hydrogen bonds found in the present crystal are all of normal distances as compared with those in other sugar structures, with average strength (Wallwork, 1962). It is interesting to note here that O(I), which is not involved in a hydrogen bond, is coordinated to two rubidium ions, whereas each of the hydrogen-bonded O(II) and O(III) deals only with one rubidium ion.

The molecules are held together tightly in the structure by these hydrogen bonds and also through the ionic interaction around the rubidium ion. It is noteworthy that the structure consists of two different types of layer, one through $a=0$, where only the ionic force around the ion exists and the other through $a=\frac{1}{2}$ where the hydrogen bonds connect molecules around the twofold screw axis.

The author is indebted to Dr A. A. Benson for the samples of the rubidium salt and many interesting discussions on the biological significance of the compound.

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A Versatile Cooling Technique for X-ray Diffraction by Single Crystals at Temperatures below 90 °K

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The customary technique for maintaining a crystal at low temperatures by a cold gas stream has been modified by the introduction of a light Dewar vessel attached to the X-ray goniometer, its contents of liquid nitrogen being controlled continuously by a constant level device.

The temperature of the cold gas stream was measured as a function both of the consumption of liquid nitrogen and of the distance of the specimen from the delivery tube. With standard Weissenberg diffraction techniques a complete sequence of equi-inclination photographs can be taken at 87 °K.

Introduction

The advantages of employing low temperatures in X-ray diffraction studies are now widely recognized. Especially in structure analyses of organic crystals, where the often large thermal motions have an adverse effect on the reliability of the determination of interatomic distances, employment of efficient cooling techniques results in a striking increase in accuracy (Cruickshank, 1960); moreover, low-tem-

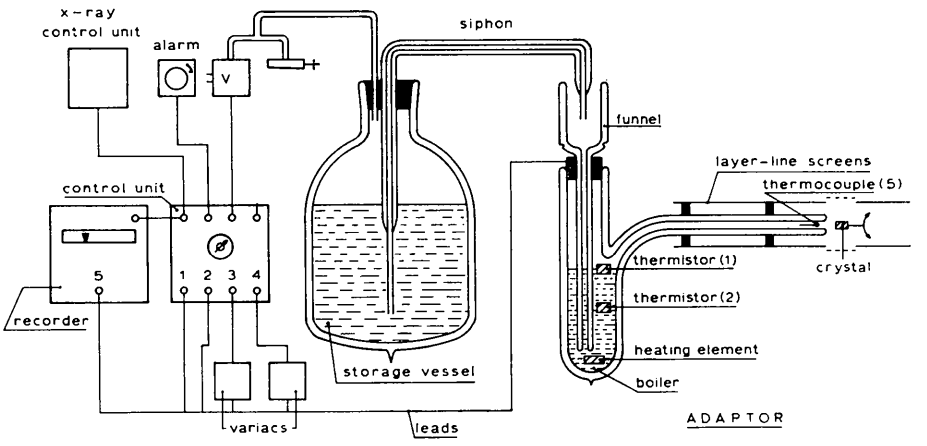

Fig. 1. Diagram showing the design of the low-temperature adaptor and the auxiliary apparatus.

perature diffraction data may afford an improved basis for a rapid solution of the phase problem as well as for subsequent refinement procedures (Mossel & Romers, 1964; Fridrichsons & Mathieson, 1962).

The general principles of low-temperature techniques in X-ray crystallography, with special emphasis upon gas-cooling, have been summarized recently by Robertson (1960) and by Viswamitra (1962).

With the above considerations in mind, a number of crystal structure determinations (see for example Romers & Altona, 1963) were carried out in this laboratory at temperatures between 175 and 130 °K. In the course of time several cooling methods were tried. In one of these, cold gas was generated by electrically controlled boiling of liquid nitrogen under a vacuum-jacketed bell placed in an open Dewar vessel. For reasons of flexibility the top of the bell was connected to a commercial delivery tube (Nonius) by means of a thermally insulated ground glass joint. It became obvious, however, that serious heat leakage occurred through this joint; the resultant loss of cooling power could be compensated for only partially by increasing the consumption of liquid nitrogen, thereby raising problems of overcooling of camera parts.

These difficulties have been overcome in the design described below, which was aimed at combining great versatility of operation with minimal loss of cold. An important feature of the apparatus is the small size of the cooling system (which we term a low-temperature adaptor), made possible by the application of an electronic level-control device. In fact, the adaptor is in essence a thermally insulated Claisen flask equipped with an insulated side arm for delivery of the cold vapour.

General description

The adaptor, as used in a standard horizontal Weissenberg goniometer (Nonius), and the auxiliary apparatus are shown diagrammatically in Fig. 1. Liquid nitrogen is boiled in a miniature Dewar vessel (capacity 170 ml). The cold vapour flows directly through a horizontal delivery tube onto the crystal. The internal diameter of the tube is 3·5 mm; the external diameter 18 mm. The vacuum jacket is silvered, except for narrow strips along the sides of the boiler. These strips allow inspection of the various electrical components inside.

Before starting operation of the equipment, the delivery tube is positioned accurately in the centre of the layer-line screens, its tip 2–3 mm from the crystal specimen. For this purpose a commercial gas-tube holder (Nonius) is well suited. The boiler vessel has no separate support: its dimensions are such that at the maximum inclination angle (40°) of the Weissenberg goniometer there is still a one cm space between the bottom of the vessel and the supporting table. During operation of the cooling assembly the inclination angle of the goniometer can be adjusted at will without touching the adaptor; however, it is convenient to remove the siphon beforehand. A shift in the position of the layer-line screens should be followed, if possible, by an equal and opposite shift of the adaptor, because the temperature of the specimen depends upon the distance between the gas outlet and the crystal (see below). For Weissenberg exposures the 'back-stream' method (Kreuger, 1955) has great advantages; therefore, the slit between the screens is covered with transparent adhesive tape during operation.

A constant flow of cold vapour is produced by means of a heating element (wire-wound resistor, 1000 ohms, 10 W) at the bottom of the boiler. A second small heating coil (not shown in the figure), placed in the cold-gas tube, can be used to adjust the temperature of the gas anywhere between 85 °K and room temperature.

A well-stoppered vertical extension of the boiler vessel serves as an inlet for a vacuum-jacketed funnel and for an assortment of wire leads. Liquid nitrogen

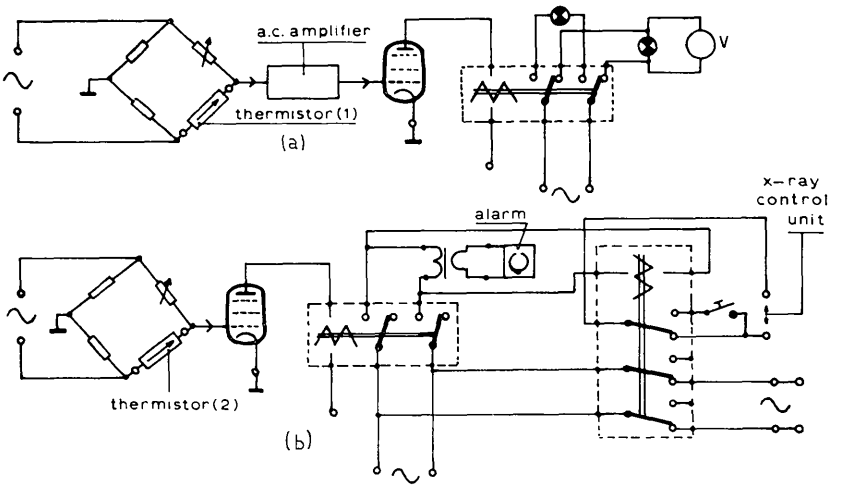

Fig. 2. (*a*) Block diagram of the level regulator. (*b*) Block diagram of the safety circuit.

from a 10-l storage Dewar vessel is automatically fed into the funnel through a glass siphon. For easy and safe removal of the siphon a piece of silicone rubber tubing is attached to its tip; the tubing fits only loosely in the relatively wide mouth of the funnel. Accumulation of ice in the stem of the funnel is prevented by placing a glass-wool cover over the mouth during operation.

Automatic level control

The level of the liquid nitrogen in the adaptor must be kept constant within narrow limits (±3 mm) for accurate temperature control. Analogous to the method devised by Verschoor & Wiegers (1961), this is achieved by making use of the high negative temperature coefficient of resistance of a thermistor (≡ N.T.C. resistor). The thermistor ((1) in Fig. 1) is situated a few mm below the top of the boiler vessel; it forms part of an on-off thyratron control circuit (Sturtevant, 1959). The circuit is shown diagrammatically in Fig. 2(*a*). It was developed from that published by Philips Nederland N.V. (1962); the sensitivity of the system was enhanced by the addition of an A.C. amplifier.

The resistance of the thermistor decreases with falling liquid-nitrogen level. At a given value of the resistance a magnetic valve *V* (Figs. 1 and 2) is closed; in a short time the vapour pressure, building up in the Dewar vessel, forces the liquid nitrogen through the siphon until the level reaches the thermistor and the valve opens again. A second thermistor, situated at half height, and an extra electrical unit (Fig. 2(*b*)) were added for safety. If for some reason the liquid level in the adaptor becomes inadmissibly low, the level regulator is switched off while *V* opens and an alarm is activated. At the same time the power supply to the X-ray tube and to the Weissenberg equipment may also be cut off automatically. As safeguard against power failure the valve *V* is of a type that opens when the current is off.

Some care must be exercised in choosing suitable thermistors.* Most industrial types have resistances of the order of 10–10^3 megohm in liquid nitrogen (Sachse, 1958). Such high values are inconvenient, however, for stray leakage resistances between the terminals, caused by gradual icing, were found to interfere with the normal operation of the switching system. No difficulties were experienced with resistances of about 1 megohm at −196 °C.

The thermistor should carry sufficient wattage, relative to its dissipation constant in air, to ensure that its temperature rises a little above ambient by self-heating as soon as the liquid level falls below the mark (see below).

Measurement of temperature

The temperature of the cold gas stream is monitored continuously by means of a chromel–alumel thermojunction connected to a chart-recorder. The thermocouple is housed in the delivery tube, about 4 mm from the exit point; the wire leads (Philips Thermocoax) run through the length of the tube to the stopper of the funnel. No correction for heat conduction

* *Note added in revision.* Mr C. P. Gerhardt and the author recently found that ordinary miniature germanium diodes (*e.g.* Philips OA 92; the forward resistance of several specimens tested was of the order of 1000–4000 ohms in liquid nitrogen) can be used as temperature sensing elements in place of thermistors. A second diode, which remains at room temperature, should then be connected antiparallel to the terminals of the cold diode. Since electronic switching systems working on this principle are now being applied in other fields of low-temperature research as well, a complete wiring diagram will be described elsewhere (Gerhardt, Kroone & Altona, 1964).

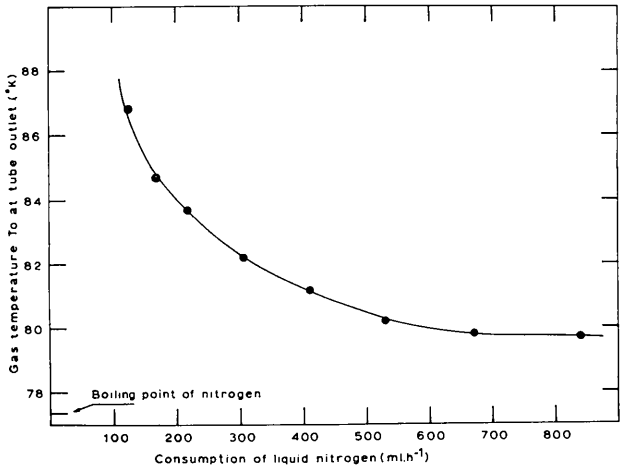

Fig. 3. Gas temperature (T_0) at the outlet of the delivery tube *versus* consumption of liquid nitrogen.

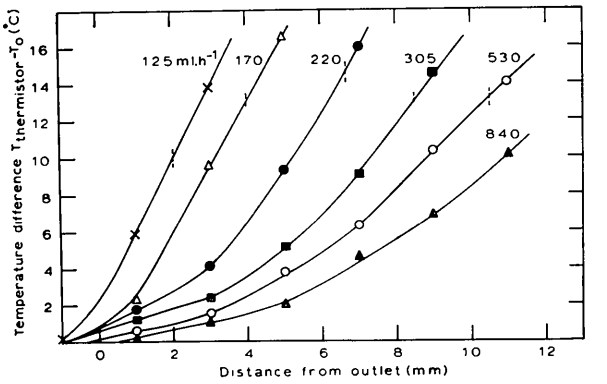

Fig. 4. $T_{\text{thermistor}}-T_0$ as a function of distance (S) from the tube outlet for various rates of boiling (B) of liquid nitrogen. T_0 is the gas temperature at the outlet of the delivery tube.

through the leads is needed, since the temperature gradient along the tube is too small to exert any effect. For the same reason we may safely assume that the temperature at the exit point is equal to that indicated by the thermocouple. A plot of gas temperature *versus* the consumption of liquid nitrogen is shown in Fig. 3.

The temperature of a small body, placed in the cold stream at a distance from the outlet, was also measured. The method employed closely imitated the cooling of a real crystal specimen: a selected miniature thermistor bead (Philips, type B 8320 04P/1 K, with the glass envelope and most of the terminals removed) was mounted upon a glass capillary by means of a little dental cement; a few centimetres of thin (30 μ) constantan wire leads were fused on and stretched parallel to the capillary. The conduction of heat through these leads and the support, and also the electrical energy dissipated in the thermistor, were considered to be negligible as compared with the effect of heat radiation to the thermistor assembly from its surroundings. The latter means of heat gain was of the same order of magnitude as that calculated by Robertson (1960) for a crystal specimen of 1 mm^3 dimensions (0·8 mcal.s^{-1}).

The resistance R of the thermistor was calibrated against a series of thermocouple readings at a high rate of use of liquid nitrogen (700 ml.h^{-1}). At this rate of use no temperature gradient could be detected between the points $S=+1$ mm and $S=-1$ mm, *i.e.* one mm outside and inside the delivery tube (Fig. 4). For safety, the calibration was carried out with the thermistor placed at $S=-1$ mm. We assume, then, that there is no temperature difference between the thermistor and the thermocouple under these conditions.

A plot of ln R *versus* T^{-1} was approximately linear between 77 °K and 100 °K; the value of R and the temperature coefficient of resistance at 80 °K were 350 megohms and $-8{\cdot}1\%$ deg.$^{-1}$, respectively. The error in the thermocouple readings amounted to 0·5–1 °K; by means of the thermistor small changes in temperature could be measured within $\pm 0{\cdot}2$ °K. A plot of the difference between the temperature of the thermistor and the temperature of the gas at the tip of the delivery tube *versus* distance S from the outlet is shown in Fig. 4. We note that, especially at a low rate of boiling, the temperature of the thermistor specimen rapidly increases with increasing distance; under these conditions the 'cooling power' of the gas stream (Robertson, 1960) seems to be insufficient to overcome the heat gain by radiation. At high rates a slow rise in temperature is observed that is perhaps caused by gradual mixing with ambient warmer gas. The thermal time constant of such a thermistor assembly is very small (a 1 degree step change in gas temperature is indicated in less than 0·1 s) and rapid fluctuations can be detected easily. The temperature of the gas stream is extremely constant (to $\pm 0{\cdot}1$–$0{\cdot}2$ °K) for the running conditions specified below. At greater distances from the outlet the amplitude of the fluctuations suddenly increases; the dotted vertical lines in Fig. 4 indicate the approximate point where, measured over a period of 15 min, the maximum deviations from the mean value exceed $\pm 0{\cdot}5$ °K.

It may seem that there is a contradiction between: (*a*) The constancy of the gas stream at the exit point during the whole of the refilling cycle, and (*b*) The requirement that, for the operation of the automatic filling process, the temperature of the thermistor should rise when the liquid nitrogen level falls. However, it is not so much the temperature difference between the liquid and the gas directly above the liquid, as the change in heat dissipation with changing medium on which the thermistor reacts (see previous section).

From Figs. 3 and 4 the temperature of the specimen can be estimated for a given rate of boiling B of liquid nitrogen and at a chosen distance S from the

point of exit. At 60% relative humidity (20 °C) of the laboratory air slight condensation of moisture is observed upon the layer-line screens when $B \geq 220$ ml.h^{-1}; at this rate and at $S=2{\cdot}5$ mm the temperature is $87 \pm 0{\cdot}5$ °K. Built-in heaters (Viswamitra, 1962), in our case a few turns of Thermocoax heating wire* on the inside of the screens, provide the means to run at much higher speeds without difficulty (*e.g.* $T = 81 \pm 0{\cdot}5$ °K at $S=2$ mm and $B=550$ ml.h^{-1}). Higher speeds are especially important when it is desired to record a complete sequence of upper layer-lines by the equi-inclination method (Buerger, 1942) at a constant temperature. For large inclination angles the minimum possible distance between the gas outlet and the specimen is necessarily large, and the rate of boiling must be increased accordingly (*e.g.* at an inclination angle of 40°, $S_{\min}=7$ mm, and $B=530$ ml.h^{-1} for $T=87$ °K). Of course, at such large distances the gas jet and the specimen should be accurately aligned.

Performance and future development

The apparatus described above has now been in routine operation for six months. It requires only scant attention, and a constant ($\pm 0{\cdot}5$ °K) specimen temperature well below 90 °K can be maintained over almost indefinitely long periods. