

2. INSTRUMENTATION AND SAMPLE PREPARATION

2.9.3.2. Capillary cells

Capillary cells, also called microreactors, exist in many variations. Depending on the application (temperature, pressure and chemical environment), capillaries may be made of polyimide, glass, quartz, single-crystal sapphire or steel. They are simple and extremely efficient devices which can accommodate a large number of different applications. The impetus for their development has mainly come from catalysis research, but they have also been successfully employed to perform *in situ* reactions on intercalation, ion exchange, gas sorption/desorption, cement hardening, hydration–dehydration, light-induced transitions, crystallization processes and polymorphism, to name a few. Capillary cells are almost always used together with temperature- and/or gas-handling (static pressure or flow) devices. In open geometry, or with simple heat shields, one can easily obtain

temperatures ranging from 80 to 1000 K with cryogenic and hot-air blowers or resistive heaters close to the sample. Static gas pressures can be as high as 30 MPa and in flow cells 2 MPa is commonly reached, as well as vacuum conditions. Capillary cells were first applied by Clausen (1991) and have been adapted numerous times (Brunelli & Fitch, 2003; Chupas *et al.*, 2008; Jensen *et al.*, 2010; Madsen *et al.*, 2005; Norby *et al.*, 1998, 2000; Palancher *et al.*, 2005) together with gas-handling systems (Eu *et al.*, 2009; Hill, 2013; Krogh Andersen *et al.*, 1998; Llewellyn *et al.*, 2009), with large 6 mm-diameter samples (Andrieux *et al.*, 2014), with supercritical solvents up to 40 MPa with a swing-in blower for rapid heating (Becker *et al.*, 2010) or with pulsed supercritical flows (Mi *et al.*, 2014) for following synthesis reactions. A recent review of several capillary cells for high-pressure reactions (Hansen *et al.*, 2015) also contains useful information on how to calculate burst pressures.

One of the most critical issues is how to create a reliable leak-tight connection between the capillary and the metallic or polyether ether ketone (PEEK) gas/liquid supply line(s). For fragile capillaries there are basically two strategies: either to glue the capillary to a metal support with high-temperature epoxy (see Fig. 2.9.1), or to use ferrules. When both ends of a capillary have to be tightened with thin-walled capillaries, the use of ferrules needs some skill (see Fig. 2.9.2).

If the working temperature permits, it is easy and reliable to use a stainless-steel bracket in which capillaries are glued such that all mechanical forces are transferred to the support instead of being taken up by the thin (glass) capillaries (van Beek *et al.*, 2011), as in Fig. 2.9.3. Gas systems are typically constructed from a combination of pressure reducers, mass-flow meters, valves and a manifold which supplies gases to the cell at controlled pressures and flow rates. It is worth pointing out the less-common back-pressure regulator used in Fig. 2.9.3. This unit allows 2 MPa of pressure to be maintained on the sample during flow experiments. Backpressure regulators for much higher pressures are commercially available, but these have so far not been used for *in situ* work. *In situ* diffraction has been coupled with stable-isotope analysis to correlate isotope fractionation with crystal structure. For this, a nonmetallic flowthrough capillary cell that avoids any contamination from the components of the cell itself was designed (Wall *et al.*, 2011). Many hundreds of studies have been performed over the last two decades with capillary devices in the above-mentioned fields.

