COMMISSION ON POWDER DIFFRACTION

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

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NEWSLETTER No. 27, June 2002

http://www.iucr.org/iucr-top/comm/cpd/Newsletters/

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Powder Diffraction in Mining and Minerals

(Lachlan Cranswick and Gert Kruger, Editors)

ISSN 1591-9552

Spray Drying for X-ray Powder Diffraction Specimen Preparation

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Introduction

One only has to look in the literature at the number of publications and variety of methods and techniques of preparing a random powder for analysis by X-ray powder diffraction (XRPD) to realize that eliminating preferred orientation (texture) is a difficult task [1,2]. The effort expended is also an indication of just how important the elusive random powder is for many applications. Making a random powder is difficult because most minerals have anisotropic shapes. The clay minerals, with which I am most familiar, tend to be platy and the slightest amount of pressure applied during the loading and mounting of the sample induces a preferred orientation. Diffraction from some planes is then over-represented whilst for others it is diminished. Many other groups of minerals are also prone to preferred orientation, particularly those with good cleavage. The feldspars and carbonates are noteworthy because they are such common constituents of many mineral samples.

Of the various methods used to prepare random powder samples the most common are probably various forms of back or side loading of a standard cavity mount. Undoubtedly this is simply because such procedures are relatively straightforward and quick to perform but even the most careful packing of a powder sample into a standard cavity holder will doubtless result in some degree of preferred orientation. This may not present a problem if reproducibility rather than truly random orientation is the key issue. If, however, a methodology, including preparing and loading of samples, is to be used by more than one person, perhaps over a long period of time when expertise in the laboratory will come and go, then guarantees of reproducibility are unlikely.

One alternative to back and side loading is a method known as spray drying. This method consists of spraying a sample, usually as an aqueous suspension, into a heated chamber where it dries in the form of the spherical spray droplets. The resulting dry product consists of thousands of tiny spherical granules of the sample components (Figure 1).

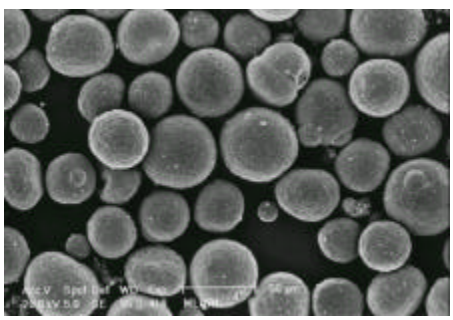

Figure 1: *Example of the spray dried clay mineral kaolinite.*

Purposely breaking open the granules or sectioning them (Figure 2) shows that the granules are by and large solid agglomerates of the individual mineral particles.

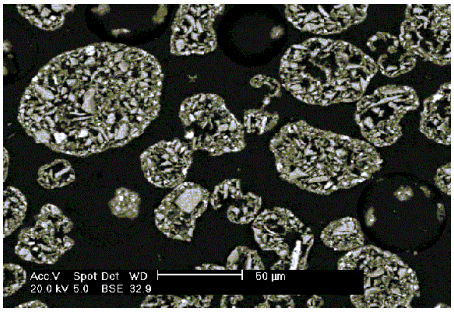

Figure 2: *Backscattered electron image of polished section through granules of a sample of sandstone prepared by spray drying.*

Typically, the average diameter of the granules is about 50 microns. Both the arrangement of any component within the spherical granules and the random way in which spherical granules pack together ensure that preferred orientation is eliminated. Spray drying is therefore a method capable of producing truly random powder samples for XRPD. In fact, spray drying is a well-known and widely used industrial process. Indeed, there have been several attempts to use it for XRPD sample preparation [3,4,5,6] but previously it has not been widely adopted. This appears to be largely due to problems of sample recovery. A method and equipment has been developed at the Macaulay Institute [7,8] that overcomes this difficulty and allows spray drying to be used as a routine method of sample preparation for mineral samples including rocks, soils, sediments or similar materials. The method is essentially a modification of that of Smith et al. [6] in that the spray is generated by a pneumatic method of atomization, but using an artists air-brush instead of a less controllable two nozzle system. Additionally, the sample is collected on a sheet of paper allowing it to be recovered easily from the drying chamber. This equipment is now in use in a number of different laboratories worldwide.

Advantages and applications of spray-drying

One of the main advantages of spray drying is that as a consequence of eliminating preferred orientation, the XRPD patterns from spray-dried samples are extremely reproducible. By way of example, Figure 3 and 4 illustrate XRPD patterns obtained by three different operators who emptied and loaded two portions of the same sample six times each. One portion was spray dried and the other freeze-dried. For the freeze-dried portion (Figure 3) no two runs were the same. Additionally, the extent of preferred orientation for each phase, as indicated by enhanced intensity, is inconsistent between phases. In contrast, the diffraction pattern from the spray-dried portion (Figure 4) is reproducible by, and between, all three operators.

