Use of an air brush to spray dry samples for X-ray powder diffraction

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ABSTRACT: The construction and operation of a spray drier is described where the spray is produced using an air brush, essentially a miniature spray gun. The spray-dried products consist of spheres 50−60 μm in diameter and typical product recoveries are 80%, a marked improvement over simple two-nozzle systems. The spray-dried samples are easy to load into XRD powder holders and present a smooth surface and relatively constant bulk density to the X-ray beam. Problems of preferred orientation are effectively eliminated and the resulting X-ray powder patterns are completely reproducible by different operators.

The importance of sample preparation for X-ray powder diffraction cannot be overemphasized (Brindley, 1984; Bish & Reynolds, 1989). One of the characteristics most commonly desired is a completely random arrangement of the individual particles in a powder sample. All types of X-ray powder diffraction, ranging from structure to quantitative analysis, rely on the preparation of such random powder samples in order to obtain the correct relative intensities of all the peaks in the diffraction pattern. Unfortunately, many materials, notably clay minerals, are orientation prone, and the preparation of a random powder sample is not a simple matter. This is reflected by the large number of methods that have been suggested in attempts to produce random powders (see Bish & Reynolds, 1989, for a recent account). Indeed, it is probably fair to say that truly random powder samples are achieved less often than not. Among the techniques used, one of the most effective is a method known as spray-drying (Jonas & Kuykendall, 1966; Hughes & Bohor, 1970; Smith *et al.,* 1979a,b). Essentially, this method consists of spraying a sample as an aqueous suspension into a heated chamber so that it dries in the form of the spherical spray droplets. The resulting dry product consists of thousands of tiny spherical agglomerates of the sample components. Smith *et al.* (1979a) evaluated this method quantitatively by comparing the intensities of observed (using both spray-dried and non spray-dried samples) with calculated X-ray powder diffraction patterns for several minerals. They concluded that problems of preferred orientation were minimized, possibly eliminated, by spray-drying.

Nevertheless, as discussed by Bish & Reynolds (1989), spray drying is not yet widely used as a method of sample preparation for X-ray powder diffraction, possibly because of the high cost of commercially available equipment (>£10,000), and possibly because it does not appear suitable for small samples of <1 g. Although commercial systems are expensive, an instrument similar to that built by Smith *et al.* (1979a) can be constructed for a moderate sum of ~£1400 (materials and labour). However, according to Smith *et al.* (1979a), product recovery with their instrument ran typically at 50% as a result of the larger spray droplets not drying before they reached the bottom of the chamber. This is in spite of the fact that the chamber was quite large, 120 cm in height and 90 cm in diameter. For many applications this probably represents an unacceptably high loss, especially if the amount of sample available is limited.

Central to the spray-drying process is the production of the spray itself. This may be

achieved by one of four different methods, namely: rotary atomization, pressure atomization, pneumatic atomization, or ultrasonic atomization. The spray dryer constructed by Smith *et al.* (1979a) used pneumatic, also known as two-fluid, atomization whereby a stream of compressed air from a nozzle impacts a water/sample slurry exiting from another closely spaced nozzle and breaks it up into a spray. Compared to the other methods of atomization, pneumatic atomization characteristically produces the widest distribution of droplet sizes (Shaw, 1990). In the course of designing a laboratory size spray dryer at the Macaulay Institute, trials were made with a design similar to that built by Smith *et al.* (1979a) using various sizes and arrangements of nozzles, and a range of air pressures. In all cases, product recovery was disappointingly low, never better than 50%, and clearly the result of the wide distribution of droplet sizes formed by this simple method of atomization. Basically, it proved impossible to avoid producing a large proportion of droplets that were much too big to dry before reaching the bottom of the chamber, the same problem encountered by Smith *et al.* (1979a).

From these tests it became clear that one of the keys to spray drying small samples on a laboratory scale, for the purpose of X-ray powder diffraction, is the production of a spray with a relatively small and uniform droplet size distribution. This can be achieved at a relatively moderate cost (<£100) by replacing the two-nozzle system of atomization with an air brush, essentially a miniature spray gun. The spray from an air brush is also produced pneumatically but the two fluids are mixed internally resulting in a narrower and more easily controlled droplet size distribution. Although rotary, pressure and ultrasonic atomization can also produce narrow droplet size distributions, rotary and pressure methods require large drying chambers due to the high exit velocities of the sprays, whilst ultrasonic equipment is expensive. Furthermore, the ultrasonic arrangement in one commercial apparatus frequently suffers from the development of large liquid drops on the probe tip, and 30% recovery is considered exceptional, although this may also be due to other aspects of its design (Chipera pers. comm.). The purpose of this paper is to describe the construction and operation of a laboratory-scale spray drier where the spray is produced by an air brush and to illustrate the results which have been obtained by this method.

