Engineering: Technical report - Annotated example

Powder X-ray Diffraction Identification of an Unknown Crystalline Compound

AIM:

Powder X-ray diffraction with a Cu Kα X-ray source and a Debye-Scherrer diffraction camera was used to identify an unknown crystalline compound.

> A clear, concise statement of what was done. The Title mirrors the Aim clearly. ✓

BACKGROUND:

X-ray diffraction from crystals has been used to solve the vast majority of known atomic structures to date. The principle behind such techniques is that X-rays of a specific wavelength, λ, will undergo constructive interference when reflected from atomic planes in crystals with spacing, d, if the angle of reflection, θ, results in a path difference of an integer number, wavelengths. This was determined by W.L. Bragg a century ago [1] and is expressed in the famous Bragg's Law which is the basis of the field of crystallography:

> Well done on introducing the topic of the experiment and giving some contextual information in the very first sentence. This allows a smooth transition to the theoretical explanation. ✓

$$2d.\sin\theta_B = n\lambda \quad (1)$$

> Avoid casual or emotive expressions that add little or no relevant information. If something is noteworthy, use a specific word that clarifies why it is significant in the context of your topic. ✏

Equation (1) illustrates Bragg's Law in relation to the arrangement of atoms in a crystal structure.

> Top marks for drawing the figure yourself. This is always best as it helps your understanding. ✓
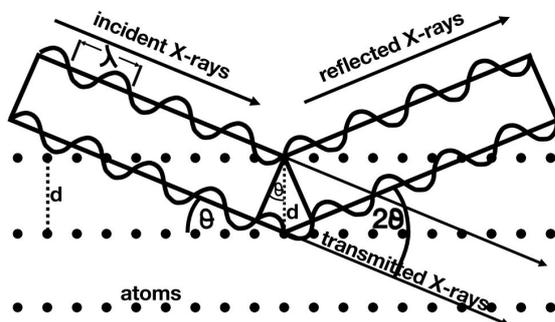

Fig. 1: Schematic diagram of X-ray diffraction from a crystal

> The caption gives sufficient detail for the reader to fully understand the figure without having to search through the text for an explanation. It states what the figure is (a schematic diagram) and what it shows (the x-ray diffraction). ✓

Legend	✓ Good practice	✏ Needs improvement	💡 Comment

When the angle of incidence, θ, of the X-rays with wavelength λ on a set of crystal planes with interplanar spacing d, results in a path difference of an integer number of wavelengths (n = 1 is shown above), then the result is constructive interference due to the exit waves being in phase with one another. This situation is described by Bragg's Law in Equation 1 above.

When Bragg's Law is satisfied, the result is a reflection that can be recorded on film or a digital detector. Given that there are many different families of crystal planes that make up a 3-dimensional crystal structure, Bragg's Law results in a diffraction pattern containing many reflections or "spots" for a single crystal. The geometric relationship between the spots in a diffraction pattern is sensitively dependent on the structure of the crystal giving rise to the pattern and the arrangements of the atoms within that crystal. Hence, X-ray diffraction has developed into a powerful set of techniques for determining atomic structures in crystalline materials.

> ✓ This is good use of a linking word to suggest logical connection between ideas.

There are two main types of X-ray diffraction techniques for determining crystal structures: single crystal X-ray diffraction and powder X-ray diffraction. While the former produces diffraction patterns containing discrete spots as described above, the latter produces diffraction patterns containing rings. Given that a single crystal diffraction pattern (see Figure 2(a)) contains discrete spots because Bragg's Law is satisfied only at specific angles of incidence for each family of atomic planes, and each family of planes has a specific orientation in a crystal, then rings in a powder diffraction pattern are explained as follows. In the case of a powder, there are many hundreds, if not thousands of single crystals, all randomly oriented. Bragg's Law applies to each of these crystals so that for a particular family of planes, there can only be constructive interference if the X-rays are incident at the Bragg angle. However, in the case of powders, a specific family of planes can have any orientation. Given that the Bragg angle must still be satisfied, the reflections span cones with semi-angles of $2\theta_B$, where θ_B is the Bragg angle. This is illustrated in Figure 2(b).