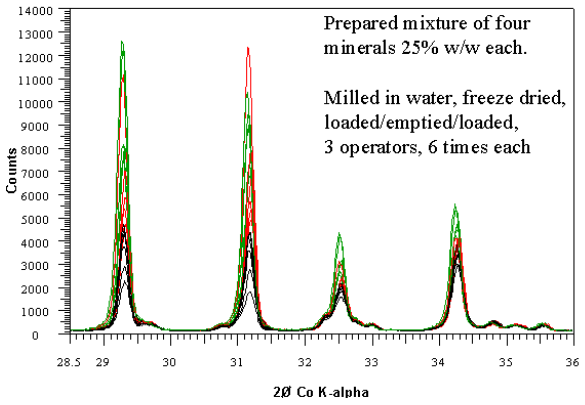

Figure 3: *XRPD patterns of a synthetic mixture of 25% chlorite, 25% muscovite, 25% albite and 25% calcite, all minerals which frequently exhibit preferred orientation. XRPD patterns from 18 separate loadings of a freeze-dried portion of the mixture by 3different operators (red, green, blue, 6 patterns each).*

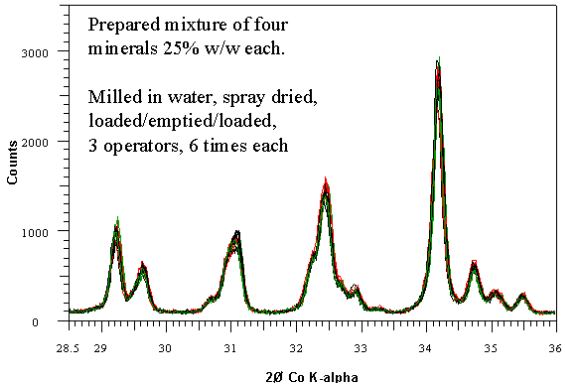

Figure 4: *XRPD patterns of a synthetic mixture of 25% chlorite, 25% muscovite, 25% albite and 25% calcite, all minerals which frequently exhibit preferred orientation. XRPD patterns from 18 different loadings of a spray-dried portion of the mixture by 3 different operators (red, green, blue, 6 patterns each).*

There can be little doubt that the problem posed by preferred orientation has been one of the biggest obstacles to the development of reliable methods of quantitative analysis of powder samples [9]. Elimination of preferred orientation by spray drying and the consequent reproducibility of diffraction data means that spray drying is an excellent starting point for quantitative phase analysis. This is especially the case if peak based reference intensity ratio (RIR) methods are used, but also means that Rietveld based procedures do not need to incorporate steps to refine preferred orientation. The practical importance of this is emphasized for example by the studies of Hill et al. [10] and Mumme et al. [11]. These authors demonstrate the wonderful potential of the Rietveld method of quantitative phase analysis for complex geological samples, but they were not successful in applying corrections to account for severe problems with preferred orientation in normal back-loaded or side drifted cavity mounts. Instead they resorted to dealing with preferred orientation by using small samples mounted in rotating capillary tubes, but with the result that each XRPD pattern took on average about 45 hours to collect. Had a means of preparing their samples by spray drying been available to these authors they could have recorded their diffraction data in much less time from normal cavity mounts.

A further practical advantage of spray drying is that in combination with wet grinding (which is preferable over dry grinding to reduce particle size) samples may be spray-dried directly from the mill in which they are ground. This is simply a matter of experience in loading the right proportions of sample to water into the mill in order to obtain a suspension of appropriate consistency to spray. Spray-dried powders are also much easier to load and handle than most other forms of powder since they can simply be poured into the cavity in excess, this is then tapped vigorously from side to side to obtain good packing, and surplus material removed.

Results of an informal Round Robin organized by Steve Norval (ICI) and presented at the British Crystallographic Association Meeting at Heriot Watt University, Edinburgh [12] showed that spray drying was the best method of preparing a random powder. The sample supplied to participants was a mixture of hydromagnesite and huntite. Figure 5 shows the sample run as received and Figure 6 the sample run after spray drying. In both figures the powder patterns are compared to reference patterns from the PDF file. The very much better correspondence of intensity data from the spray-dried sample to the reference patterns is obvious.