EQUIPMENT AND METHODS

Construction of the spray dryer

The spray dryer consists of two parts, the spraying system and the drying chamber (Fig. 1). The construction of the drying chamber is similar to that described by Smith *et al.* (1979a), but is smaller in size. The chamber is made from 2 mm aluminium sheet formed into a cylinder of 45 cm diameter and 90 cm in height. A Watlow Thinband Heater of two-piece construction (drawing 1500 W per half, and connected to form a band 45 cm in diameter and 15 cm in height) is clamped around the base of the cylinder. Due to differential contraction and expansion of the cylinder and the heater, strips of aluminium are fixed above and below the heater to hold it in place. The heater is controlled via a United Automation solid-state temperature controller with a range of $0-150°C$ connected to a stainless steel temperature sensor. The lid of the chamber is made from a sheet of aluminium formed into a $90°$ cone with a 2.5 cm diameter hole at its apex through which the samples are sprayed. The lid is permanently fixed to the cylinder by brackets and the joint sealed with thermal cement. The base of the chamber is supported 0.5 cm above the workbench by two insulated blocks of aluminium bolted to the sides.

The spray is produced by a Crescendo No. 175-7 air brush manufactured by Badger Air-Brush Co. 9128 Belmont Av., Franklin Park, IL 60131, USA. The air brush is fitted with its largest spray head regulator (slightly enlarged from 1.6 to 2 mm diameter) and needle designed for spraying the most viscous materials. Samples are fed into the air brush via a disposable plastic pipette trimmed to fit with the air brush sample inlet via a small piece of silicon rubber tubing. Larger samples, up to 60 ml, can also be fed from the paint bottles supplied with the brush, but the gravity-fed arrangement using the pipette is usually more convenient as it ensures that all of the sample is sprayed. The air brush is arranged to spray vertically downwards into the chamber and is simply held in position while spraying by hand. Holding the air brush by hand also enables the suspension to be continuously agitated during spraying, or even to stop, shake, and restart, in order to avoid problems of segregation or increasing viscosity due to sedimentation in the container.
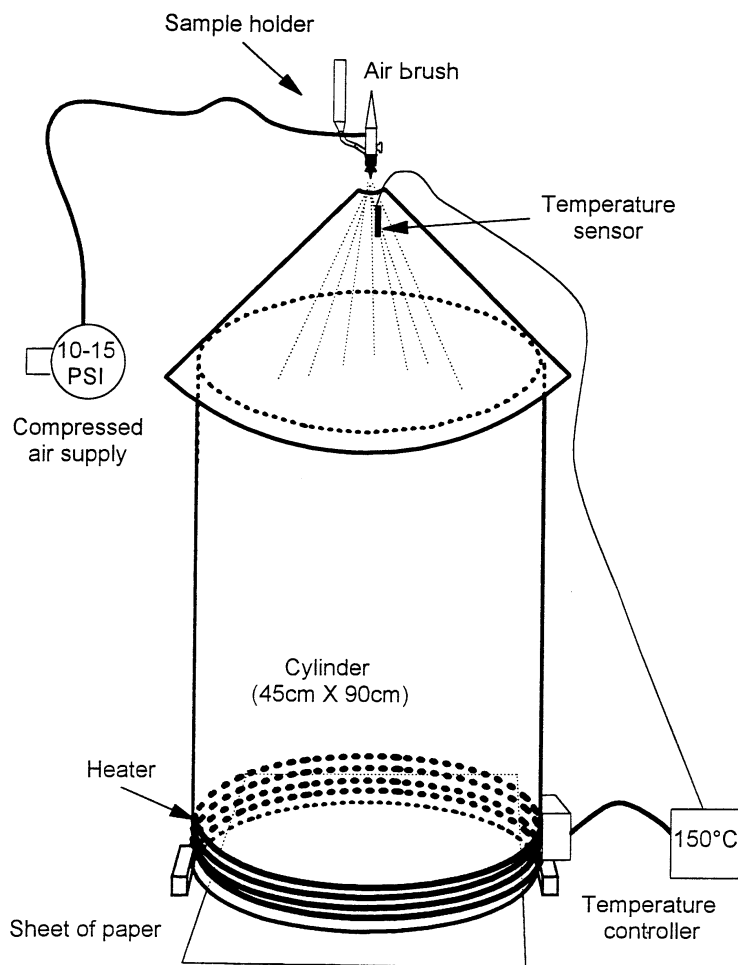
FIG. 1. Diagram to show the construction and operation of the spray drier.
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Sample preparation