> ✎ Could do better: Your clear and detailed explanation shows you have researched the topic thoroughly – but where are the citations? You need to show where you found all this information.
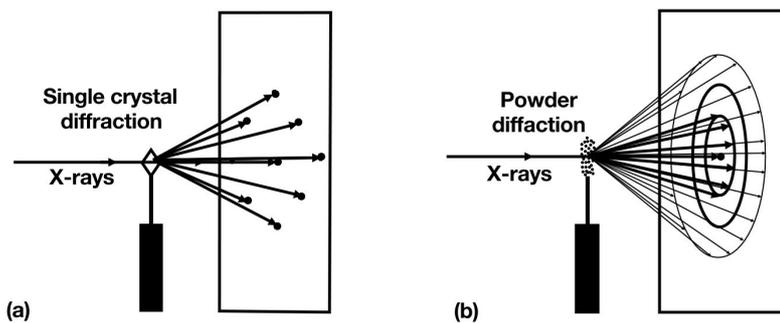
Fig. 2: Schematic diagrams of how X-rays scatter from single crystals and polycrystalline powders.

> Letters are used to clearly label and refer to each part of a multi-part figure. ✓

Diffraction from a single crystal (a) produces a discrete diffraction pattern where each reflection manifests as a spot. Diffraction from a powder (b) produces a diffraction pattern consisting of concentric rings which are the result of the detector plane intersecting diffraction cones whose semi-angle is twice the Bragg angle, $2\theta_B$, for the corresponding set of crystal planes.

Considering figure 2(b) more carefully, the useful information available from a powder diffraction pattern comes from the diameter and intensity of each of the rings. The diameter is directly dependent on the Bragg angle for each set of crystal planes contributing to a ring as well as the distance of the sample from the detector, whilst the relative intensities of the rings are dependent on the strength of each set of planes as scatterers of X-rays. These scattering strengths are directly related to the area density of atoms in each plane.
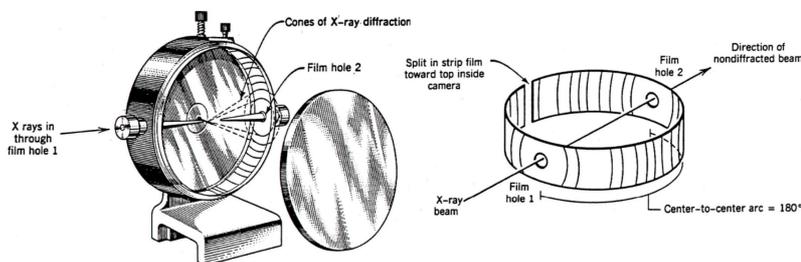

Fig. 3: Diagram of how a Debye-Scherrer camera works in powder X-ray diffraction.

> Is this your original diagram? If not, it requires a citation and reference. ✎

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A Debye-Scherrer camera places the specimen at the centre of a cylindrical detector of well-known radius. The cones of X-ray diffraction are recorded on the strip detector (in this case film) over all scattering angles spanning 360°. This is the simplest approach to collecting a complete powder diffraction pattern and is also extremely simple to manufacture and implement. The diffraction pattern appears as a series of curved lines at the specific Bragg angles for each set of crystal planes that give rise to the corresponding reflections. Figure taken from [2].

"Taken from" means that the figure was copied from a source without alteration. "Adapted from" would indicate that some changes have been made to the figure.

The schematic in Figure 2(b) is not the most efficient way to collect powder diffraction information because the detector is planar and subtends a limited range of scattering angles. A Debye-Scherrer camera overcomes this by placing the specimen at the centre of a cylindrical camera where the detector itself (film in the present experiment) completely circles the specimen, allowing the recording of powder diffraction patterns over all scattering angles (see Figure 3 above). The detector is essentially a strip that intersects each diffraction cone to record a curved line. The scattering angle (Bragg angle) of each line of reflections is easily determined from the well-known geometry of the camera and this in turn, via Bragg's Law (see Eq. 1), gives the interplanar spacing, d, of the set of planes giving rise to each line.

The interplanar spacings of a vast number of organic and inorganic compounds have been measured by powder X-ray diffraction. The relative intensities of the lines in powder diffraction patterns coupled with interplanar spacings (commonly referred to as d-spacings) provide a simple "fingerprinting" approach for identifying unknown compounds. The Hanawalt method [3] involves measuring the d-spacings associated with the strongest lines in a powder diffraction pattern and listing these d-spacings in order of decreasing line strength for at least the three strongest lines. It is then a matter of matching one's experimental observations with values tabulated in the Hanawalt Search Manual Powder Diffraction File [3], which indexes compounds in exactly the same manner, thereby identifying one's unknown material.

METHOD:

A small bottle containing granules of a white substance was received. Each granule appeared to be regularly facetted (a characteristic of many crystalline materials) and approximately 1 - 2mm in size. A stainless steel spatula was used to transfer a small arbitrary quantity (4 – 6 granules were more than adequate) to an agate mortar and these granules were crushed to a fine white powder with the complementary agate pestle. A ~2cm length of 1mm diameter glass capillary tubing was filled with the white powder from the mortar using a needle to aid with the transfer.The filled capillary tube was then mounted into the centre of the Debye-Scherrer camera with plasticine. Both glass and plasticine are relatively X-ray transparent and because they are amorphous (non-crystalline) materials, they are non-diffracting and would not interfere with the recording of the powder diffraction pattern.

Top marks for observing more than just the obvious. The comment in parentheses is extremely relevant because a non-crystalline material will not diffract.

Well done. This explanation shows you understand the physical principles underlying the experiment and were listening to the demonstrator's explanations during the lab.

The camera with the mounted powder specimen was taken into the darkroom near the X-ray diffractometer laboratory and a roll of X-ray sensitive film removed from the darkroom film fridge (low temperatures slow the degradation of the reagents in the film) after the lights had been extinguished and the film safe red lights switched on. A special guillotine was used to cut a strip of film to a pre-set length corresponding to the inner circumference of the Debye-Scherrer camera. The guillotine had two built-in hole punchers that allowed the entry and exit holes for the X-ray beam to be punched into the film at the correct positions to allow the film to be mounted into the camera and the X-ray beam collimators to be fitted. The cut and punched strip of film was mounted into the camera and retained with spring-loaded brackets at each end to keep the film flat against the inner cylinder wall of the camera. This was done with great care in order to avoid disturbing the specimen target at the centre of the camera. The collimators were inserted and the camera lid replaced prior to transfer out of the dark room. See Figure 3 for a view of these components.

Back in the X-ray diffractometer laboratory, the camera was mounted into a Futuron 1560 X-ray diffractometer and the entry collimator of the Debye-Scherrer camera was locked into the exit port of the X-ray source. The source itself was a copper anode filtered to emit Cu Kα1 radiation which has a wavelength of 1.5405Å [4].

After the safety screens were lowered on the diffractometer, the diffractometer was switched on and the potential and current across the X-ray tube were slowly increased to the pre-set limits. The shutter was then opened, commencing the exposure of the film to X-rays scattered from the specimen at the centre of the camera.

After an exposure time of 30 minutes the shutter was closed and the diffractometer powered down. The camera was removed and taken back into the dark room and opened under the film safe red lighting. The retaining mechanism was loosened and the film carefully removed so as not to disturb the specimen target at the centre of the camera. A film clip was attached that allows the film strip to be hung into both the developer and fixer tanks. The film was suspended in the developer with mild agitation for 4 minutes and then rinsed in a flowing water bath for 1 minute. The film was then placed into the fixer and kept there under mild agitation for 6 minutes. It was then washed in the flowing water bath for 30 minutes, with the darkroom lights on.

After 30 minutes in the water bath, the film was removed and hung in a drying cabinet for 30 minutes. Initial inspection of the film before placement into the cabinet showed that the experiment had succeeded in producing a number of lines on the film of different intensities. After 30 minutes of drying, the film was ready for analysis on the light table in the diffractometer laboratory.

Describing the equipment used with all the relevant technical detail here will make it easier to refer to it later, in the analysis of results

Smart move. Checking the film as soon as possible, even when still wet, was a prudent step which could save time in the event of an initial failure of the experiment.

RESULTS & DISCUSSION:

Figure 4 is a scan of the film negative from the powder diffraction experiment. The negative is transparent and all measurements were made on a light table using a ruled guide with a minimum increment of 0.5mm. The length of the negative and distance between the X-ray beam entry and exit holes were measured to be 372.0±0.5mm and 188.0±0.5mm respectively. The error margins are estimated on the basis of half the smallest measurement increment multiplied by 2. This additional factor of two in the estimated error comes from the uncertainty associated with the positioning of the two ends of the negative and the two holes when measuring the distances.
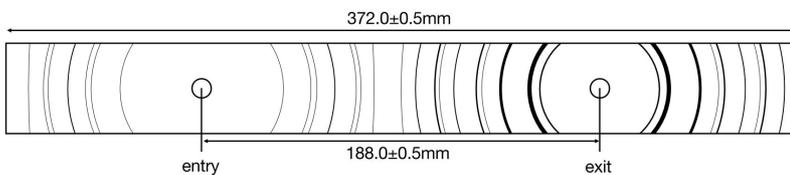
> Top marks. This is vital information that establishes the precision of the measurements. ✓

> Well done for not only stating the numerical uncertainty, but also for explaining how and why the magnitudes of the uncertainties differ from the standard approach. ✓

Fig. 4: A scanned image of the negative film which recorded the diffraction of X-rays from the unknown powder.

> Long captions are used in some engineering fields. Note that the content is limited to an explanation of what can be seen in the figure. ✓

The X-ray beam entered the camera through the hole in the film marked "entry" and left the camera through the "exit" hole. These holes are separated at an angle of 180°. Segments of the rings arising from X-ray diffraction by the powder were recorded as shown on the film. The most intense rings surround the exit hole which is the direction of low-angle or "forward" scattering, whilst higher angle diffraction results in the rings closer to the entry hole, i.e. in the backwards scattering direction.

Given the entry and exit holes in the film correspond to an angle of 180° in the camera (i.e. the angle between the incident and transmitted X-ray beams), the distance between these holes can be used to convert the positions of each of the diffracted rings into angles. Given the known wavelength of the X-rays used (Cu Kα1, 1.5405Å [4]), Bragg's law (Eq. 1) can be used to obtain the d-spacing for the sets of crystal planes corresponding to each ring.

> Top marks for adopting the simplest approach to deriving the required information from a set of measurements. ✓

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These results are presented in Table 1 for the 6 most intense rings (a minimum of the 3 most intense rings is required for the Hanawalt method of identification [3]).The details of how the Bragg angles, θ_B, and d-spacings were determined from the ring diameter measurements are given with the accompanying error analysis in Appendix 1.

Where working from measurement to result need only be carried out once, there is no need for an appendix. The working can be included in the main text in the Results section. Having determined the d-spacings of the crystal planes associated with the 6 most intense diffraction rings, the Hanawalt Search Manual [3] was consulted according to the indexing procedure detailed therein and not repeated here for the sake of brevity. The two most intense rings led very quickly to a likely candidate, namely NaCl, however, [3] lists d-spacings of 1.63Å and 3.26Å for the third and fourth most intense diffraction rings respectively (compared with 3.21±0.07Å and 1.61±0.02Å shown in Table 1 for this experiment). From Table 1, it is apparent that these rings were very closely matched in intensity and could easily be swapped in order, which would result in a match within the uncertainty interval associated with the current experiment.

Table 1: The table of experimental results.