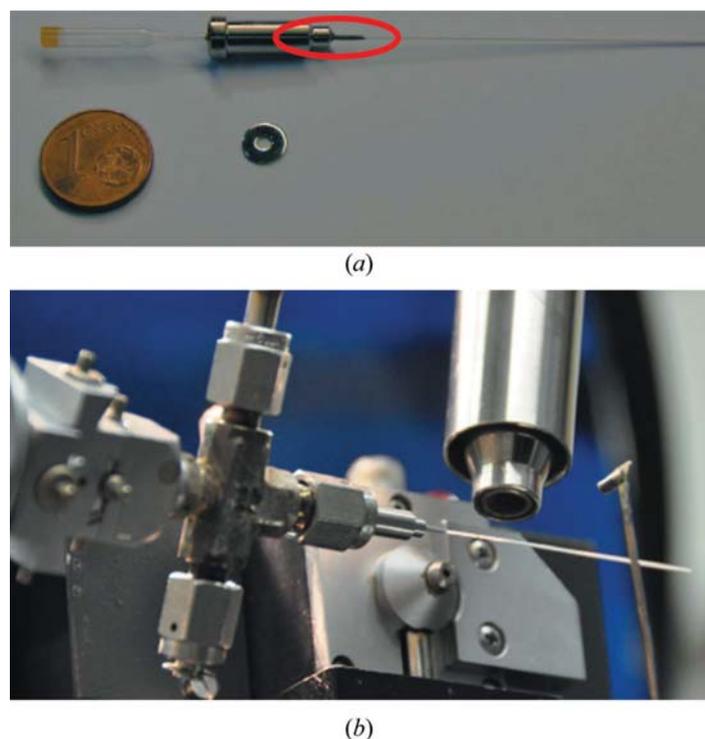


Figure 2.9.1
(a) Swagelok VCR gland with an epoxy-glued capillary (red ellipse). (b) VCR capillary cell on a beamline with a cryostream (adapted from Jensen *et al.*, 2010).

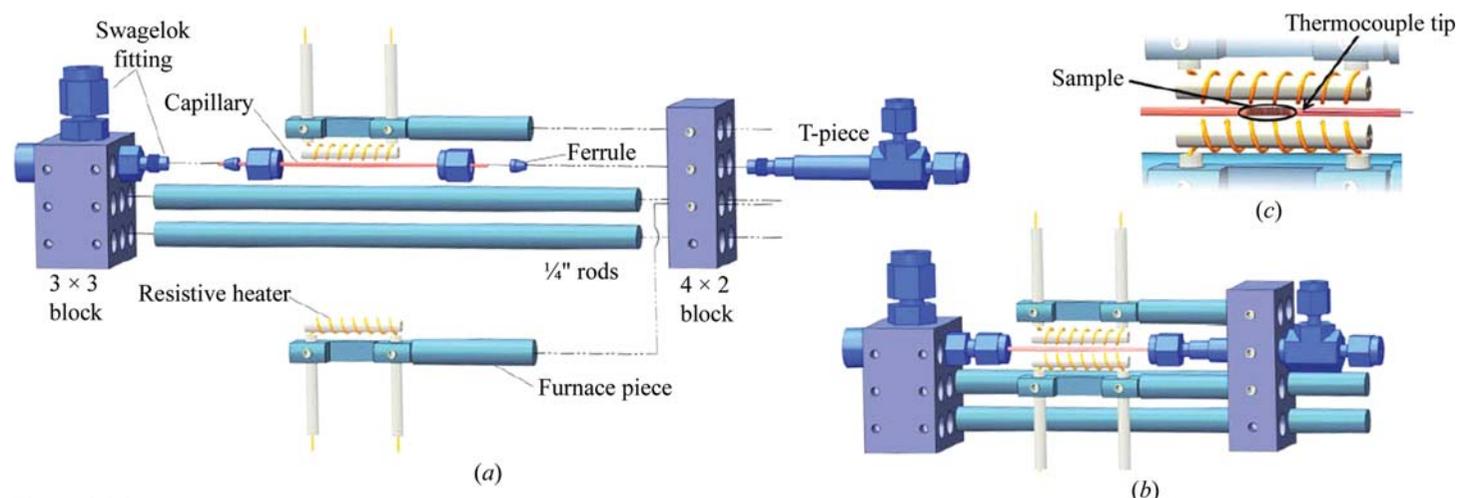


Figure 2.9.2
(a) An exploded representation of the flow-cell/furnace components, indicating how they fit together. (b) The fully assembled flow cell/furnace. (c) An expanded view of the sample region, indicating the relative position of the sample and thermocouple tip within the furnace hot zone (adapted from Chupas *et al.*, 2008).