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Powder X-ray diffraction detection on a paper-based platform

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ABSTRACT

We developed paper-based powder X-ray diffraction (PP-XRD) to implement phase identification and/or crystal structure determination on paper-based platforms. These aims are not possible with other paper-based detectors, such as Raman spectroscopy and mass spectrometry. PP-XRD overcomes these limitations. Here we reported the simple and low-cost in situ PP-XRD protocol for phase identifications of inorganic and organic materials. We demonstrated that sample amounts of lead nitrate on paper substrate can be reduced into 1/30 of conventional ones by using the standard glass substrate at the same signal-to-noise ratio (S/N) of the X-ray diffraction (XRD) pattern. The paper-based method was comparable in sample quantity and intensity with zero background holder method, even though single crystal Si(100) substrate as zero background holder was used for the specimen preparation of CTAB ($C_{19}H_{42}BrN$). More importantly, paper substrates helped reduce preferred orientation that was generally present in routine powder XRD. Also, combined with paper chromatography, overlap peaks were eliminated in the XRD detection patterns of lead nitrate and cobalt nitrate hexahydrate. This new PP-XRD protocol may accelerate the process to identify phase or determine the molecular structures of new materials using trace sample directly. It also includes a hyphenated technique of powder XRD with a simple paper-based microfluidic separation of chemical solutions.

1. Introduction

Portable and cheap paper-based analytical devices [1–4] have many unique advantages, such as power-free fluid transport via capillary action, high surface area-to-volume ratio and the ability to store reagents within fiber network. In fact, paper as a separation substrate dates back to the early 19th century. Its big breakthrough was the invention of paper chromatography [5–7]. One crucial step of paper chromatography or other paper-based separation devices is able to quantify or identify the analytes. On paper-based separation platforms the detection techniques such as colorimetric [8], electrochemical [9,10], chemiluminescence [11,12] and surface enhanced Raman scattering [13] were proposed to analyze complex samples with different characteristics. However, in principle, these detection techniques could not be used for phase identifications or structural determinations at the atomic level of known or unknown materials.

Knowledge of molecular structure of matter at the atomic level is a prerequisite to understand and predict material properties. Single-crystal XRD [14,15] was recognized as the most reliable structural determination method. However, for most materials it was very difficult to prepare a stable single crystal with sufficient sizes, and many natural or synthesized compounds are in polycrystalline states [16–18]. Powder XRD was an alternative approach for the determination of crystalline structure in this case [19]. Besides determining crystal structures of unknown materials, the powder XRD method could be frequently used for the identification of multi-phase samples [20]. It is well known since the observed powder diffraction pattern of a multi-phase sample is the sum of phase pattern of many components. However, the peak overlaps need a lot more time to perform the phase identifications. In addition, preferred orientation and impurity phase from powder XRD data may potentially limit the successful application of XRD techniques for structure determinations. Thus, the specimen preparation methods are of the utmost importance to obtain reliable diffraction data through reducing the effect of preferred orientation. To best of our knowledge, little attention was focused on hyphenating paper chromatography with powder XRD detection for the multi-component separations and simultaneous phase identifications of mixed samples from liquid to solid.

In this article, paper-based powder XRD protocol, called PP-XRD for short, was presented for the phase identification of inorganics, organics and amino acids in situ. With PP-XRD, three polycrystalline preparation methods were used: the soaking, spotting, and wicking of

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paper strips. The sample amount of lead nitrate was reduced into 1/30 of the conventional amount at the same signal-to-noise ratio, as compared to traditional powder XRD. The detection limit of lead nitrate was dropped to about 660 μg. In addition, the PP-XRD method was comparable in sample quantity and intensity with using single crystal substrate in conventional one. Furthermore, in situ phase identifications of a mixture of lead nitrate and cobalt nitrate hexahydrate were achieved by combining paper chromatography with powder XRD. This PP-XRD protocol will be useful to identify phase with trace amount discover new drugs and natural products from complex chemical and biological samples.

2. Experimental

2.1. Materials and chemicals

Whatman chromatography paper #1 (20.0 cm×20.0 cm) was from GE Healthcare Worldwide (Pudong Shanghai, China). Filter paper (Hangzhou, China) and microporous filter membranes (Shanghai, China) were from Xi'an Hairmer Biotechnology Co., Ltd (Xian, China). Nitrocellulose membranes were from Merck Millipore Ltd. Si (100), (111) and (110) substrates were purchased from Zhe Jiang Lijing Silicon Materials Co., Ltd. Chalcanthite, cobalt nitrate hexahydrate, lead nitrate, hexadecyl trimethyl ammonium bromide (CTAB, C_{19} H_{42} Br N) and L-leucine (C_6 H_{13} O_2 N) and absolute alcohol were from Aladdin Industrial Inc. (Shanghai, China). All reagents were analytical reagents. Water with 18.2 MΩ cm resistances was obtained from Ulupure purification system (Milli-Q Gradient, Millipore).

