Procedures for Preparation of Sealed Powder Patterns and Single Crystal Samples for X-Ray Diffraction Methods in Controlled Atmosphere without Dry Box

M. ZIKMUND and A. VALENT

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava 9

Received September 29, 1969

In the present paper device and procedures are described for preparation of flat powdered samples of air-sensitive substances in an inert atmosphere without the application of a dry box. The samples are to be submitted to measurements with X-ray diffractograph and with the Guinier method. Further a method for filling single crystals into capillary tubes of Lindemann glass for measurements with the Weissenberg method are reported.

X-ray diffraction methods, both of the powder and single crystal types, have been used to identify and check the purity and crystal structure determination of air--unstable substances. In the course of their preparation and during the measurement itself the samples of these substances must be protected against the atmospheric air. A standard technique has been developed for filling suitable capillary tubes (*e.g.* of Lindemann or silica glass) with highly air-sensitive powdered substances in inert atmosphere [1, 2].

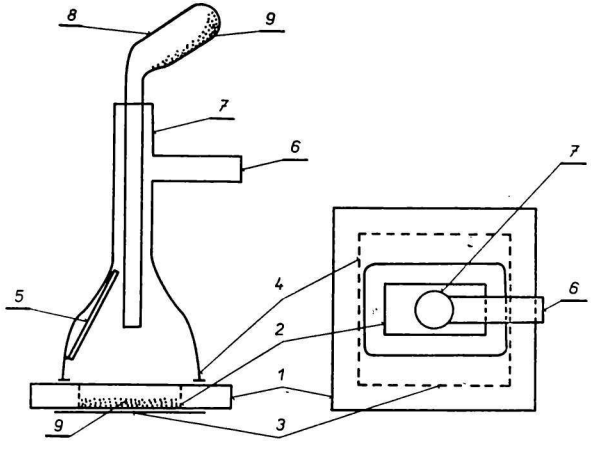

Fig. 1. Device for preparation of flat powdered samples.

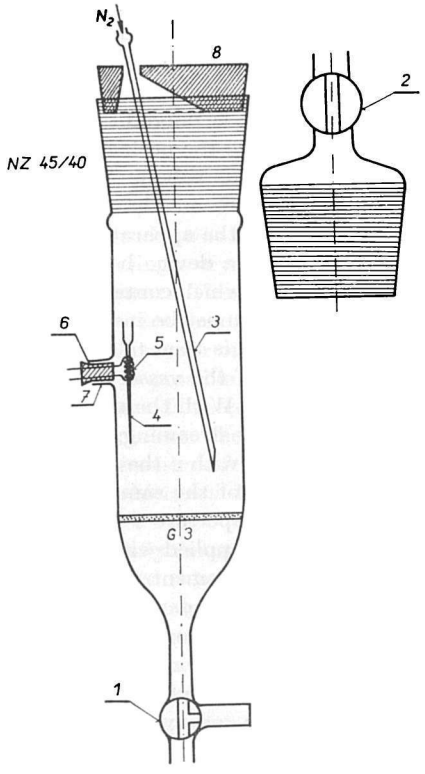

Fig. 2. Apparatus for filling single crystals into Lindemann capillary tubes.

On the other hand, essentially less attention has been given to the development of the technique for filling single crystals of air-sensitive substances into glass X-ray capillary tubes in inert atmosphere [3] so that these could be examined *e.g.* by Weissenberg or precession methods. Analogously the technique for filling unstable powdered samples into flat holders used for measurements with diffractograph or with the Guinier camera by Hägg is relatively little developed. In this case the sample of flat shape placed in holders between little absorbing X-ray amorphous foils is used [4].

In the present work procedures and devices are described by which flat powdered samples are made (Fig. 1) and with the aid of which single crystals are filled into Lindemann capillary tubes (Fig. 2) in protective inert atmosphere without using the glove box.

Powdered specimens

The flat powdered sample is made with the aid of a holder consisting of the frame *1* whose dimensions (Fig. 1) are compatible with the used X-ray apparatus. In the middle of the frame an oblong aperture *2* is cut out which, on the lower side of the frame, is closed by a thin foil *3* made of an X-ray amorphous and little absorbing material. The foil is fastened to the frame (made *e.g.* of plexiglass) and made air-tight by applying

a suitable sealing agent (*e.g.* with acetone lacquer). To the upper part of the frame the glass head *4* with the ground bottom is sealed. On the inner wall of this head an about 1 mm thick polyethylene plate *5* is fastened whose dimensions are identical with those of the aperture *2*. Before the holder is filled with the powdered specimen, the inner area of this assembly is purged thoroughly with nitrogen flowing partly through the inlet tube, inserted into the neck *7* which reaches just over the bottom of this apparatus, and partly through side tube *6*. Nitrogen, which during the whole procedure comes through the tube *6* and flows out through the neck *7* provides a slight overpressure owing to which the inner part of the apparatus is protected against the air atmosphere.

After the whole device has been filled with nitrogen, the neck *7* is opened and the glass ampoule *8*, which contained the sealed specimen *9*, and which was opened immediately beforehand, must be inserted quickly through this neck *7*. From the ampoule *8* the powdered sample is then filled through the aperture *2* so that a sufficiently thick layer on the bottom of the vessel should be formed, and afterwards the ampoule is removed from the neck *7*. With the aid of a glass rod or of a hypodermic needle through which nitrogen is slowly streaming, the polyethylene plate *5* is carefully removed from the wall of the head *4* and with it the aperture *2* is trapped, whereupon, owing to the slight pressure, a compact layer of the sample *9* is formed. Places of contact between the plate *5* and the walls of the aperture *2* can be cemented with an appropriate cementing agent (*e.g.* acetone lacquer) applied with the aid of a hypodermic syringe through the neck *7*. After hardening of this cement the area over the polyethylene plate *5* may be filled with an appropriate filling (*e.g.* with molten paraffin or dentacryl). After removing the frame of the head *4* from the frame *1* the sample in the holder is prepared for measurements.

Single crystal specimens

Filling of glass capillary tubes with single crystals of substances sensitive towards the active components of the air may be performed with the aid of an assembly shown in Fig. 2. It consists of a glass tube wherein the sintered disc *G3* is sealed. A capillary tube of Lindemann glass, 0.5 mm in diameter, is fastened to the wall of this tube with the aid of a fine wire spiral. This spiral is fixed in a rubber stopper *6* placed in the aperture *7* and which, so as to be air-tight, is covered with picein. Through a T-bore tap placed in the lower part of the tube closed with a glass stopper with straight-bore tap *2*, air is removed by evacuation and by repeated purging with nitrogen. Then, through the tap *1*, nitrogen is brought into the tube which provides an inert atmosphere in the course of the whole procedure. The nitrogen flow being kept rather strong, the glass stopper *2* is replaced by the rubber stopper *8*. The conical opening of the rubber stopper makes it easier to handle the hypodermic needle *3* (purged with nitrogen), with the aid of which the single crystals are inserted into the capillary tube.

The investigated crystals, taken from a freshly opened sealed ampoule, have to be put with great care into the tube through the opening in the stopper *8*. Then the tube is fixed in horizontal position and with the aid of the Greenough stereoscopic microscope the suitable crystal is chosen on the bottom of the tube and with the blunt tip of the hypodermic needle *3* this crystal is taken and put into the enlarged neck of the capillary tube. Then the tube is carefully replaced in vertical position, whereupon the single crystal drops into the narrow part of the capillary tube. Its position may be checked by the stereoscopic microscope.

The hypodermic needle *3* is removed from the glass tube and the rubber tube about 1 cm long, with inner diameter equal to the diameter of the enlarged part of the capillary

tube, is put over the needle, through which nitrogen is allowed to pass slowly. The needle is inserted into the tube through the opening in the stopper and it is introduced into the enlarged part of the capillary tube which is then removed from the apparatus. Then the rubber tube is carefully put over this part of the capillary tube, with a fine hypodermic needle this tube is pierced and nitrogen is allowed to flow through the needle and further it is allowed to escape out of the capillary tube.

The bigger hypodermic needle is then taken out from the enlarged part of the capillary tube and is replaced by an about 2 cm long tip of a Lindemann glass capillary tube (diameter 0.3 mm) which, prior to being sealed on both ends, was thoroughly purged with nitrogen. With the aid of this tip the position of the single crystal in the 0.5 mm capillary tube is fixed for the whole duration of the measurements. Then the two capillary tubes are sealed with a small hot flame. The nitrogen stream escaping out of the capillary tube keeps the atmosphere inert during the procedure and moreover on sealing the capillary tube, it inhibits formation of a bubble in the glass. It is possible to check with the stereoscopic microscope whether the sealing has been faultless. If there were fine fissures in the capillary tube of Lindemann glass, it is advisable to cover the tube with a fine film of X-ray amorphous lacquer which prevents contamination of the single crystal by the atmospheric oxygen and by atmospheric moisture which are bound to damage the capillary tubes of the Lindemann glass.

The capillary tubes of Lindemann glass are needed especially for specimens with very low linear absorption coefficient. For other specimens capillary tubes of Pyrex or silica glass may be taken, which, however, are more difficult to be sealed and there is always the possibility that the specimen would be attacked by heat in the course of sealing.

When designing this kind of devices, similarly as when construction of other overpressure devices is planned, it is advisable to test their aerodynamical properties (*e.g.* to check whether there is turbulent flow inside the apparatus) by adding some gas to the flowing nitrogen which forms fumes when mixed with the gas in the atmosphere. It is possible to use for this purpose the reaction of ammonia with hydrogen chloride and the formation of the ammonium chloride fumes at the opening of the apparatus.

References

1. D'Eye R. W. M., Wait E., *X-Ray Powder Photography in Inorganic Chemistry*, p. 54. Butterworths, London, 1960.
2. Bartlett N., in *Preparative Inorganic Reactions*. (W. M. Jolly, Editor.) Vol. 2, p. 317. Interscience, New York, 1965.
3. Holloway J. H., Peacock R. D., Small R. W. H., *J. Chem. Soc.* ***1964***, 644.
4. Scaife D., Watts J. A., *J. Sci. Instrum.* ***41***, 569 (1964).

Translated by V. Šašková