affects the freezing of water, and to determine the effect of adding various crystallisation nuclei.

Chemicals and laboratory glassware

- demineralised water
- tap water
- mineral water
- ice
- balance
- NaCl
- grain of sand
- glass stirring rod
- electric heater
- magnetic stirrer
- several small beakers (100–150 mL)
- plastic container
- two bottles with a volume of 500 mL
- digital thermometers
- laboratory spatulas
- watch glass

Procedure

1. Part of the experiment: Freezing of demineralised water

At the start of the experiment, fill two 500 mL bottles with demineralised water and place them carefully in the freezer for approximately 1 hour and 45 minutes. After this time, remove them gently from the freezer, avoiding any shaking or sudden movements.

Firmly strike one of the bottles against the workbench. This increases molecular movement, raising the probability of homogeneous nucleation and causing the supercooled water to freeze. Carefully pour the contents of the second bottle in a thin stream onto a large watch glass on which a small piece of ice has been placed beforehand.

Upon contact with the ice, the supercooled liquid freezes, forming a "stalactite". Record and comment on your observations.

2. Part of the experiment: Supercooling of different water samples

Pour approximately 30 mL of each demineralised, tap, and mineral water into three glass beakers. Prepare 400 mL of a saturated NaCl solution (the solubility of NaCl in water at room temperature is approximately 36 g per 100 g H_2O). Weigh the required mass of NaCl and add the calculated volume of water, allowing for a 10 % excess of NaCl. Stir the solution on a magnetic stirrer for at least 15 minutes. There must be an excess of undissolved substance remaining at the bottom of the beaker; if not, add more NaCl.

Fill the white plastic container to two-thirds of its height with finely crushed ice and add 150 mL of the saturated NaCl solution. Measure the temperature of the cooling mixture with a thermometer. The temperature must reach at least −13 °C.

Place the smaller beakers containing demineralised, tap, and mineral water into the white plastic container. Ensure that ice surrounds all sides of the beakers to achieve the lowest possible ambient temperature. Insert a thermometer, attached to a stand, into each beaker, ensuring the thermometer does not touch the wall or bottom of the beaker. Monitor the temperature changes in all three beakers. Record the temperature to which the water can be supercooled without crystallisation, and also note the time. Observe how the temperature changes upon crystallisation. Perform each measurement in duplicate. Record and comment on your observations.

3. Part of the experiment: Supercooling of previously boiled water samples

Repeat the second part of the experiment using demineralised, tap, and mineral water that has been previously boiled (boil for at least 5 minutes) and then cooled to room temperature in a larger beaker with tap water.

Pour approximately 30 mL of boiled and cooled demineralised, tap, and mineral water into three glass beakers.

Fill the white plastic container to two-thirds of its height with finely crushed ice and add 150 mL of the saturated NaCl solution, adding extra NaCl if needed. Measure the temperature of the cooling mixture with a thermometer. The temperature must reach at least −13 °C.

Place the smaller beakers with boiled demineralised, tap, and mineral water into the prepared container. Ensure that ice surrounds all sides of the beakers and that the ambient temperature is as low as possible. Insert a thermometer, attached to a stand, into each beaker, ensuring the thermometer does not touch the wall or bottom of the beaker. Monitor the temperature changes in all three beakers. Record the temperature and time at which the water can be supercooled without crystallisation. Observe how the temperature changes upon crystallisation.

Record and comment on your observations. Compare the results with those obtained in the second part of the experiment.

4. Part of the experiment: Effect of various additives on crystallisation

Fill the white plastic container to two-thirds of its height with finely crushed ice and add solid NaCl in a 1:1 ratio. Measure the temperature of the mixture with a thermometer. The temperature must reach at least −12 °C.

Cool three beakers of demineralised water on the ice–salt mixture to a temperature of at least −3 °C or −5 °C (it may be lower, but ensure spontaneous crystallisation does not occur). Add a small piece of ice to the first beaker and observe the result. Add a grain of sand to the second beaker and observe the result. In the third beaker, attempt to initiate crystallisation by stirring with a glass rod.

