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1.5×10^{-5} W m^{-1} K^{-1}. N_2 boils at 77 K; propane remains liquid between 83 and 228 K. It is often thought that a gas bubble that can form around an object dipped in liquid N_2 makes it less effective as a coolant than liquid propane, which is much less likely to form bubbles. However, from model calculations, Bald (1984) suggested that the gas insulation problem in liquid N_2 would not be significant in the cooling of small objects of low thermal conductivity, because there is not enough heat transport to the surface to maintain the gas layer. He also concluded that liquid N_2 could potentially yield the highest cooling rate among commonly used coolants. But in a review of plunge-cooling methods, Ryan (1992) gives preference to liquid ethane. Walker *et al.* (1998) measured the cooling rates in N_2 gas (100 K), liquid N_2 (77 K) and liquid propane (100 K) of a bare thermocouple and of a thermocouple coated with RTV silicone cement. The thermocouples were made from 0.125-mm wire and the coating was about 0.20–0.25 mm thick. With the gas stream, cooling of the centres of the samples from 295 K to 140 K took 0.8 and 2 s, respectively; with liquid N_2 the times were 0.15 and 0.6 s, and with liquid propane they were 0.15–0.18 and 1.2 s (time reproducibility is to within $\pm 10\%$). Given the simplicity of liquid-N_2 immersion, there seems little reason to choose the more complicated and more hazardous liquid-propane technique.

10.1.3. Principles of cooling equipment

There are many ways to construct a low-temperature apparatus based on the cold-stream principle that functions well, but they are all made according to a small number of basic principles.

All gas-stream crystal-cooling devices must have three essential components: (*a*) a cold gas supply, (*b*) a system of cold gas delivery to the crystal, and (*c*) a system for frost prevention at the crystal site.

10.1.3.1. *Cold gas supply*

Two methods are commonly used: generation of gas by boiling liquid N_2 with an electrical heater, and cooling of a gas stream in a liquid-N_2 heat exchanger.

Because precise voltage and current control are easily realized, the boiler method has the advantage of providing very accurate control of the flow rate with minimal effort. Precise control of the flow rate is typically not attained when the rate is controlled with standard gas-flow regulators, because they control volume, not mass.

In addition to control of the flow rate, precise control of the temperature requires exceptional insulation for the cold stream. The longer the stream path, the higher the requirements for insulation. As a rule, temperature rise during transfer should not exceed 15 K at a flow rate of 0.2 mol N_2 min^{-1}; preferably, it should be significantly lower. Higher cooling loss leads to excessive coolant consumption and to instability caused by changes in ambient temperature. High flow rates also tend to cause undesirable cooling of diffractometer parts. No commercially offered device should be accepted if it does not meet the criterion given above.

Appropriate insulation can be readily attained either with silvered-glass Dewar tubing or with stainless-steel vacuum tubing. Glass has the advantage of being available from local glassblowing shops; it generally provides excellent insulation. The main disadvantages are fragility and a rigid form that makes accurate positioning of the cold stream difficult. Stainless steel can provide superb insulation, given an experienced manufacturer; unsatisfactory insulation is quite common. A major advantage is the availability of flexible transfer lines that greatly simplify the positioning of the cold stream relative to the diffractometer.

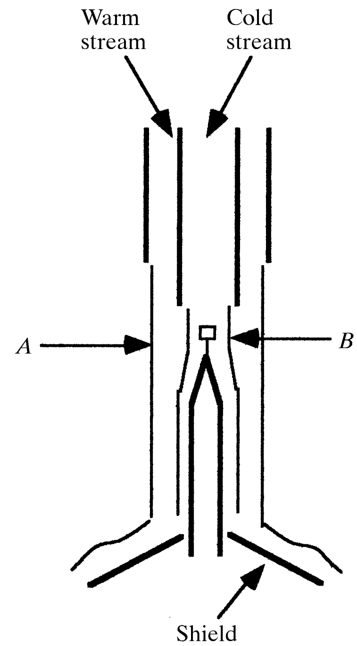

Fig. 10.1.4.1. Schematic drawing of a dual-stream setup with the streams parallel to the diffractometer φ axis. The top part represents the outlet end of the stream delivery device. *A* represents the outline of the warm shield stream and *B* represents the interface between the cold stream and the warm stream. The goniometer head (not shown) is protected by a shield.

10.1.3.2. *Frost prevention*

Three areas must be kept frost-free: the crystal, the crystal mount and the delivery end of the transfer tube. The first successful solution to this problem was the dual-stream design of Post *et al.* (1951). It provides for a cold stream surrounded by a concentric warm stream. If the warm stream is sufficiently dry, this will prevent frost around the outlet. The crystal will remain frost-free only if mixing of the two flows occurs downstream from the crystal. For a stream aligned with the axis of the goniometer head, an additional shield is needed to keep the goniometer head frost-free.