2.2. PP-XRD detection protocol

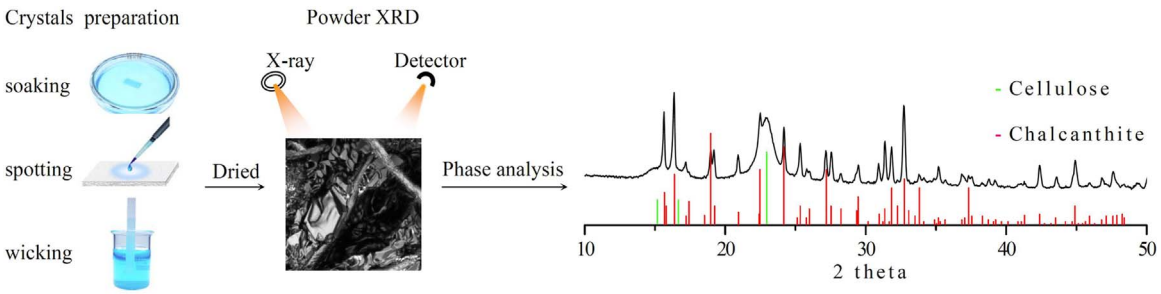
Scheme 1 indicates the operation steps of the PP-XRD protocol. Three polycrystalline preparation methods were used – soaking, spotting, and wicking of paper strips. *In soaking*, the entire cellulose paper strip, e.g. 1.0 cm×2.0 cm, was immersed into the solution filled in glass petri dish at room temperature for a period of time, then removed from the solution, and dried on a hydrophobic polyethyle (PE) glove (Guanming Brand, Haimen Yangzi Medical Equipment Co., Ltd) for the diffraction analysis. *In spotting*, the droplets of the solution were spotted onto the paper strip (e.g., 1.0 cm×1.0 cm) by a pipettor. For very low concentration solutions, spotting repetitions and drying times were correspondingly increased. Each spotting must be done after the solvent (e.g., water) on the paper strip were completely evaporated last time. In wicking, one end of a long paper strip, e.g. 1.0 cm×20.0 cm, was plunged below 1 cm–2 cm of the liquid level, and the other end of paper strip was clamped on a rack. The solution was placed in the beaker, whose mouth was sealed with aluminum foil, only leaving a gap to make the paper strip insert expediently. As a mode molecule, the copper sulfate in the solution was lifted upward a certain height on the strip due to capillary force. As the solution evaporated, blue crystals of copper sulfate accumulated on the leading edge of the paper strip. The wicking time was mainly depended on the concentration of solution under constant temperature and humidity. After the wicking was finished, the paper strip was removed from the solution. Then, the strip was dried on the PE glove, a 1.0 cm×2.0 cm paper strip contained maximum crystals was cut down by a scissors. In principle, the wicking can be applied to low concentration solutions of other inorganic, organic, and amino acid samples, etc. Wicking is the preferred of the three methods, because it requires less effort than spotting, and chemical separation, or hyphenation, does not occur with soaking or spotting. The temperature was control by a drying oven (DZF 6021, Shanghai Jing Hong Laboratory Instrument Co., Ltd).

Once the paper strips were dried, they were placed directly onto the backside of amorphous glass to obtain the XRD spectra. X-ray diffraction analysis was performed on the powder Diffractometer (PANalytical's X'Pert Pro) using CuK_α radiation at 40 kV and 40 mA with $\lambda = 1.5406$ Å. The divergence, anti-scatter and acceptance slits were 1°, 2° and 6.6 mm, respectively. The step size was 0.0334225. The X′ Celerator detector was used to collect the diffraction data.

3. Results and discussion

3.1. XRD patterns from different paper substrates

The effects of PP-XRD patterns of target molecules depended on the characteristics of paper substrates, such as their compositions, pores and thicknesses, etc. In the PP-XRD protocol the apparent diffraction patterns (Fig. 1A) were made with chalcanthite as target molecules and paper cellulose. The XRD patterns of seven kinds of paper substrates on a glass slide were collected (Supplementary Fig. S1). The patterns 1–4 (Supplementary Fig. S1) show the diffraction patterns of four filter papers composed of pure cellulose, but with the different thicknesses, respectively. They showed a broad main peak at 22.867° (2 theta) and two spread shoulders at 14.848° and 16.567°. In the patterns 5–7 (Supplementary Fig. S1) non-crystalline peaks appeared since the microporous filter membrane and nitrocellulose membrane were non-crystalline materials. Thus, the XRD information of chalcanthite in patterns 1 and 2 (Fig. 1A) was directly obtained without interference from paper substrates. However, in pattern 3 (Fig. 1A) it was necessary that the diffraction peak of the cellulose, shown as three light gray lines from the standard card of Powder Diffraction File (PDF-2004), was deducted from the apparent one to acquire the diffraction data of the target molecule. When the pure cellulose paper was chosen as the substrate in the crystal preparations, the detection limit of the PP-XRD increased due to the interference of the paper substrate. Namely, the sample amounts of target molecules needed were increased. In the pattern 3 (Fig. 1B) the fine diffraction data was collected from the 160 μm thickness filter paper. However, on the two kinds of filter papers with 668 μm and 360 μm thickness, very few diffraction peaks of chalcanthite appeared in patterns 1 and 2 (Fig. 1B) with the same sample quantities as those in pattern 3 (Fig. 1B). It means that most target molecules on the thick paper strips cannot be detected outside the effective penetration depth of given X-ray wavelength. Therefore, larger sample amounts were needed with thicker paper strips. The pore sizes of the paper strips also affected the grain sizes of target molecules (Supplementary Fig. S2). In filter paper with 11–15 μm pore size, the



Scheme 1. Powder XRD analysis on a paper-based platform.