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Laboratory Experiment

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An Inquiry-Based Project Focused on the X-ray Powder Diffraction Analysis of Common Household Solids

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Supporting Information

ABSTRACT: While X-ray powder diffraction (XRPD) is a fundamental analytical technique used by solid-state laboratories across a breadth of disciplines, it is still underrepresented in most undergraduate curricula. In this work, we incorporate XRPD analysis into an inquiry-based project that requires students to identify the crystalline component(s) of familiar household products. Centering the project on materials which students encounter in their everyday lives helps to demystify the technique, making it accessible to everyone with a basic understanding of crystallinity and unit cells. In an XRPD study, each crystalline component generates a unique set of peaks in the diffractogram. Comparing the collected diffractogram to a library of diffractograms for known crystalline materials allows students to identify the crystalline components in their unknown. Students must determine for themselves the chemical compositions of the possible unknowns, and link their findings back to the analysis of the collected data. Initially challenging, this is the part of the work they respond to most strongly. This lab includes a data collection component, but its inquiry-based objectives can still be achieved by providing the students with simulated diffractograms when the appropriate instrumentation is unavailable.

KEYWORDS: *Upper-Division Undergraduate, Inquiry-Based/Discovery Learning, Crystals/Crystallography, Qualitative Analysis, Solids, X-ray Crystallography, Interdisciplinary/Multidisciplinary, Laboratory Instruction*

■ INTRODUCTION

As the breadth and interdisciplinary nature of science continues to expand, the central role that chemistry plays brings new challenges to the undergraduate curriculum. A significant part of that challenge has been ensuring that the instrumental methods the students are taught match the skills they will need in their postbaccalaureate careers. In 2008, Sojka and Che reported the frequency with which a host of analytical techniques were used in six ACS journals.[1] While NMR and IR were the most common, X-ray diffraction (XRD) was the third most frequently used technique among the 18 analyzed. In two of the six journals (*Journal of Solid State Chemistry* and *Journal of Catalysis*), XRD was the most-often reported technique.[1] As part of their work, Sojka and Che compared their findings to the frequency with which each technique was reported in this *Journal*, and concluded that coverage of XRD has been disproportionally low.[1] Additionally, a report by the American Crystallographic Association (ACA) and the United States National Committee for Crystallography (USNC/Cr) documented a lack of sufficient X-ray diffraction education and training among undergraduate students in recent years.[2] This report explicitly identified primarily undergraduate institutions (PUIs) as key agents in improving the integration of crystallographic topics and methods into teaching and research.[2]

There are many chemical and physical methods that can be used for identifying compounds; however, most of these techniques cannot provide phase information. A phase is defined as a compound with a specific chemical composition and a particular crystal structure. Some characterization methods provide ambiguous results for compounds of very similar stoichiometry and many are unable to differentiate between polymorphs, which are materials of the same chemical composition but different crystal structure. Since each crystalline phase has its own X-ray powder diffraction pattern, which can be used as a fingerprint to identify it, X-ray powder diffraction is a very powerful and definitive technique for the identification of crystalline solids.

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The literature does contain a number of excellent contributions describing applications of both single-crystal[3−5] and X-ray powder diffraction (XRPD),[6−21] as well as some recent papers that use XRPD as one of several characterization tools.[22−24] Unfortunately, none of these incorporated inquiry-based methodologies in the manner we were seeking. In response, we developed a new laboratory that merges the analytical power of XRPD with the innate curiosity all students have for the world around them. With the use of XRPD, students record and analyze the diffraction patterns of unknown white crystalline powders to determine their chemical compositions, and then match them to their corresponding commercial products.

■ EXPERIMENTAL OVERVIEW

As part of their prelab preparation, students are asked to assume the role of chemist at a major manufacturing plant that produces a wide variety of common household products. A number of vials containing white powders have been found, and they are asked to identify each of them so that the materials may be safely and properly disposed of. Their prelab materials briefly review atomic/ionic/molecular packing in crystalline materials and the basics of Bragg's law of X-ray diffraction.

Upon entering the lab, all students are first given a safety lecture on the proper use of the XRPD instrumentation. Each student then receives two unknowns, and is shown how to load them into the appropriate sample holders. (For convenience, the students are provided with samples that have been preground for them. For small classes with additional time, students could also be asked to grind their samples prior to loading.) A PANalytical X'Pert Pro MPD X-ray powder diffractometer operating in Bragg−Brentano geometry and equipped with a Cu K_α X-ray source was used to collect data in a continuous, absolute scan from 5 to 50° 2θ with a 0.017° step size, requiring approximately 6 min per sample. Students then used the PANalytical X'Pert HighScore Plus software package[25] to match the peaks in their diffractogram against the reference X-ray powder diffractograms of known crystalline phases. In some instances, their sample was a single phase, pure compound, and in other instances, it was a mixture containing two or more crystalline components. Typically, each student was given one of each type to analyze. The PANalytical software performs the search using references from the Powder Diffraction File (PDF),[26] a database maintained by the International Centre for Diffraction Data (ICDD). This database is the primary reference for powder diffraction data and includes tabulated *d*-spacings (determined from the angle of diffraction and the wavelength of the X-rays) and the corresponding diffracted intensity. The database contains both experimentally measured (deposited) patterns and those calculated from crystal structures.