10.1.4. Operational considerations

10.1.4.1. *Dual-stream instruments*

Fig. 10.1.4.1 shows a schematic drawing of the region around the crystal in a traditional dual-stream apparatus, first described by Post *et al.* (1951). The device provides for a cold stream surrounded by a concentric warm stream. The diameter of the cold stream is typically around 7 mm with a shield stream of 2–3 mm. The two streams flow parallel to the axis of the crystal mount. In a properly functioning apparatus, the warm stream supplies enough heat to keep the tip of the tube carrying the cold stream above the dew point. It is important that the streams do not mix, or the crystal temperature will not be stable. This is achieved by careful balancing of flow rates to minimize turbulence. (Absence of turbulence can be judged by the shape of the shadow of the cold stream in a parallel beam of bright light.) In a laminar cold stream, the crystal is well protected and no unusual precautions are needed. The region of constant, minimum temperature will typically have a diameter of about 3 mm. Turbulent flow will result in no constant-temperature region, so it is important to verify the stream quality.

The cold stream has sufficient heat capacity to cool down the goniometer head, and sometimes other adjacent equipment parts as well. A simple solution consists of an aluminium cone equipped

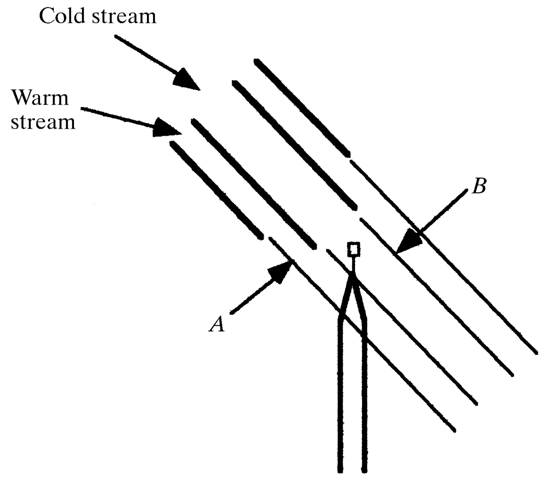

Fig. 10.1.4.2. Schematic drawing of a dual-stream setup with the streams angled relative to the diffractometer φ axis. *A* and *B* are the same as in Fig. 10.1.4.1. The cold stream misses the goniometer head, so no shield is required.

with a heating coil on the back. A shield that functions well has been described by Bellamy *et al.* (1994).

Fig. 10.1.4.2 illustrates a situation where the stream direction deviates substantially from the head-on direction in Fig. 10.1.4.1. An angle of 35–55° will give good results. An advantage of an angled delivery is that the goniometer head will not be touched by the cold stream, therefore the heated stream deflector is not needed, resulting in simplified installation and operation.

Analysis of the dual-stream apparatus reveals a twofold function of the outer stream: it keeps the nozzle frost-free and it supplies heat to the mounting pin. Protection of the crystal is, in reality, already provided by the laminar cold stream. The nozzle can be kept frost-free simply with an electric heater. Ice formation on the crystal mount can be easily suppressed by appropriate design of the mounting pin and mounting fibre, and attention to their interaction with the cold stream. A successful solution is sketched in Figs. 10.1.4.3 and 10.1.4.4.

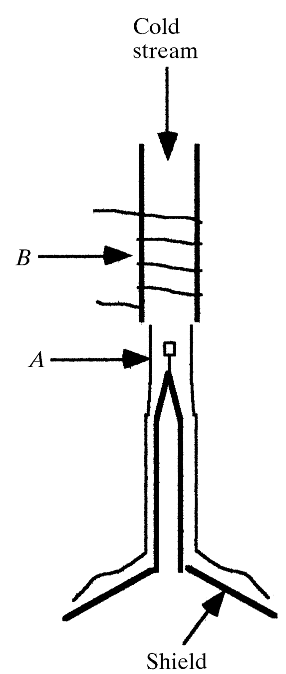

Fig. 10.1.4.3. Schematic drawing of a single-stream setup with the stream parallel to the diffractometer φ axis. *A* represents the outline of the cold stream. The tip of the outlet end is heated above the dew point with a heating coil *B*. The goniometer head (not shown) is protected by a shield.

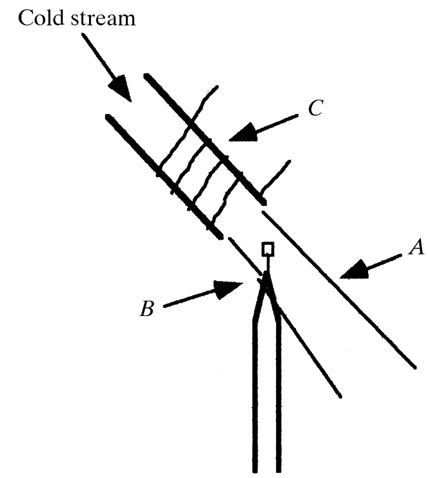

Fig. 10.1.4.4. Schematic drawing of a single-stream setup with the stream angled relative to the diffractometer φ axis. *A* represents the outline of the cold stream. At *B* the crystal mounting pin protrudes 1–2 mm into the cold stream. This prevents frost from forming on the mounting fibre. The tip of the outlet end is heated above the dew point with a heating coil *C*. The cold stream misses the goniometer head, so no shield is required. In general, the simplest operation is attained with a setup similar to that shown here.