Essentially, the preparation of samples for spray drying involves nothing more than making a concentrated aqueous suspension of the material that can be sprayed through the air brush into the drying chamber. However, the preparation of samples for spray drying is one of the most important aspects of the process and probably the one that is most likely to result in failure (Lusasiewicz, 1989). This is because sample preparation involves a delicate balance between two conflicting aims. On the one hand, the sample

suspension needs to have as high a content of solids as possible in order to minimize drying time and to ensure that the droplets retain a spherical shape as they dry. On the other hand, the suspension must still be sufficiently dilute to be sprayed easily through the air brush at low pressures without clogging. Experience has shown that the best results, in terms of product recovery, are obtained by spraying at as low a pressure as possible (10−15 psi). Observation suggests that this is because the higher the pressure, the higher the proportion of very small droplets that are produced, in fact so small (<10 μm) that they tend to remain

in suspension in the hot air, and are carried away in the atmosphere rather than sedimenting to the bottom of the chamber. In addition, low pressures allow the droplets to pass more slowly through the chamber giving a longer contact time with the hot air and a better chance of drying before they land on the paper underneath. The concentration (viscosity) of the suspension also affects the size of the spray droplets that form, more concentrated suspensions forming larger droplets, but being more difficult to spray at low pressures.

Sample suspensions are prepared by dispersing the solid material in a 0.5% (w/v) aqueous solution of polyvinyl alcohol (PVA) of 30,000−70,000 molecular weight. The PVA acts as a binder giving strength to the dried product. However, for samples with a high clay content it has been found that the addition of a binder is not essential. Addition of a single drop of 1-octanol ($CH_3(CH_2)_7OH$) prevents foaming during dispersion, makes transfer of samples between containers easier, and reduces the incorporation of air bubbles into the dried granules. As mentioned previously, the suspension needs to have as high a content of solids as possible, but the amount of solid that can be suspended in the PVA solution depends on the nature of the solid itself. For samples of muscovite, wollastonite, pyrite, siderite and corundum, Smith *et al.* (1979a) used 3−4 g of powder suspended in 6−7 ml of a 1% aqueous solution of polyvinyl alcohol (PVA). This equates to solid to liquid ratios (w/v) ranging from 1:1.5 to 1:2.3. In the present investigation, all non-clay minerals have been successfully spray dried using a solid to liquid ratio of ~1:2. In contrast, the solid/liquid ratios for clay minerals are much more variable and some clays need to be diluted considerably in order to make a suspension with the desired rheological properties. In general, the finer grained the sample and/or the greater the amount of swelling clay layers present, the more PVA solution necessary to make a suitable suspension. This is because for a given volume concentration of solids in suspension, the mean distance separating particles decreases with decreasing particle size resulting in more interaction between particles (Lukasiewicz, 1989). An extreme case is illustrated by that of Na-montmorillonite. For the raw product (SWy-1) suspended by shaking, a ratio of 1:13 was necessary to make a suspension that can be sprayed, and for a well dispersed <2 μm fraction of this clay, this ratio was increased to 1:60.

Because of the large quantities of PVA solution required, smectites are undoubtedly the most difficult samples to spray dry. In addition to the fact that the high water content of the droplets makes them more difficult to dry, it also tends to result in many more smaller particles, which are much more difficult to recover from the air stream, and a more irregular shape than those which are recovered, probably due to the drastic change in volume of the droplet during drying. Nevertheless, by operating at pressures as low as 5−10 psi, even clay fractions consisting of smectites can be successfully spray dried with solid product recoveries of up to 70%.