Once the student had identified the chemical composition of their sample, they then had to match it to the corresponding commercial product. Table 1 lists both the commercial product name and its corresponding crystalline component(s). In the lab, students were only provided with the common household name and were expected to research the composition of each product on their own. Finally, as part of their lab report, students were asked to visualize the packing structure of each crystalline component in their materials and create figures by searching out its crystallographic information file (CIF) to read into the Mercury software package.[27]

Table 1. A Sample of Commercial Products Used as Unknowns in This Lab[a]

Commercial Product	Crystalline Chemical Components	CAS No.	Challenge Level
Advil	ibuprofen	15687-27-1	1
Alka-Seltzer	acetylsalicylic acid	50-78-2	3
	citric acid	77-92-9	
	sodium bicarbonate	144-55-8	
OxiClean	sodium carbonate	000497-19-8	3
	sodium carbonate peroxide	015630-89-4	
Table sugar	sucrose	57-50-1	1
Tums	calcium carbonate	1317-65-3	2
	sucrose	57-50-1	
Tylenol	acetaminophen	103-90-2	1

[a]The full table listing all 25 samples is provided in the Supporting Information.

■ HAZARDS

Properly installed and maintained, modern XRPD instruments expose operators to no additional radiation above background. Basic X-ray radiation safety should be covered in class prior to students using the instrumentation.

While most of the samples used in this lab are either food-grade products or common household products of minimal risk, students originally encounter them as unknowns, so all of the materials should be treated as potential hazards, and proper safety protocols (including gloves, lab coats, and safety glasses) should be used when handling and disposing of them. A full list of the chemical components and their CAS numbers are provided in the Supporting Information.

■ DISCUSSION

Helping students build effective linkages between the atomic theory of matter and the tangible world around them can be frustratingly difficult. Gases are almost always invisible, while the intricate, symmetrical, and false-colored atomic lattices supposedly representative of all crystalline solids typically displayed in the classroom bear little resemblance to most "solids" of the macroscopic world, which are substantially more complex and often heterogeneous mixtures. While we know that a key step in learning chemistry is the ability to "see" the world at the level of atoms, ions, and molecules, guiding students to this appreciation remains a challenge.

In this laboratory, our ultimate goal is to have students discover for themselves that crystalline materials are a part of their everyday lives. An important first step along this path is to introduce them to the types of analytical instrumentation that allow chemists to explore the structures of materials. All of the samples used in this laboratory are white powders, which when finely ground are visually indistinguishable from each other. When analyzed by XRPD, the first insight students gain is that the resulting diffraction patterns are clearly different from each other. Even if they do not appreciate why initially, the point that they must have different structures is readily made.

Next, students match their diffractograms against a commercial library of inorganic crystalline materials. For properly prepared single-component samples, this step can be quite quick and engaging. As students progress in skill and confidence, they can be further challenged with a sample containing a mixture of crystalline components. Figure 1A compares the diffractogram for a single component sample, table salt, with pure sodium chloride, while Figure 1B shows

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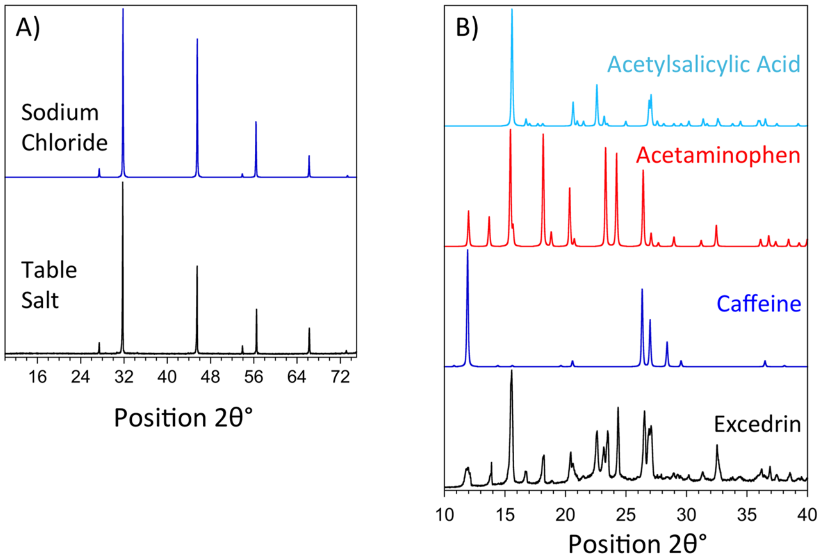

Figure 1. Diffractograms of household solids, table salt and Excedrin, shown on the bottom in (A) and (B), respectively. For each example, the reference diffractogram(s) of the crystalline component(s) are provided as well, on the top. *Y*-axis signals are relative diffraction signal intensity, normalized to the largest peak in each pattern.

data for Excedrin. The latter sample contains three crystalline active components, having distinctive diffraction patterns, producing a much more complex diffractogram.