10.1.4.2. *Electrically heated nozzle*

Fig. 10.1.4.3 shows the functional equivalent of Fig. 10.1.4.1. Instead of the warm stream, an electrical heating element is used to keep the tip of the delivery tube ice free. An actual construction will usually consist of a nozzle that can be attached to the delivery tube. The heating element is made from standard resistance wire (*e.g.* Nichrome). About 5 W will usually be enough to prevent frost or condensation. The head-on direction results in reliable frost protection for the crystal, but the goniometer head must be equipped with a heated stream deflector.

Fig. 10.1.4.4 shows the functional equivalent of Fig. 10.1.4.2. This arrangement leads to the simplest design, though some precautions are needed. The mounting pin itself supplies the heat needed to prevent ice formation on the pin. The cone-shaped tip of the pin (full cone angle about 20°) should be smooth in order to prevent turbulence. About 1–2 mm (but not more) of the tip must protrude into the cold stream (see region *A* in Fig. 10.1.4.4). If too much of the pin is in the cold stream, the rest of the pin can become too cold and ice up. If the pin is too far out of the stream it will also fail, because glass or other insulating mounting materials will invariably collect frost at the cold/warm interface. As frost prevention depends on heat conducted from the rest of the pin, it must be made from copper. This design has been extensively tested and has been used for many years for the collection of a large number of data sets. Results are uniformly good, with simple operation and reliable frost prevention even in high humidity.

Omission of the warm stream results in significant design simplification. The entire apparatus for production of the outer stream is left out, resulting in real savings in manufacture, operation and maintenance. There is no obvious disadvantage. Ice protection is as good as with the dual stream. The main cost to the user is in the requirement that the mounting system be constructed within somewhat narrower limits. The fact that operator errors tend to become apparent through frost formation can actually be an advantage. With a dual-stream device, an improperly positioned cold stream or an improperly prepared crystal mount may not produce overt signs, even though the crystal temperature is ill-defined.

In all configurations shown, correct positioning of the cold stream is essential. The centre of the stream should not miss the centre of the diffractometer (and hence the crystal) by more than 0.5 mm.

10.1.4.3. *Temperature calibration*

Measurement of the temperature at the crystal site with thermocouples or other devices that require attached leads is very difficult, mainly because of heat conduction along the leads. The preferred method of calibration makes use of the known temperature of a phase transition of a crystal in the normal data-collection position. KH_2PO_4 (often referred to as KDP) has a sharp transition at 123 K from tetragonal to orthorhombic, and is commonly used. Another possibility is KH_2AsO_4, which has a corresponding phase transition at 95 K.

Two readout temperatures suffice, one at room temperature and one at the phase transition. The difference between readout temperature and crystal-site temperature can be assumed to vary linearly with T, so interpolation or extrapolation is simple.

10.1.4.4. *Transfer of the crystal to the diffractometer*

Inspection of Figs. 10.1.4.1–10.1.4.4 reveals that the mounting of a crystal on a mounting pin *via* the traditional placement of the pin in the hole of a standard goniometer head is not simple, because the cooling nozzle is in the way. The solution to the problem is a design that allows side entry. Two methods are in use. One depends on a side-entry slot on a modified goniometer head; the slot is equipped with a spring-loaded catch that allows a very smooth, but stable, catch of the pin. The other method relies on a magnetic platform on the goniometer head and a corresponding magnetic base on the mounting pin.

The use of liquid-N_2 cooling and side entry, and the requirement of reproducible knowledge of crystal temperature, led to the development of a set of tools for crystal mounting, as described by Parkin & Hope (1998). The tools include special transfer tongs used for moving crystals from liquid N_2 to the goniometer head. The temperature of the crystal is maintained by the heat capacity and low heat conductance of the tongs. The operation is independent of the orientation of the goniometer head, since there is no liquid to contain.

10.1.5. Concluding note

With correctly functioning low-temperature equipment and appropriate techniques, a crystal can be maintained frost-free for the duration of a data-collection run. Formation of frost on the crystal indicates malfunction of the equipment, or operator error. The most likely cause is operator error, but faulty equipment cannot be ruled out. The techniques described here have been used for collecting thousands of data sets from ice-free crystals and crystal mounts. There is no reason to accept frost problems as an unavoidable part of cryocrystallography.

references