Record and document the events during all parts of the experiment, and comment on your observations.

Further reading

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EXPERIMENT 2

Crystallisation of NaCl in the presence of urea

Theoretical background

Crystallisation from solutions is a fundamental phenomenon of great importance in science and industry. NaCl crystallises in a face-centred cubic structure, which is one of the simplest ways to pack ions in a crystal lattice. NaCl from aqueous solutions usually crystallises as cubes, corresponding to its crystal structure (crystal growth along the {100} planes). However, for more than two centuries, it has been known that NaCl from solutions containing urea (and some other compounds, such as formamide) crystallises as octahedra (crystal growth along the {111} planes). Nevertheless, the theoretical foundations of this phenomenon remain poorly understood to this day.

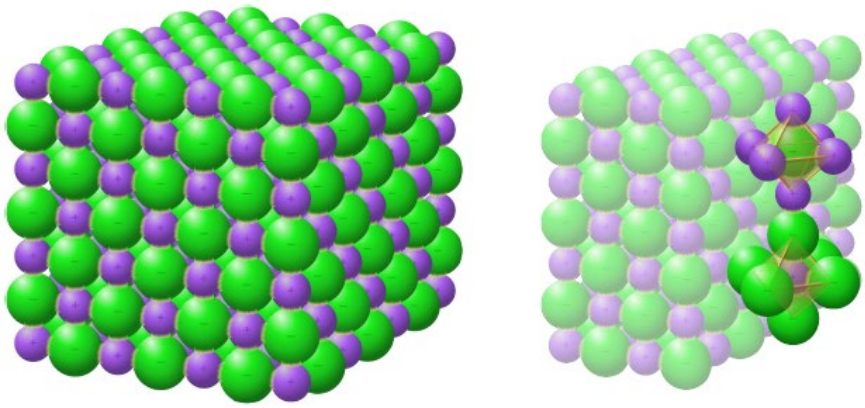


Figure 2: Cubic and octahedral forms of NaCl
Source: Crystal structure of NaCl with ionic bonds, avtor: Goran_tek-en, Wikicommons.org, 2021.

Objective of the experiment

To investigate the effect of additives on the crystallisation of NaCl and to determine how different additives and their concentrations influence the shape of NaCl crystals.

Chemicals and laboratory glassware

- demineralised water
- NaCl
- urea
- potassium hexacyanidoferrate(II), $K_4[Fe(CN)_6]$
- magnetic stirrer
- funnel
- filter paper
- beaker 500–1000 mL
- several beakers (200–250 mL)
- laboratory spatulas
- watch glasses
- glass stirring rod
- tweezers

Procedure

Prepare 400 mL of a saturated NaCl solution (the solubility of NaCl in water at room temperature is approximately 36 g per 100 g H_2O, and the density of the saturated solution is 1.2 g/mL). Add NaCl with a 10 % excess to the calculated volume of water and stir the solution on a magnetic stirrer for at least 15 minutes. An excess of undissolved NaCl must remain at the bottom of the beaker; if not, add more NaCl. Filter the solution through filter paper to remove the undissolved NaCl. Divide the filtrate into several smaller beakers so that each contains an equal volume of solution (approximately 50 mL).

a) Beaker 1 is the control: leave it in air so that the solvent slowly evaporates. Monitor the precipitation of NaCl daily and carefully remove well-formed crystals from the solution with tweezers.
b) Add different amounts of urea to beakers 2, 3, and 4 so that the urea concentrations are approximately 10 %, 20 %, and 30 %. Use a magnetic stirrer to assist. After

dissolving the urea, filter the solution again through filter paper and leave the filtrates in air as described in point a).

c) Add $K_4[Fe(CN)_6]$ to beakers 5 and 6 so that the concentrations of $K_4[Fe(CN)_6]$ are 1 % and 5 %. Use a magnetic stirrer to assist. After dissolving the $K_4[Fe(CN)_6]$, filter the solutions again through filter paper and leave the filtrates in air as described in point a).

