The McCrone Sample Preparation Kit

The McCrone Sample Preparation Kit was designed to rapidly and easily reduce large particles to suitable sizes for the McCrone Micronizing Mill. It consists of a Percussion Mortar, Sieve and Sieve brush.

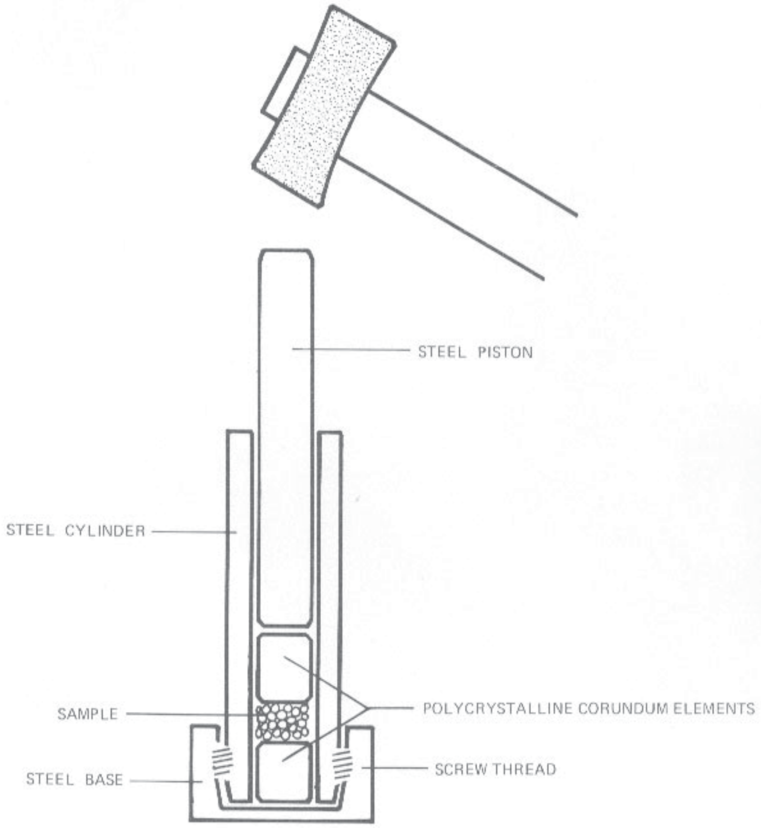

Fig. 1 The McCrone percussion mortar

Plate 2. The McCrone Sample Preparation Kit

The Percussion Mortar

The effort, tedium and losses associated with grinding by mortar and pestle have been eliminated by the McCrone Percussion Mortar. The particle size of hard, tough materials is reduced within seconds.

No sample loss occurs, because the steel cylinder contains all crushed fragments. External contamination of samples is prevented in the same manner.

Operation is simple. The steel base and cylinder are screwed together. The dry sample, of maximum dimensions 12mm diameter and 40mm length, is loaded into the cylinder between the two polished 12mm diameter cylindrical, polycrystalline corundum crushing elements. The steel piston is loaded above these. A series of taps with a one-kilogram hammer will reduce most samples to a powder of which a considerable proportion will pass through a 0.4mm aperture sieve. Larger particles can be returned to the mortar for further treatment.

Internal contamination has been reduced to a minimum. Polycrystalline corundum has a hardness approximately equal to that of cobalt-bound tungsten carbide. The sintered corundum anvil surfaces do not flake or pit during the course of normal use even with the most coherent materials. Analyses of the reduced samples have shown that iron pickup is negligible. The steel cylinder serves only to contain the sample. The base and cylinder can be unscrewed for easy cleaning and rapid oven drying.

Dimensions
Height – 108mm
Maximum diameter – 38mm
Weight – 410g

Also supplied with the Percussion Mortar are:

The McCrone Percussion Mortar Sieve, which consists of a 50mm diameter disc, mounted on a 25mm deep anodized aluminum ring. The metal sieve disc is not of woven mesh, but has 0.4mm square openings. This aperture size is slightly less than the maximum size of particles acceptable to the McCrone Micronizing Mill.