Intensity (arbitrary units)	Diameter, D (mm)	Bragg angle, θ_B (°)	d-spacing(Å)
100	66±1	15.8±0.3	2.82±0.05
60	95±1	22.7±0.3	2.00±0.03
20	58±1	13.9±0.3	3.21±0.07
20	119±1	28.5±0.3	1.61±0.02
15	157±1	37.6±0.4	1.26±0.01
10	176±1	42.1±0.4	1.15±0.01

Repetitive working should be summarised in a single example showing every step of the process used to derive results from the raw data. Present it in an appendix, along with a full quantitative error analysis. Don't forget to refer to the appendix by number at the appropriate point in the Results section.

Nice work - you not only describe inconsistencies but also try to explain them. This shows that you fully understand what you are doing.

Tables are captioned like figures, but the caption appears at the top. Give sufficient detail in the column headings (and row headings if relevant) for the reader to easily understand the content. Always give units in the column headings.

The d-spacings for the fifth and sixth most intense rings match the fifth and sixth listed d-spacings (in order of intensity) for NaCl in the Hanawalt Search Manual, lending confidence to the conclusion that the unknown compound is NaCl.

The measured diameters of the 6 most intense diffraction rings are listed in order of decreasing intensity (estimated on an arbitrary scale from 0 to 100 where 100 is the most intense ring), together with the Bragg angle and d-spacing determined from the diameter measurements. See the appendix for a fully worked example (including error analysis) using the most intense ring. To verify if the third and fourth entries in Table 1 could be switched, it was necessary to ascertain from the literature whether the expected intensities of these two rings should be similar as observed in the present experiment. Reference to [4] shows that this is indeed the case for NaCl. The comparison between the present experimental results and the literature values for NaCl is made in Table 2, with the third and fourth rings listed in Table 1 swapped for the sake of making this comparison.

Top marks for doing extra research to inform your explanation and treatment of discrepancies.

When comparing your results with published values, it is essential to provide citations for the published values.

Table 2: Comparison of the present experimental results and the literature [3 & 4] for NaCl.

Intensity – this expt. (arbitrary units)	Intensity from [4] (arbitrary units)	d-spacing – this expt. (Å)	d-spacing from [3] (Å)
100	100	2.82±0.05	2.82
60	55	2.00±0.02	1.99
20	15	1.61±0.02	1.63
20	13	3.21±0.07	3.26
15	11	1.26±0.01	1.26
10	7	1.15±0.01	1.15

Intensities and d-spacings from this experiment and the literature [3 & 4] are laid out side by side for ease of comparison and entries 3 and 4 from Table 1 have been swapped as the intensities of the rings were indistinguishable from one another in the experiment. Given the arbitrary nature of assessing the intensities of the different diffraction rings with respect to one another in this experiment, it is not surprising that the estimated intensities are only in approximate agreement with those given in the literature [4]. Rings 3 and 4 could easily be interpreted in a different order as suggested by the lack of distinction between them in the experiment as well as their closeness in the literature [4]. The accurate assessment of intensities is also compromised by the non-linear response of film.)

Based on the above comparisons, the unknown material has been confidently identified as NaCl, or common table salt. All d-spacings measured here agree with the literature values [3] to within the experimental uncertainties. The form of the as-received material is also entirely consistent with this identification.

CONCLUSIONS:

Powder X-ray diffraction with a Debye-Scherrer camera was carried out on an unknown material in order to identify it. The six most intense diffraction rings in order of decreasing intensity allowed an unequivocal determination that the material was NaCl. All d-spacings determined from these rings were in agreement with the literature values for NaCl [3], to within the level of uncertainty of the experiment.

> Well done for describing associated circumstances that can lead to errors of judgement; i.e. qualitative errors.

> Well done on this fully justified but compact statement of how the aim has been achieved. It relates previous observations to the conclusion and shows that no other observations contradict the result. For example, if the material had been blue it is highly unlikely to have been NaCl. The form of the material was discussed earlier in the report, so this ties up the Discussion neatly.