Clearly label the beakers with the prepared solutions and leave them on the laboratory bench. Every day, for one week, at least one member of the group should monitor and document the solutions and observe the crystallisation. When crystals a few millimetres in size form, carefully remove them from the solution with tweezers, remove the mother liquor by gently touching a piece of paper towel, and place the crystals on a watch glass. Observe the differences in crystal shape. Photograph the solutions and the formed crystals daily.

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EXPERIMENT 3

Use of the X-ray powder diffractometer for qualitative analysis of samples

Theoretical background

X-ray powder diffraction (XRD) is a technique used to qualitatively and quantitatively analyse crystalline materials in powder form, and it can also be applied to the analysis of bulk materials. It is one of the most important methods for characterising substances in solid-state chemistry.

X-rays are electromagnetic radiation that, when interacting with matter, cause electrons to oscillate. These oscillating electrons then emit secondary electromagnetic radiation in all directions, known as scattering. In crystals, where atoms and therefore electrons are arranged periodically, interference of the scattered radiation occurs. Owing to this property, X-rays are suitable for determining crystal structures. If the geometric condition described by Bragg's law is met, diffraction of X-rays takes place. The resulting diffracted beams travel in specific directions, and their intensity is measured by a detector.

Bragg's law is expressed as:

$$(n \cdot \lambda) = 2 \cdot d \cdot sin\theta \qquad (3.1)$$

where:

n - a natural number,
λ - the wavelength of the X-rays,
d - the distance between planes in the crystal lattice,
θ - the angle between the direction of the incident beam and the lattice plane.

In powder X-ray diffraction, the analysed sample is usually in the form of a fine powder, so the crystals are randomly oriented. For diffraction of X-rays to occur, some of the crystals must be oriented so that their crystal planes make an angle θ with the incident beam, thus satisfying Bragg's law.

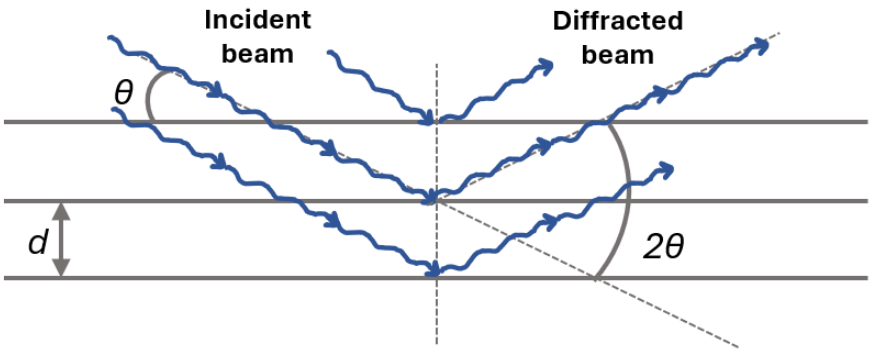


Figure 3: Illustration of Bragg's law
Source: own.

The diffracted beam forms an angle of 2θ with the incident beam, known as the diffraction angle. The instrumental implementation of the diffractometric method is based on placing the sample at the centre of the measuring circle, while the detector moves along this circle to detect the diffracted X-ray radiation. During measurement, the sample rotates at half the angular speed of the detector, so the incident angle of the X-ray beam changes continuously. The measurement produces a diffractogram, which displays the intensity of the diffracted X-ray radiation as a function of the angle 2θ. The shape of the diffractogram allows assessment of whether the substance is amorphous, partially crystalline, or crystalline. By comparing the positions and intensities of the diffraction peaks with a reference database (PDF – *Powder Diffraction File*), the substance can be identified.