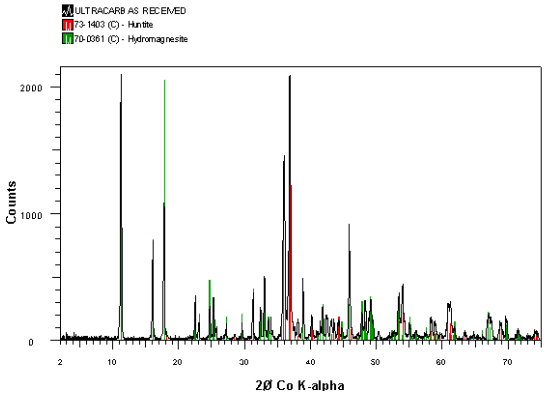

Figure 5: *Sample consisting mainly of huntite and hydromagnesite run as received. Note obvious and common discrepancies of measured intensity and intensity as indicated by PDF files (calculated patterns) for these minerals.*

Additionally, this sample also revealed another potential advantage, namely the more reliable use of intensity data for search match procedures. Since the intensity data of the spray dried sample is not affected by preferred orientation it became obvious that the sample also contains minor/trace amounts of magnesite and calcite. This conclusion is not at all obvious for the non-spray dried sample because one cannot easily separate discrepancies in intensity data that arise from preferred orientation from those that have other causes.

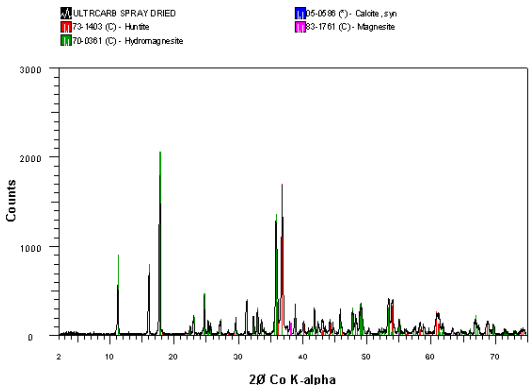

Figure 6: *Sample consisting mainly of huntite and hydromagnesite run after spray drying. Note obvious much better agreement between measured intensity and intensity as indicated by PDF files (calculated patterns) for these minerals compared to previous figure. Note also that minor/trace calcite and magnesite are obvious in this pattern.*

Disadvantages of spray drying

As with any method there are of course some disadvantages with spray drying. Firstly, spray drying produces dust and it is imperative that proper and appropriate precautions and regulations relating to health and safety issues regarding dusts are implemented and followed.

As far as disadvantages for powder diffraction are concerned the main one is that it is inevitable that some sample will be lost in the process. Typically recovery will be 50-80%. The losses occur as material left in the mill (assuming the sample is sprayed directly following wet grinding), material left in the holder from which the sample is sprayed, and material that is not recovered from the oven. This is not normally a problem for a sample if there is plenty of it and many mineral samples fall into this category. For a precious sample, however, of which there is less than 1g spray drying is not yet the answer. At the Macaulay Institute we usually begin by milling 3g of sample and end up collecting ~1.5g in a vial.

For most practical purposes the oven may be cleaned between samples simply by using a jet of compressed air. Experience has shown that trace amounts (<0.5%) of contamination of one sample by another may occur if this procedure is adopted. For many geological materials this is entirely acceptable and an experienced operator can then mill and spray dried as many as 30 samples in a day. If contamination must be avoided at all costs, then the oven must be switched off and cleaned between samples.

The only other disadvantage of spray dying is that some minerals may be susceptible to phase changes at the temperatures used. Typically the sample 'sees' an air steam heated to about 170°C for a few seconds or more. Whilst this does not cause any problems for clay or other common rock forming minerals, phase transformations can occur in many sulphates such as gypsum which dehydrates forming bassanite. Doubtless other temperature sensitive minerals may be similarly affected. One way to combat such problems is to spray dry at lower temperatures using a liquid other than water, and such a procedure may also be adopted for materials which would react with water such as Portland cement which can be successfully spray dried from ethanol (Figure 7). Departures from using aqueous suspensions obviously require that all health and safety aspects should be adequately assessed and appropriately controlled and monitored.

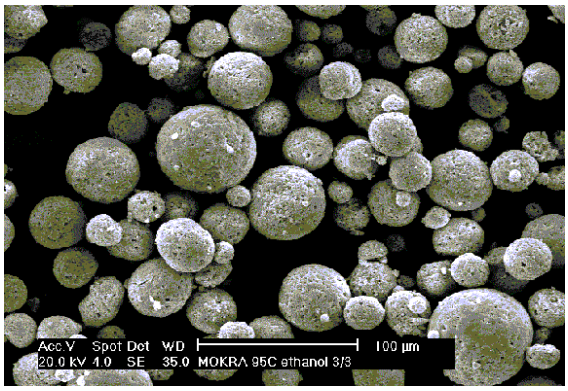

Figure 7. *Ordinary Portland cement spray dried from ethanol.*

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