A sieve brush with coarse bristles and 8 additional polycrystalline corundum crushing elements complete the Sample Preparation Kit.

Features of the McCrone Micronizing Mill

The problems associated with preparing solid samples for infrared absorption and x-ray diffraction analysis can be summarized as follows:

1. Control of particle size distribution.
2. Introduction of crystal lattice disturbances.
3. Contamination from grinding elements and cross contamination.
4. Sample loss.
5. Oxidation, hydrolysis or other chemical degradations of the particles.
6. Prolonged grinding times.

The McCrone Micronizing Mill has been designed specifically to minimize or overcome these problems.
It rapidly reduces the particle size of troublesome samples by a unique grinding action. Each cylindrical element moves with respect to its neighbors, so as to produce line contact blows and planar contact shears.
Wet grinding in airtight containers reduces crystal lattice deformation and oxidation.
Virtually the whole sample is recovered. If required, the very low levels of contamination by the grinding elements can be calculated for precise quantitative analysis1.
The Mill was designed to reduce the size of particles from 0.5mm diameter to the fine micrometer sizes required for most physical analytical techniques. It is widely used in sample preparation prior to quantitative analysis.
Sample Capacity: the Mill will handle a sample volume up to 4 ml (e.g. if the sample has a density of 2.5g./ml, a 10 g sample could be used for milling).
Choice of Grinding Elements: Corundum and agate elements are available which allow the Volborth Dual-Grind technique1 to be used to obtain the true composition of samples.
Inert polypropylene jars allow a wide choice of grinding liquids to be used, although water, propan-2-ol or cyclohexane are most often used. These jars suffer little abrasion from hard samples, provided that the sample is passed through a 0.4mm aperture sieve prior to grinding. This is provided with the Sample Preparation Kit.
The process timer is calibrated in one minute intervals up to 35 minutes. Processing is started by switching the red, illuminated rocker switch to the “ON” position. A red dot shows the elapsed time during a run and the initial time set is permanently displayed.

Applications of the McCrone Micronizing Mill

PREPARATION OF SAMPLES FOR QUANTITATIVE ANALYSIS

X-Ray Diffraction, X-Ray Fluorescence and Infra-red Spectroscopy:

An upper limit on particle size is undoubtedly the most critical factor in accurate quantitative analytical techniques using XRD, XRF (pressed self-bonded disc) and IR.

X-Ray Diffraction and Infra-red Spectroscopy:

Wet grinding results in the least damage to the samples’ crystal structure, which is crucial for XRD and IR. It also makes for easier total sample recovery, eliminates manual element and vessel cleaning and reduces sample oxidation and cross contamination. It is superior to dry grinding in that it yields much smaller particles, narrower particle size distributions and gives more uniform phase distributions.

X-Ray Diffraction:

Dry grinding can be used to induce microstrains in the crystal lattice for the determination of ultrastructural damage by XRD line broadening measurements. Sample weight, grinding element type and grinding time are the only variables that need to be specified when describing the amount of induced lattice deformation.

Atomic Absorption Analysis:

In the case of samples that are difficult to dissolve, grinding with the mil is found to greatly facilitate subsequent acid digestion or alkali fusion.

The McCrone Micronizing Mill

The McCrone Micronizing Mill was designed to reduce a few grams of material to micrometer size particles of a narrow size range, minimizing contamination, time, cost, and mess.

What kind of grinder is it?

It is a vibratory laboratory mill powered by a 1/30 HP motor. The grinding vessel consists of a 125 milliliter capacity polypropylene jar fitted with a screw-capped, gasketless, polythene closure. The jar is packed with an ordered array of identical, cylindrical, grinding elements. The elements normally supplied with the mill are of fine-grained, nonporous, polycrystalline corundum. They are packed in 6 regular layers of 8 elements each, making a total of 48 in each jar. Agate grinding elements are also available.