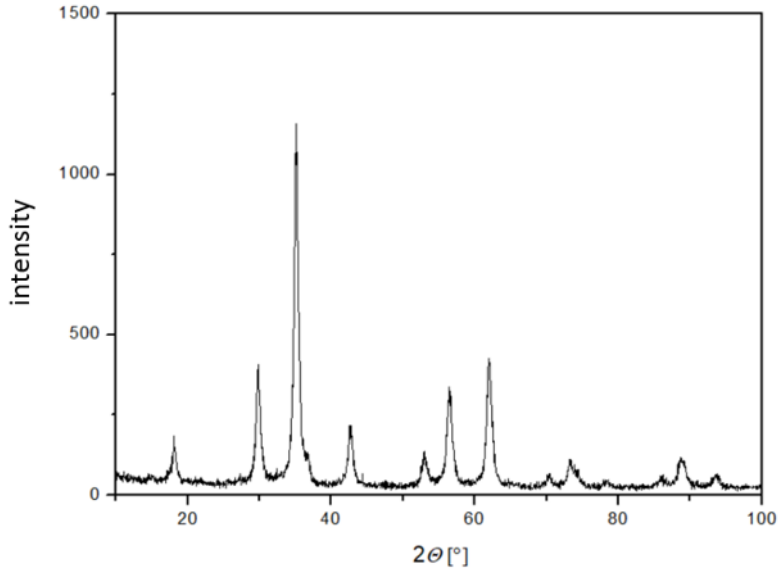


Figure 4: Diffractogram showing the intensity of radiation as a function of the diffraction angle
Source: own.

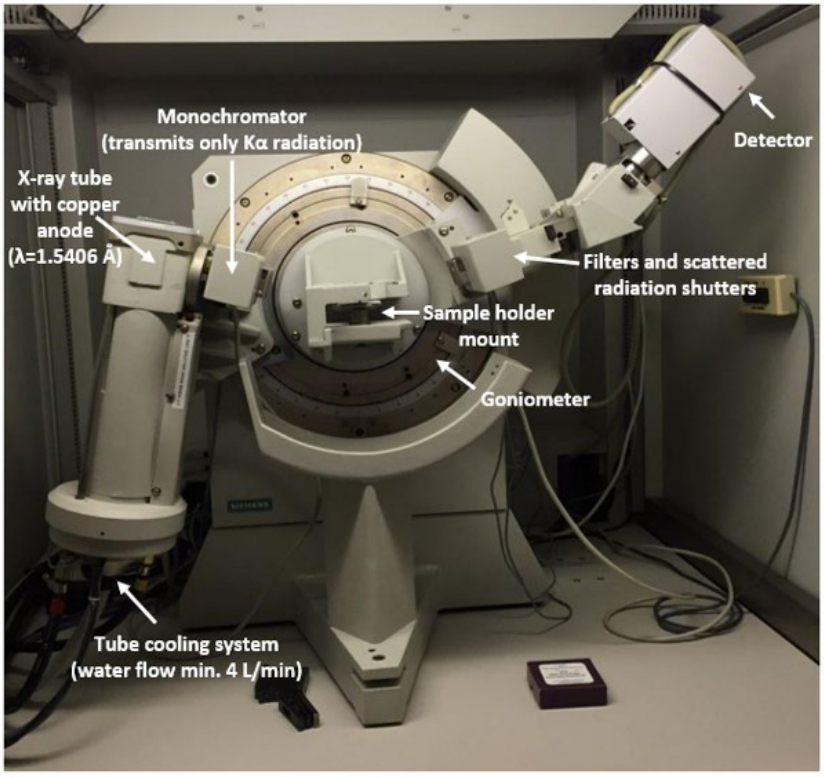


Figure 5: Powder diffractometer Bruker/Siemens D5005
Source: own.

Proper sample preparation is essential for obtaining high-quality data. A common error in X-ray powder measurements is using an insufficiently ground sample, which is particularly problematic for anisotropic crystals. A diffractogram recorded in this way may show some diffraction peaks overly emphasised, while others are too weak or entirely absent. Another

source of error is improper sample application, such as applying a layer that is too thick, which can be partially corrected using appropriate software tools for data processing.

Preferred orientation occurs when crystallites in the powder tend to align in a particular direction. Random orientation of particles is achieved only if the particles are approximately spherical. In real samples, preferred orientation is almost always present, and therefore the measured intensities of diffraction peaks may be distorted.