As far as clay minerals are concerned, a simple method of determining a reasonable concentration of solid to PVA solution is to add the solution progressively to the clay until such point that the resulting suspension does not adhere to the sides of its container after vigorous shaking. As a general rule, most suspensions are limited to between 30−40% solids by volume before viscosity increases excessively (Lukasiewicz, 1989).

Operation of the spray dryer

The first step is to heat the drying chamber. The exit air temperature from the chamber is monitored by the sensor and typically takes ~10−15 min to reach the maximum temperature of 150°C. At this maximum setting, the air temperature on the surface beneath the chamber reaches ~90°C. Exit air temperatures of 100−150°C are suitable for most samples, lower temperatures resulting in insufficient drying. Once the desired temperature is attained, a sheet of A2 paper is placed beneath the chamber. The temperature sensor is then removed from the chamber, the air brush positioned above it, and the sample immediately sprayed into the chamber through the hole in the lid. This typically takes one to a few minutes, depending on the air pressure and the viscosity of the sample. Once all the sample has been sprayed, the paper is removed from beneath the chamber and the sample collected by pouring it into a vial. Between samples the air brush is easily cleaned by spraying and back-flushing water at high pressure (40 psi). The sample chamber does not normally require any cleaning between samples, but can be blown out with compressed air if desired, and is cleaned periodically when not in use.

RESULTS AND DISCUSSION

Product form and recovery

Typical examples of spray-dried products are shown in Fig. 2. Based on measurements made on these and many other similar photomicrographs, the products consist of spheres with an average size ~50 μm. Weighing measured volumes of the products and assuming typical densities and a porosity ~30%, both between and within the spheres, i.e near ideal close packing, suggests that the majority (~75%) are solid rather than hollow spheres. Three of the samples are of spray-dried <2 μm clay fractions (Fig. 2A,B,C,D), that of the muscovite and kaolinite produced quite smooth and uniform spheres, whereas the spheres of the montmorillonite have a more irregular surface. One of the samples shown illustrates the effect of the grain size of the materials on the form of the product (Fig. 2E). Although the granules of the spray-dried talc are roughly spherical, they have a quite irregular surface due to the relatively large size of the component particles. Examples of a shale and sandstone which have been prepared by spray drying the slurry obtained directly from a McCrone mill are also shown (Fig. 2G,H).

Product recovery was determined by weighing the amount of material recovered by pouring it off the sheet of paper after spraying measured amounts of suspensions of known concentrations. Two clays were used for this purpose: Na-montmorillonite (SWy-1) and a kaolinite (AIPB) of unknown origin. The results are given in Table 1. For both samples the best recovery was obtained at the lower pressure of 10 psi, especially for the montmorillonite. In both cases the total loss is due to the loss of two fractions: the fraction of droplets so small that they remain in the air stream, and the fraction of droplets which are not dry and so splatter on the paper as they land.

Most of the loss appears to be due to the former mechanism, but losses by both are reduced by spraying at low pressure. The difference in recovery between the samples is probably due to the effect of suspension concentration. At 40% (w/v) the kaolinite suspension is much more concentrated than the montmorillonite suspension at 7.1% (w/v). Although not all of a sample is recovered, for most materials recovery of ~80% is typical, and represents a significant improvement on the 50% attained by Smith *et al.* (1979a). Without doubt the most difficult samples to process are clay fractions of well dispersed (e.g. Na-saturated) smectites for which recovery may be as low as 20%.

Random powder patterns

The aim of spray drying materials for X-ray powder diffraction is to produce a sample which can be loaded into a powder holder without inducing a preferred orientation to any of the phases present. To assess the effect of spray drying as a means to this end, powder patterns were recorded from samples of chlorite (CCa-1) and kaolinite (KGa-2) prepared as both freeze-dried and spray-dried powders. The samples were mixed in a 1:1 proportion by weight with corundum, wet ground and homogenized in a McCrone mill for 12 min, and the resulting slurries freeze dried. After freeze drying, a portion of each sample was re-suspended in 0.5% PVA solution and spray dried. Both chlorite and kaolinite are prone to orientation with respect to 00*l*, whereas corundum is generally considered to be free from problems of preferred orientation to the extent that it is frequently chosen as an internal standard for quantitative phase analysis. Both freeze-dried and spray-dried samples were loaded into powder holders and XRD patterns recorded from $2-75°2\theta$ on a Siemens D5000 with a θ/θ goniometer, using Co

TABLE 1. Results of product recovery tests.

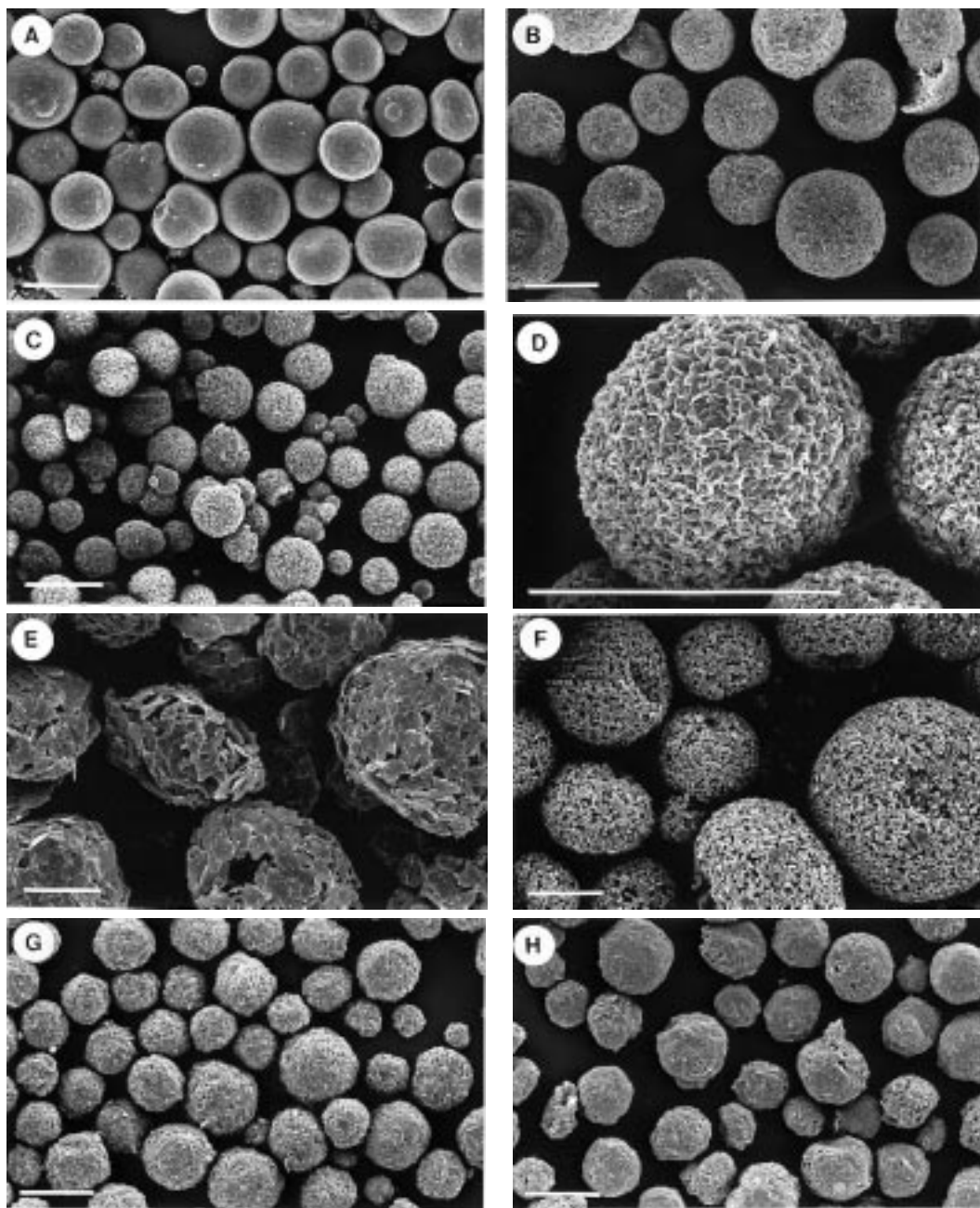| Sample	Identity	Origin	Air pressure (psi)	Concentration of clay (wt%)	Wt of clay sprayed (g)	Wt clay recovered (g)	% clay recovered
Kaolinite	AIPB	Unknown	10	40	6.34	5.39	85
Kaolinite	AIPB	Unknown	15	40	7.41	5.99	81
Smectite	(SWy-1)	Wyoming	10	7.1	1.07	0.82	77
Smectite	(SWy-1)	Wyoming	15	7.1	0.97	0.56	58