Is it necessary to maintain this configuration of grinding elements?

Absolutely necessary. During grinding, each element moves with respect to its neighbors, grinding between the plane ends and along the cylindrical sides of the elements. The powder continuously circulated between these surfaces is ground much more rapidly than in a ballmill, for example, with its point contacts. The edges of the Micronizing Mill grinding cylinders have been chamfered to reduce point contact damage to the elements.

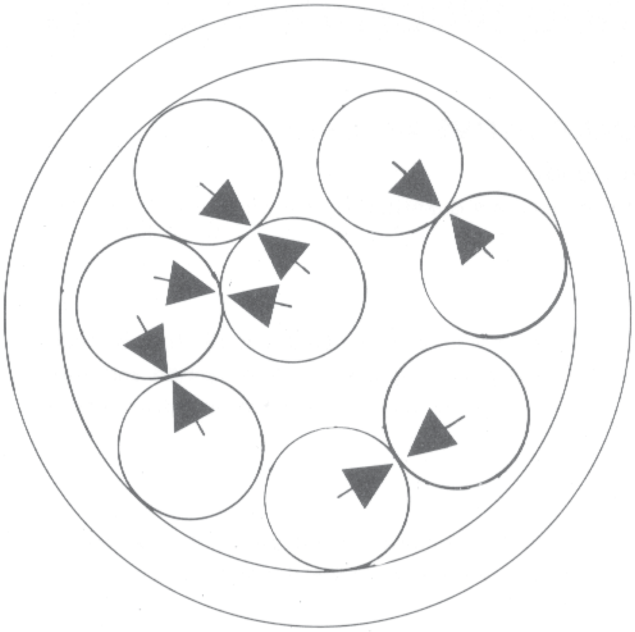

Fig. 2 Cross section of grinding jar, showing movement of grinding elements

What charge and particle size sample does it take?

It can accept up to about 4 ml of material. This corresponds to a sample weight of 20g if the material has a particle density of 5g/ml, or to a sample weight of 4g if the particles have a density of 1g/ml. However, an optimum grinding efficiency is usually achieved with 2 ml of sample.

The largest particles presented to the mill should not exceed 0.5 mm diameter. Any sample fraction remaining on top of a No. 30 mesh British Standards sieve should be crushed in a mortar to pass through this aperture size.

What is the smallest particle size produced?

Almost all substances can be reduced to sub-micrometer sizes. Soft materials, like some plastics and metals, cannot be successfully ground to these sizes. Even in the presence of suitable liquids they show a tendency to reweld. However, several authors have reported success with some metals (nickel, iron, cobalt), and the difficult platey minerals (mica, talc, graphite). Through the use of selected grinding aids (certain inorganic salts) and grinding liquids, it has been found possible to reduce these to 0.1μm[2,3].

The mill must be secured by substantial wood screws or bolts to a rigid bench. It is highly important that neither the mill nor the bench vibrates during operation. All the vibrational energy available should be directed to the grinding jar and holder and not to any other structure. Indeed, the mill will operate at its greatest efficiency if the rubber pads on the base are removed before bolting it tightly to the bench. Ideally, vibration of the mill unit should scarcely be detectable.

How long does it take to grind a sample?

On wet grinding runs, the mill is operated for periods ranging from 2 to 30 minutes, depending on the fineness of product required and the fineness, volume and grinding resistance of the starting sample. Changes in grinding time affect the particle size distribution of the product. The mill is fitted with a process timer, graduated in one minute intervals up to 35 minutes, to ensure reproducibility of sample size.

Does it work with really hard substances?

Few substances cannot be ground. Even silicon carbide and various metal carbides, nitrides and borides can be ground effectively, although as they abrade the corundum grinding elements, agate grinding elements are recommended.

What is a typical performance?

EXPERIMENT 1

Conditions: Charge of 1.0g of biotite mica, passed through 400µm aperture sieve; 10 ml of propan-2-ol. Ground for 10 minutes with corundum grinding elements.