Within a relatively short time frame, every student can determine the chemical identity of the crystalline components in their sample(s), but this is only the starting-point for the true discovery step. As part of their lab assignment, students are provided only with the commercial brand-names of the possible sample materials. To successfully match their samples to the unknowns, they need to discover for themselves the chemical compositions of the products. At this step, students also notice that some of the household products contain more compounds than those which they can "see" in the diffraction pattern because some components are amorphous in nature or present in very small quantities, below the detection limit of X-ray powder diffraction about <5%. In pharmaceutical products, for example, the active pharmaceutical ingredients (APIs) are usually, but not always, the crystalline components, and the excipients, inactive components added to the formulation for other reasons, such as time release agent, filler, glidant, colorant, etc., are most often amorphous or present in very small quantities.

The collective ingenuity, resourcefulness, and teamwork our classes have displayed in completing this assignment has been impressive. Food and drug products, for example, are required to list their contents as part of their packaging, but many other household materials are less explicit with respect to what they contain. A good resource for finding the contents of nonfood and nondrug items is the household solids database maintained by the U.S. Department of Health and Human Services.[28] In the process of completing this part of the assignment, students gain a much deeper appreciation of the fact that the "products" they use every day are, in fact, "chemicals"; many have since told us that they have started reading product labels at the grocery store much more closely. One class even took a field-trip to a local store as part of their lab.

To complete the association between the chemical composition of a product and its fundamental chemical makeup, students are asked to use the Mercury software platform, provided free of charge from the Cambridge Crystallographic Data Center, to generate representations of the unit cell and the packing structure of each crystalline material. In the process of generating these images, students learn to use a powerful visualization tool, are able to examine details such as bond lengths and angles, and build connections between the physical solid in their sample and the details of its crystalline packing. Students are graded on the effectiveness of these figures; all atoms must be visible and labeled in the image and all bonds must be properly drawn.

We have most often used this laboratory with chemistry majors in our upper-level integrated laboratory, from which student feedback for this laboratory has been very positive. Students here are already familiar with the level of intellectual independence and self-initiative this type of lab approach requires, and they were easily engaged. While this lab now lists 25 possible unknowns, it was first introduced with an original list of less than 15. It has grown over the years thanks to the suggestions of students who, not only completed the assigned tasks, but also took the time to research other consumer products. The fact that the upper-level students find the XRPD technique both simple and powerful is supported by our observation that these students now use this technique more frequently in settings where they are asked to choose for themselves how to analyze samples.

When used with a group of honors general chemistry students, formative feedback gathered via surveys was still favorable but less enthusiastic. About half of the students rated it equivalent to other laboratories, well over a quarter of them preferred it to other laboratories, and only a few liked it less. Students in this cohort were still being introduced to the expectations of structured-inquiry laboratories, and it is challenging to dissect student reaction to the topic from the discomfort many of them experienced when asked to think for themselves in a lab setting. Adaptations for using this approach in a first-year setting are discussed in more detail below.

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■ ADAPTATIONS AND ALTERNATIVE IMPLEMENTATIONS

This lab, as described above, served to both familiarize students with the use of an X-ray powder diffractometer and guide them through an investigation of the crystalline nature of common household products. While XRPD instruments continue to become more compact and user-friendly, access to this sort of instrumentation is not universal. In this event, instructors have the option to simulate single-phase diffraction patterns by imputing crystallographic information available in the literature into an upgraded version of the Mercury software package. The inquiry components of this lab can still be accomplished by asking students to identify the chemical compositions of their unknowns and trace this back to their commercial products. Complicated mixtures and components that are hard to discriminate by eye have been omitted from this data set.

The level of difficulty in this lab is dictated primarily by the complexity of the mixture to analyze, and the number of commercial products provided as possible answers. Even with a good library of diffractograms and the library-matching software provided with the instrumentation, some mixtures are challenging. In the Supporting Information, we have ranked the challenge level of each household product, allowing instructors to match the difficulty with the level of the students with whom they are working. Additionally, the time it takes to link an identified sample to its commercial product scales with the number of potential choices that must be eliminated. The balance between learning about lots of common products and the frustration that arises after too many negative results can be ameliorated by paring down the number of total choices provided.

Although highly recommended, completing this lab does not require a fundamental understanding of the diffraction process; many instructors may wish to include this option. A number of papers provide excellent materials that could be integrated.[29−34] As noted above, the Mercury visualization software can calculate powder diffraction patterns from CIFs obtained from the literature. For advanced students, this offers the ability to complete the learning cycle by having them calculate new powder patterns for materials they have not yet tested. An excellent series of articles in this *Journal* provides additional applications of the Mercury visualization software and associated materials available from the Cambridge Structural Database.[35−38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00008.

Student handouts, instructor notes (PDF, DOCX)
Experimental X-ray powder diffractograms and crystallographic data necessary for simulated powder X-ray diffractograms of household solid components (XLSX
Household items references (XLSX)

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Notes

The authors declare no competing financial interest.

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