> Top marks for a short, concise Conclusion. All you need is to summarise what you learned from the experiment in relation to the aim, i.e. what you found and what it means.

REFERENCES:

[1] W.L. Bragg, Proc R Soc Lond, A Contain Pap Math Phys Character 89(610) (1913), 248–277.

[2] Museum Optischer Instrumente, Germany (http://www.musoptin.com/sale/debye_scherrer.html).

[3] Hanawalt Search Manual – Inorganic Phases, Powder Diffraction File, International Centre for Diffraction Data (Pennsylvania, USA, 1995).

[4] B.D. Cullity and S.R. Stock, Elements of X-ray Diffraction – 3rd Ed., (Prentice Hall, New Jersey, USA, 2001), 278.

APPENDIX 1 – determination of d-spacings from diffraction ring diameter measurements:

The first, most intense diffraction ring listed in Table 1 is taken as the example showing how each diameter measurement in Table 1 was used to determine the d-spacings. The following working from diameter to d-spacing includes the error analysis required to state the experimental uncertainty associated with each d-spacing determination.

The error associated with the diameter of each diffraction ring was determined to be ±1mm. This is because the line width for each ring was of the order of 1mm so half of this width is taken as the uncertainty in the position of each side of a ring. The diameter requires the relative positions of opposite sides of a ring to be measured, doubling the uncertainty to ±1mm. The uncertainty associated with the smallest measurement increment on the ruled guide is ±0.25mm and even if doubled to ±0.5mm, this falls well within the ±1mm associated with the line width. This larger value is taken as the overarching error margin.

The radius of a diffraction ring corresponds to the total scattering angle from the incident (and therefore transmitted) X-ray beam direction by the relevant crystal planes. According to Figure 1, this is twice the Bragg angle, θ_B. Therefore, the diameter of a diffraction ring corresponds to 4 times θ_B. The determination of the Bragg angle for the first ring in Table 1 is therefore expressed as:

$$\theta_B = (66\pm1mm).180°/(4.(188.0\pm0.5mm)), \quad (2)$$

or:

$$\theta_B = 15.8° \pm (1.5\% + 0.3\%), \quad (3)$$

and so:

$$\theta_B = 15.8 \pm 0.3°. \quad (4)$$

In Equation 2, 180°/(188.0±0.5mm) converts distance on the film to an angle in degrees, given the separation between the entry and exit of the X-ray beam spans 180° and a distance on the film of 188±0.5mm.

A full numerical analysis should be included in every lab report that deals with measurements and the derivation of results and conclusions based on those measurements. This allows the reader, and equally important the experimenter, to grasp the levels of uncertainty associated with each result and conclusion.

Top marks for a full explanation of the uncertainties in the measurements.

All units relevant to measurements and quantities must be shown. Errors are calculated based on individual uncertainties. When calculating final error margins, the convention is that for addition and subtraction, simply sum the error margins. E.g. (100±2mm) + (20±1mm) = 120±3mm. For all other operations (multiplication, division, trigonometric functions, etc), use the sum of the percentage errors associated with each component as in the present case (see Equations 2–4).

Equations, even when on separate lines and numbered, are considered part of a sentence. Therefore, punctuation between equations must be maintained, as in the present example which also contains words that interlink the equations.

Bragg's Law (Eq. 1) is now used to convert the angle given in Eq. 4, into a d-spacing:

$$d = \lambda/(2.\sin\theta_B) = 1.5405/(2.\sin(15.8 \pm 0.3°)), \quad (5)$$

$$d = 2.82\text{Å} \pm 1.8\%, \quad (6)$$

$$d = 2.82 \pm 0.05\text{Å}. \quad (7)$$

This working is repeated for the determination of all θ_B and d-spacing values shown in Table 1.

Never express more significant figures in your results than are warranted by the uncertainty. For example: 2.821263894 ± 0.051246346Å is redundant because the uncertainty in the value already lies in the second decimal place. This should always be truncated to 2.82 ± 0.05Å.