Results: 1.0g of dried product recovered. Average diameter of product was 5µm. Largest particle present was 10µm.

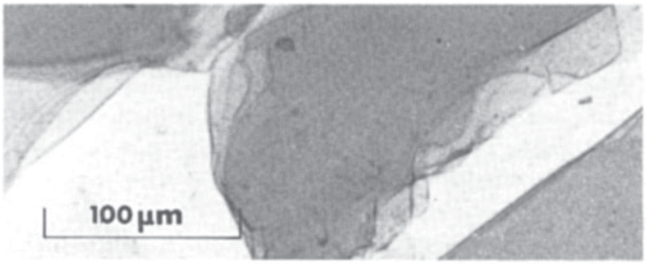

Plate 3. Biotite mica before grinding

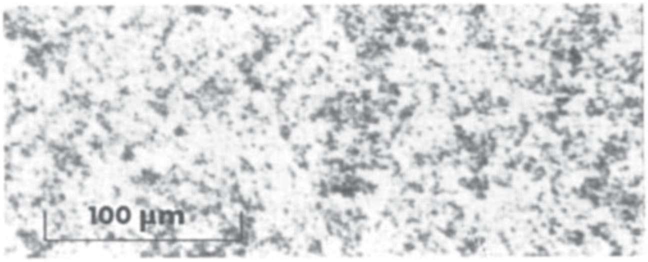

Plate 4. Biotite mica after grinding

EXPERIMENT 2

Conditions: Charge of 2.0g of graded Belgian optical glass silica sand of particle size 285µm + 15µm; 10 ml of water. Ground for 10 minutes with corundum grinding elements.

Results: 2.0g of dried product recovered. Average diameter of product was 6µm. Largest particle present was 14µm.

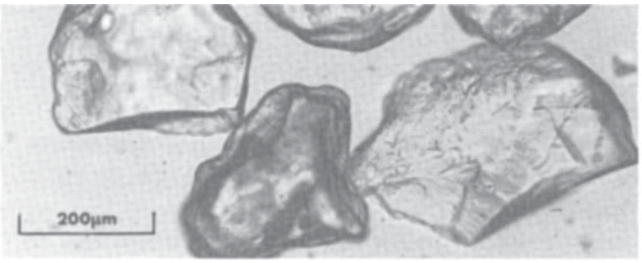

Plate 5. Belgian optical sand before grinding

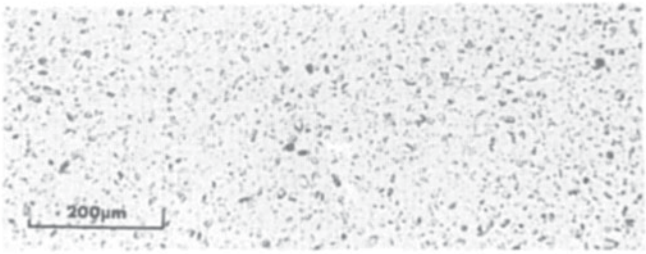

Plate 6. Belgian optical sand after grinding

Is grinding done dry or in a liquid slurry?

Either way, but slurry grinding has advantages over dry grinding. It is now the preferred method in most laboratories.

First of all, a liquid slurry helps ensure that none of the sample compacts into corners where it escapes the grinding elements. Comparisons of dry and slurry grinding show that slurry-ground products always have the narrowest particle size ranges.

Secondly, for comparable grinding times, slurry grinding produces the finer product.

Thirdly, much less microstructural damage occurs both to the product and to the grinding elements. This product damage is less, probably because of the presence of a thermally conducting liquid which limits the momentary local high temperatures and pressures produced at impact sites. Thus, rewelding of particles or the formation on their surfaces of “amorphous” Bielby layers is less likely to happen[4]. (See diagram below)

Lastly, various inert liquids can be chosen to protect the sample from unwanted reactions arising from the presence of moisture, carbon dioxide or oxygen.

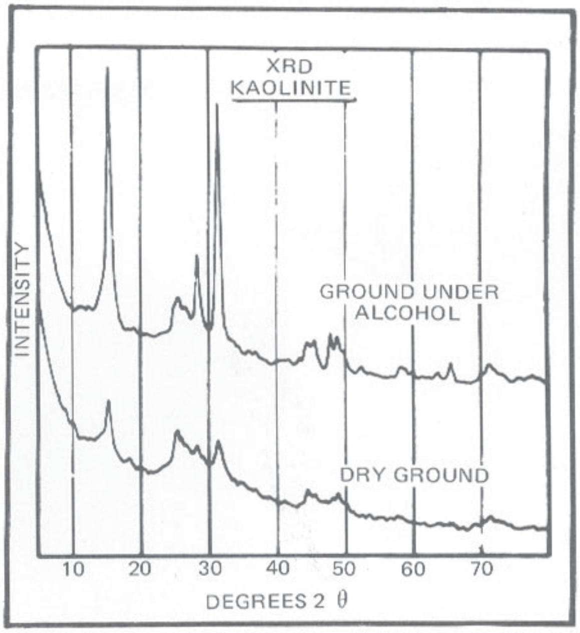

Fig. 3 Comparison of results after slurry grinding and dry grinding[5]

Surely wet grinding is more trouble than dry grinding?

Surprisingly, no. With wet grinding, the total recovery of the ground sample and the cleaning of the jar and grinding elements is simpler.

It is accomplished by removing the closure at the end of the run and replacing it with a similar closure but having two diametrically-opposed holes of about 6mm diameter. The ground slurry is then poured out through one of these and the jar with the elements in place is washed two or three times with intermediate shakings. This procedure yields the combined pourings and washings, together with a clean jar, and with the grinding elements clean and their packing unaltered.

The conversion of a slurry into a dry powder is not such a messy step as it appears. Clear supernatant liquid can be safely decanted. If water is the liquid, the remainder can be replaced by acetone. As the acetone is a lighter and less viscous liquid than water, the ground powder settles out more rapidly. After decanting off the clear acetone layer, the remaining small amount of acetone can be evaporated off in a few minutes under an infrared lamp.

Some low boiling organic liquids may be used directly. One of the best liquids for grinding Portland cements for analysis is propan-2-ol. Cyclohexane is also used.

The low density polypropylene jar is inert to most non-polar hydrocarbons and alcohols.

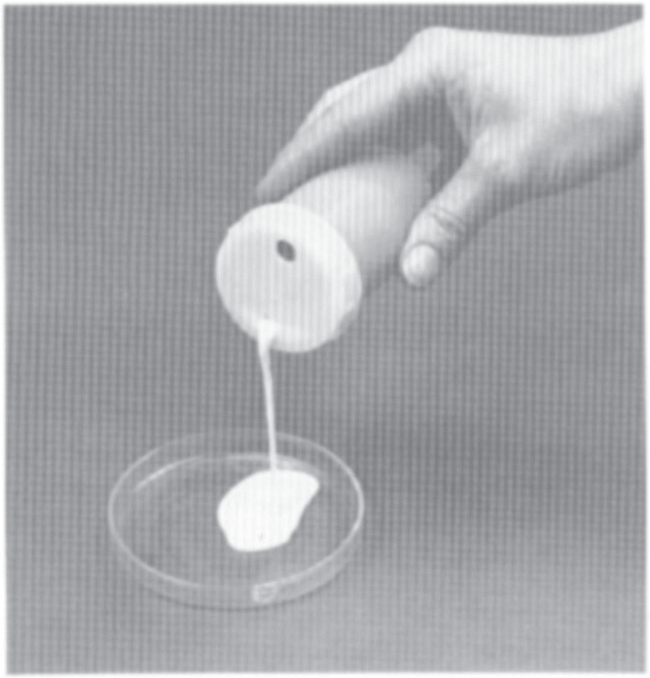

Plate 7. Pouring slurry from grinding jar

Is there any occasion when dry grinding is preferable?

Yes. When it is required to study the relationship between the amount of mechanical work put into a sample with the amount of ultrastructural damage produced.

The work of Burton[6] on the production of gram quantities of materials with unusual properties for research and development purposes is a good example of this.

Increasing attention is also being given to the examination of various crystallographic transformations and tribochemical reactions induced by prolonged dry grinding [7, 8, 14].

Lewis and his colleagues[9] have made use of the x-ray line broadening effects observed when powders are dry-ground for different times. They were able to measure the amount of lattice microstrain produced in brittle substances as diverse as calcite, lithium fluoride, corundum and tungsten carbide. Such measurements have been shown to be of great value in fundamental studies of the sintering of metal powder compacts. The McCrone mill has the virtue that close control can be maintained over every aspect of the strain-inducing milling operation.

With the quantity of sample and the grinding time as the only variables, the McCrone Micronizing Mill is the appropriate quantitative tool for such studies.

What about contamination from the grinding elements and the container?

In all grinding operations, some abrasion of both parts will inevitably occur no matter how hard or tough the materials are.

The densities of practically all the liquids used in wet grinding are greater than that of polypropylene, the container material. As a consequence, any abrasion particles from this source will appear as a faintly visible layer on top of the supernatant liquid. This is easily removed. In practice, the jar seldom needs replacement as a result of wear.

The density of the corundum abrasion product is 3.7g/ml. If the densities of the constituent phases of the sample product are different from 3.7, then complete removal of the traces of corundum particles is theoretically possible. This is done by using a heavy liquid suspension centrifuging technique. It would only be appropriate in the preparation of extremely pure micronized products.

How then can the true or original elemental composition of a rock, glass, cement, or ceramic sample be obtained?

To do this, the sample has to be subjected to two parallel grinding operations, each introducing entirely different kinds of contamination. The most convenient method involves grinding in two separate jars, one filed with the standard corundum elements and the other with agate elements. A 5 ml sample, say, is split into equal volumes and ground in the separate jars. Each ground product is then completely analyzed, using any of the appropriate methods, such as classical wet analysis, ultraviolet emission analysis or X-ray fluorescence analysis. By simple calculation, the true composition is then derived[1]. Dual grinding is almost a mandatory procedure when analyses of the very highest quality are required.

Can this mill produce samples suitable for quantitative x-ray diffraction analysis?

Yes. Indeed, the development of the McCrone Micronizing Mill arose out of a sponsored study. The study was undertaken in an attempt to improve the hitherto poor performance of X-ray diffraction as a strictly quantitative tool.

There are seven factors involved in X-ray diffractometry that must be kept under tight control if good quantitative performances are to be obtained.

The first four are respectively:

a) the degree of preferred orientation of the crystals.
b) the specimen's X-ray absorption characteristics.
c) the X-ray beam geometry.
d) the X-ray intensity stability.

Less attention has been given to the remaining three factors. These are:

e) the degree of primary and secondary extinction.
f) the depth of the non-crystalline layer of the crystal.
g) the degree of "spottiness" of the Debye-Scherrer lines.

The effect of (e) and (f) is well illustrated in the graph Fig. 4 shown below. It is taken from a report [10] on a study of the variation of the relative peak intensity of a strong diffraction line of quartz with the crystal size of the diffracting particles. It shows that line intensity is only constant over a relatively short interval of crystal size, i.e. between approximately 3 and 30µm. Above a size of 30µm, the effect is due to extinction and below 3µm it is due to the presence of non-crystalline layers on the crystals.

Grinding techniques and sample origin influence factor (f).

Factors (e) and (g) have one feature in common, the effect of size. If the size of the particle is less than 30µm, and preferably below 10µm if a non-rotating specimen holder is used (factor g), then the errors from these two factors are eliminated. It is not too much to claim that by far the largest share of errors in quantitative X-ray diffractometry arises from these two factors.