FIG. 2. Scanning electron photomicrographs of spray-dried samples. (A) kaolinite (KGa-1b) <2 μm fraction; (B) muscovite (No 5 Macaulay collection) <2 μm fraction; (C) montmorillonite (SWy-1) <2 μm fraction; (D) close-up of C; (E) talc (No 8 Macaulay collection) as supplied by Hopkins & Williams Ltd; (F) corundum (No 3 Macaulay collection) <10 μm as supplied by Aldrich/Sigma Chemicals Ltd.; (G) shale, Reading beds, McCrone milled 12 min; (H) glauconitic sandstone, Denmark, McCrone milled 12 min. All scale bars are 50 μm long.

radiation, diffracted beam monochromator, 1° slits and counting for 1 s per 0.02°2θ step.

Because the spray-dried powders flow very easily, loading of the powder holder is accomplished simply by pouring in an excess of powder, gently tapping to distribute it evenly across the cavity and swiping away the surplus powder by passing the edge of a glass slide across it to leave a smooth flat surface. Indeed, the spray-dried powders are so fluid that problems of sample stability might be anticipated with a θ/2θ goniometer if the sample is tilted far from horizontal. In contrast, the freeze-dried powders were both lumpy and fluffy, and much more cohesive than the spray-dried samples. As such, gentle tamping of the sample surface was unavoidable in loading them into the holders.

The low-angle portions of the resulting XRD patterns are shown in Fig. 3. All four samples were run twice, the second run after a different operator had emptied and reloaded the sample holders. In all patterns the intensities of the reflections from corundum are virtually identical, except for being slightly less intense in the spray-dried samples, presumably due to a somewhat lower bulk density of these powders. Similarly, the patterns for each spray-dried mixture are identical. Patterns recorded from the freeze-dried samples, however, show marked and variable increases in the intensity ratio of the basal to the non-basal reflections of the clay minerals compared to the spray-dried patterns. Clearly, the increases in intensity of the 00l reflections in the freeze-dried samples must be due to preferred orientation acquired during the loading of these samples into the holder. In contrast, for the spray-dried samples, the degree of any preferred orientation is clearly much less, and is unaffected by the loading and packing process.

In an attempt to assess the degree of preferred orientation in the samples, observed XRD patterns were compared to patterns calculated using the Rietveld quantitative phase analysis program, Siroquant. In all cases without refinement of preferred orientation, the fit between observed and calculated patterns was best for the spray-dried samples. When refinement of preferred orientation was included in the analysis, the March function (Dollase, 1989) for the spray-dried chlorite:corundum mixtures refined to 0.99, indicative of virtually no preferred orientation. In contrast, the March function for the freeze-dried samples refined to 0.82 and 0.75 indicating significant preferred orientation, equivalent to compaction of the chlorite plates from a uniform distribution by 18 and 25%, respectively. For the kaolinite:corundum mixtures, a similar trend was observed with the March function refining to 1.01 and 1.03 for the spray-dried samples, and to 0.94 for both of the freeze-dried samples. Quantitative phase analysis results from Siroquant were accurate to within 2% absolute for all spray-dried samples regardless of whether or not preferred orientation was refined. In contrast, analyses of the freeze-dried chlorite:corundum mixtures were not accurate (66% chlorite, 34% corundum, in the worst case) unless preferred orientation was refined. Although neither of the Rietveld refinements of the clay minerals is exact due to the presence of stacking disorder, as far as it is possible to judge by this method, it appears that the samples which have been spray dried are randomly oriented, whereas the freeze-dried samples show significant preferred orientation.