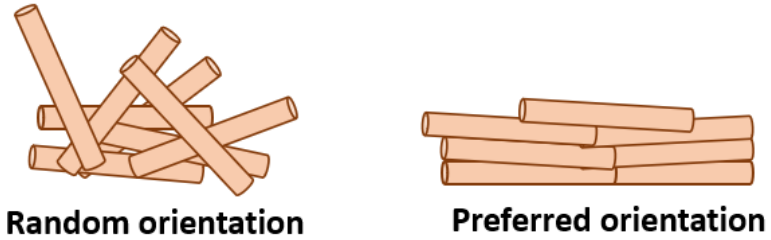


Figure 6: Effect of crystal orientation
Source: own.

Various sample holders are available for measurements. Standard holders enable simple and reproducible preparation of powder samples, such as geological materials. Bulk samples (e.g., coins) are mounted at the appropriate height in deeper holders, ensuring correct sample positioning during measurement and preventing peak shift. Steel holders with different cavity depths are available, designed for either powder or bulk samples. Pharmaceutical compounds and other weakly absorbing materials are prepared on silicon holders with low background contribution, reducing the influence of the holder on the diffractogram and limiting peak broadening. Samples sensitive to air or moisture can be protected with hermetically sealed holders, where the sample is covered, for example, with Kapton foil. These holders also reduce operator exposure to hazardous substances. They are available as standard holders or as holders with a silicon insert. Back-loading holders reduce the effects of preferred orientation by improving the random distribution of crystals [1].

Objective of the experiment

To investigate the effect of sample preparation on measurement quality. To determine the influence of crystallite size, sample quantity, and the sample holder on the measurement results.

Chemicals and laboratory glassware

- sodium carbonate decahydrate, $Na_2CO_3 \times 10H_2O$
- agate mortar
- spatula
- isopropanol
- various sample holders for XRD: Si single crystal, polypropylene holder

Procedure

Apply sodium carbonate decahydrate directly to the polypropylene holder as instructed by the assistant and perform a measurement using the X-ray powder diffractometer. Then, crush the sodium carbonate decahydrate into a fine powder and repeat the measurement on the polypropylene holder and on the Si holder. Compare the results and comment on your observations.

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EXPERIMENT 4

Determination of the composition of a binary sample using the X-ray powder diffractometer

Theoretical background

X-ray powder diffraction (XRD) enables both qualitative and semi-quantitative analysis, including the estimation of the composition of binary and even ternary mixtures of powdered crystalline samples. Two methods are used: the first measures the heights of diffraction peaks on diffractograms, and the second measures the areas under the peaks. The ratio of peak heights or areas corresponds to the ratio of the mole fractions of the two components:

$$\frac{h_1}{h_2} = const \times \frac{x_1}{x_2} \tag{4.1}$$

$$\frac{A_1}{A_2} = const \times \frac{x_1}{x_2} \tag{4.2}$$

Here, h_1 and h_2 represent the heights of the diffraction peaks for components 1 and 2, A_1 and A_2 the areas of the corresponding peaks, and x_1 and x_2 the mole fractions of components 1 and 2.

The calibration curve is prepared by plotting the ratio of the mole fractions of the individual components in the mixture (x_1/x_2) on the x-axis, and the ratio of the intensities of the selected diffraction peaks on the y-axis – either the ratio of peak heights (h_1/h_2) or the ratio of peak areas (A_1/A_2).

Two evaluation methods can be used when determining peak heights and areas. One can choose between the maximum height or the net height of the peak (max height/net height) and between the total area or the net area of the peak (max area/net area), where the net values account for background subtraction.

The use of peak areas is generally more appropriate, as the area better reflects the total diffraction contribution and is less sensitive to possible changes in peak shape or width. Peak heights may be more sensitive to peak broadening, instrumental effects, or signal overlap, and are therefore more suitable primarily in cases of well-separated and symmetrical peaks [2].