Why then, are particle size considerations so often neglected? Partly because of a common failure amongst diffractionists to appreciate the almost dominating importance of particle size. This failure has, no doubt, arisen because conventional powder diffractometers have photon counters which are unable to reveal the presence of crystals between 40µm and about 150µm diameter in the stationary or rotating specimen. Only a diffractometer having arrangements for photographic as well as counter recording would be able to do this effectively[11].

(The Nelson X-ray Diffractometer has been designed for both counter and photographic recording. For further details: contact McCrone Research Associates.)

Can the mill be used to prepare specimens for quantitative infrared absorption analysis?

Yes. Two kinds of specimen are usually used, the thin, self-supporting, pressed KBr or Csl disc containing the embedded specimen particles or the Nujol mull type.

In both types, if the particle size is much greater than about 5µm, heavy radiation losses occur due to optical scattering, and quantitative measurements are insensitive and unreliable. There is also a likelihood of the spectra showing spurious peaks arising from the Christiansen effect. With the KBr or Csl pressed disc type, optical homogeneity of the finished disc is particularly important. To ensure this, the KBr powder and the previously ground specimen powder can be milled together.

A good example is an account of the successful quantitative IR determination of water in granites[12]. The authors state that, ideally, the particle size should be below 3µm (i.e. the wavelength band of the OH-stretching modes in silicates). They also stressed the point that this size would give a much needed control of the mull thickness between the KBr windows.

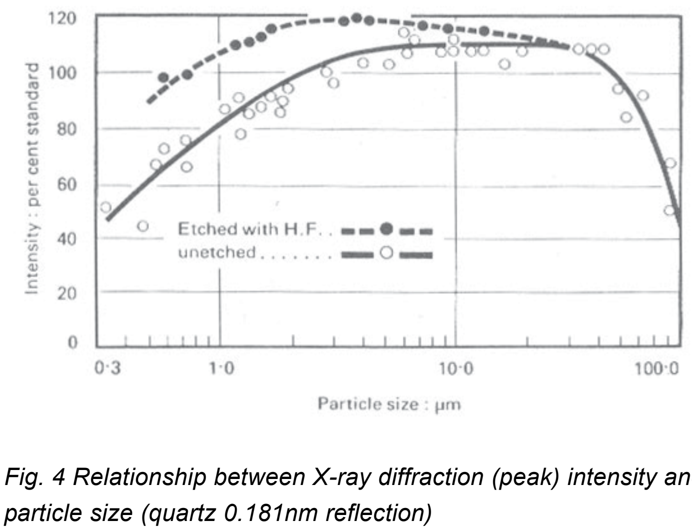

Fig. 4 Relationship between X-ray diffraction (peak) intensity and particle size (quartz 0.181nm reflection)

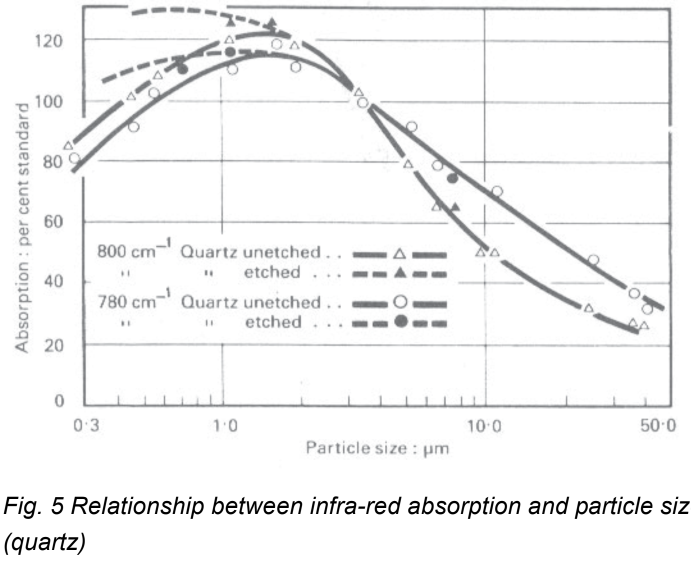

Fig. 5 Relationship between infra-red absorption and particle size (quartz)

The effects of particle size on x-ray diffraction and infrared absorption. The quartz was from many sources and was compared with a Belgian sand (Snowit). Size determination was by microscope and when necessary size fractioning was by sedimentation.

Figs. 4 and 5 above are Crown copyright and were supplied by Health and Safety Executive's Laboratories in Sheffield.

Is sample size reduction an important factor in x-ray fluorescence analysis?

Yes. Specimen preparation remains an area where attention to tighter particle size control could yield considerable improvements in speed, convenience and accuracy.

Specimen preparation techniques in common use are of two general types:

A direct analysis of ground, pressed powder compacts[1],

and

B analysis of glasses produced by fusion of the sample at 1100° C in a graphite crucible with a flux such as lithium tetraborate. The fused glass buttons are crushed, ground and pressed into specimen compacts.

Method A was the earlier scheme. It was, and still is, used by many workers. The objection to it, in spite of its great sensitivity, was that such specimens gave unreliable and erratic measurements. This was claimed to be linked to the presence of platey or lamellar constituents (micas, clays).

The accuracy was restored by converting the sample into a homogeneous, glassy specimen. The improvement was obtained, however, at the cost of sensitivity, speed and convenience.

There appears to be a movement back to the direct method, with a realization of the need for a much more rigorous control of specimen particle size.

Other Applications:

Whilst designed originally as a highly specialized laboratory tool, in general it can deal with any task that requires small quantities of materials reduced in size, dispersed in liquid or very intimately mixed together.

Illustrations of recent successful applications are:

(1) Preparation of specimens for the quantitative analysis of Portland cements by x-ray diffractometry, infrared analysis and x-ray fluorescence analysis.

(2) Preparation of industrial clay minerals and their products for x-ray fluorescence analysis.

(3) Grinding and dispersion of a number of highly toxic organic compounds in glycerol.

(4) Size reduction of various zirconia-based pottery pigments in turpentine.

(5) Maceration of fibers (paper, straw, ramie, sawdust, asbestos, high tensile carbon fibers) and liver and muscle tissue.

(6) Size reduction of sectile minerals such as shale, talc, mica, vermiculite and graphite. These substances have proved to be very difficult to grind in any other vibratory mill. The success with the present mill is believed to be due to the planar shearing contribution.

(7) Submicrometer grinding and milling of various metallic silicides and glasses for phase equilibrium studies. Regrinding the frits was done to further homogenize the final fired body. The same kind of procedure was used in solid state reaction studies of pure oxide mixtures with chromites and cerates.

(8)Used as a device for obtaining the abrasion pH[13] of a series of oxidizable, pure, inorganic compounds (various solid solutions of manganous and ferrous carbonates).

(9) Preparation of various x-ray opaque dispersions for a study of blood vessel distribution using x-ray stereo-microradiography.

(10) Crushing of the cell walls of penicillin mycelia to extract the cell contents.

(11) Reducing the aspect ratio of crystals in pharmaceutical products. Slurry grinding results in minimal crystalline damage.

(12) Grinding of segments of teeth and bone for X-ray diffraction analysis.

Mill Specifications The mill measures 48 x 20 x 16.50 cm. It weighs 9 Kilograms when charged with grinding jar containing corundum grinding elements. Models are available for use at either 220-240 volts 50Hz, or 110 volts 60Hz. Please specify voltage required when ordering. The mill is supplied complete with separate operating instructions.

Replacement of Parts & Accessories All spare parts are readily available. Replacements of flexible mountings and polypropylene grinding jars are occasionally required. Where the mill has been used to reduce the size of exceedingly hard substances, agate grinding elements have needed replacement only after an estimated grinding time of 2,500 hours. The rubber flexible couplings and corundum grinding elements are the only other replacements requested in over 12 years of mill sales.

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