Figure 2.10.33
Commercial holder for air-sensitive samples. This particular holder for small samples has a flat silicon zero-background plate and a polymer dome which screws down against a rubber o-ring seal.

One of the most common questions asked by users of laboratory instruments is how to deal with small sample sizes. In an ideal world, a specialist microdiffraction system or capillary geometry could be used, but many laboratories do not have access to such equipment. How problematic such samples can be depends to some extent on the mass absorption coefficient of the sample. Conventional powder diffraction data relies on having a sample with an 'infinite sample depth'. However, that depth can be very small for samples with very high absorption coefficients. In those cases, spreading the sample in a very thin layer can still yield reasonable relative intensities across a large range of 2θ angles. With low-absorbing samples such as organics the relative intensities will drop off at higher angles as the sample is no longer

Figure 2.10.34
Filling a commercial back-loading sample holder. The holder is held against a base surface (sandpaper in this case) while filling, the back is replaced and then the holder is flipped over to reveal the sample surface once the clips are removed.

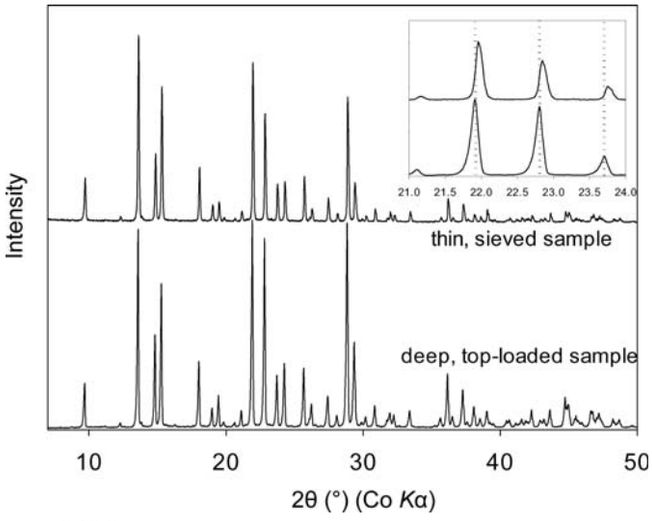

Figure 2.10.35
Data from powdered sucrose on a Bragg–Brentano instrument, with the peak intensities normalized to the first reflection. The thin sample was prepared by sieving onto a low-background silicon plate made slightly tacky using hairspray. The inset shows that there is a slight peak shift between the two data sets as well as the predicted decay in relative intensities with the thin sample with 2θ angle.

'infinitely thick', as shown in Fig. 2.10.35. However, the peak positions will be more accurate than with deeper samples because of the lack of transparency effects in thin samples. Consequently, it is not uncommon to obtain two data sets from such samples: from a thin sample to obtain good peak positions, and from a deep one to obtain better relative intensities. The details of sample penetration are given in Chapter 5.4.

Most modern holders are circular and the specimen is often loaded into a round cavity. As the beam 'footprint' is rectangular, this is not the most efficient use of the material, as a significant portion will always remain outside the beam. Prior to the introduction of sample spinners, square and rectangular cavities were quite common. It is good practice to know the footprint of the beam at various diffraction angles by observing the illuminated area of a fluorescent specimen. Should the material be in particularly short supply and sample spinning is not absolutely necessary, the powder may be mounted in the minimum rectangular shape to be illuminated by the incident beam. Such an approach may be combined with the use of motorized divergence slits to maintain a constant beam length on the sample. Although most analysis software assumes constant divergence slits, the correction is well known and implemented in most commercial software.

In order to avoid background from the sample holder, thin specimens are usually mounted on flat zero-background plates. It is useful to have the surface of the plate lower than the reference surface (50 μm is a common value) to minimize specimen displacement effects. In practical terms, thin samples are historically referred to as smear mounts. Slurry mounting using ethanol or acetone often yields a self-adhesive specimen, but it is tricky to obtain the correct slurry rheology to produce a non-lumpy, thin and even layer across the surface; surface roughness is often apparent in the pattern. Loose, friable samples may be problematic with spinning specimens or the tilting specimens in θ–2θ geometry. A number of materials have been used over the years to adhere thin powder samples to flat plates; common ones are thin smears of Vaseline or grease, but analysts often have their own favourites. The particular material used to stick the sample to the surface is often the result of testing a large number