CONCLUSIONS

Spray drying on a laboratory scale is easily accomplished with a small drying chamber by using an air brush to produce the spray. The product consists of spheres with an average diameter of 50 μm, and 70−80% recovery is typical for most samples. The spray-dried powders are easily loaded into XRD powder holders in a form with a smooth surface and relatively constant bulk density. The resulting XRD powder patterns are reproducible and appear to be random, exhibiting no preferred orientation. Consequently, this method of sample preparation is ideally suited to problems such as quantitative phase analysis. Furthermore, because wet grinding is preferable to dry grinding for the reduction of particle size for X-ray powder diffraction, a scheme such as McCrone milling followed by spray drying of the resulting slurry, can be used as a routine, rapid, and reproducible method of sample preparation.
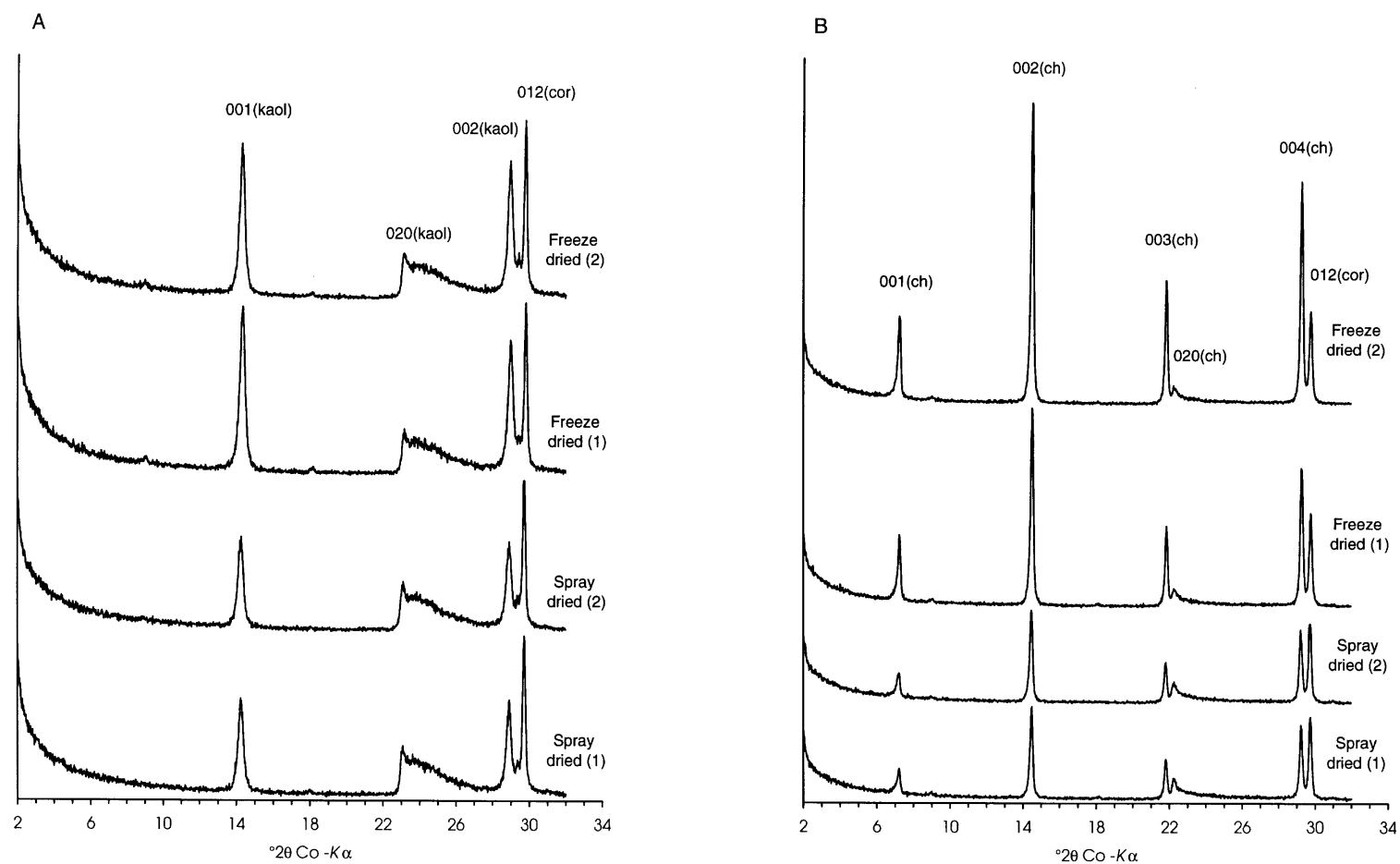
FIG. 3. Portion of XRD patterns of kaolinite:corundum (A) and chlorite:corundum (B) 1:1 mixtures. For each mixture and preparation (1) and (2) refer to the same sample run twice, after the sample holders have been emptied and reloaded by a different operator. Note the reproducible and lower intensities of the 00l peaks in patterns from spray-dried samples compared to patterns from freeze-dried samples.

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