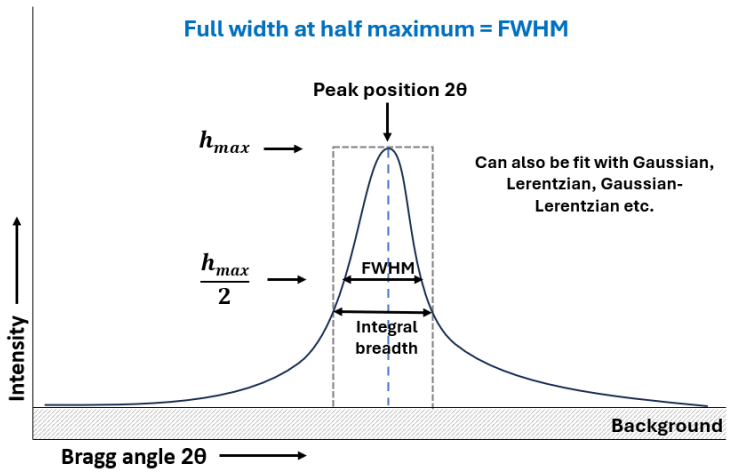


Figure 7: Schematic of a diffraction peak with labelled parameters for diffractogram analysis, including FWHM, peak position, and background
Source: own.

Table 1: Example results obtained with the powder diffractometer (Bruker/Siemens D5005) for a binary sample NaCl : Na_2CO_3.

n(NaCl) : n(Na_2CO_3)	1 : 2	1 : 1	2 : 1	Unknown sample
h_{max} (NaCl)	1404 Cps	1635 Cps	4077 Cps	2177 Cps
h_{max} (Na_2CO_3)	1267 Cps	738 Cps	864 Cps	660 Cps
h_{net} (NaCl)	1377 Cps	1595 Cps	3957 Cps	2106 Cps
h_{net} (Na_2CO_3)	1243 Cps	690 Cps	836 Cps	647 Cps
A_{max} (NaCl)	438	545	1144	620
A_{max} (Na_2CO_3)	337	204	207	147
A_{net} (NaCl)	429	533	1132	612
A_{net} (Na_2CO_3)	330	195	193	142

Objective of the experiment

To prepare a calibration curve for the NaCl : Na_2CO_3 (salt 1 : salt 2) system and determine the composition of an unknown sample.

Chemicals and laboratory glassware

- salt 1 (NaCl)
- salt 2 (Na_2CO_3)
- agate mortar
- spatula
- isopropanol
- Si sample holder for XRD

Procedure

Thoroughly grind both salts in the mortar. For the calibration curve, prepare mixtures with molar ratios $n(1) : n(2) = 2 : 1$, $1 : 1$, and $1 : 2$ and measure their diffractograms. When preparing the sample, apply the experience gained from Experiment 3. Using the appropriate software and following the assistant's instructions, identify one diffraction peak belonging to component 1 and one diffraction peak belonging to component 2. If the peaks are well separated, the strongest (highest) peak is usually selected for both components. In the case of partial peak overlap, it is better to select the second or third highest peak that is well separated from the others. Prepare two calibration curves: plot the ratios of mole fractions (x_1/x_2) on the x-axis, and on the y-axis plot the ratios of peak heights (h_1/h_2) for the first curve and the ratios of peak areas (A_1/A_2) for the second curve. The curve can be drawn manually on graph paper or using any appropriate computer program. Under the same conditions, measure the diffractogram of the unknown sample and determine the mole and mass fractions of the individual components from it.

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Structural Chemistry: Laboratory Course Manual

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The laboratory manual for the Structural Chemistry course describes four experiments focused on crystallization phenomena and the structural characterization of crystalline materials. The first experiment investigates supercooling of water, examining the conditions under which water can remain liquid below its freezing point and the influence of impurities, crystallization nuclei, and prior boiling on nucleation processes. The second experiment studies the crystallization of NaCl in the presence of additives, particularly urea, and evaluates how different additives and their concentrations affect the morphology of NaCl crystals. The third experiment introduces X-ray powder diffraction (XRD) as a method for the qualitative analysis of crystalline materials, with emphasis on proper sample preparation and factors influencing measurement quality. In the fourth experiment, XRD is used to construct a calibration curve for the NaCl–Na_2CO_3 system and to determine the composition of an unknown binary mixture based on diffraction peak intensities.

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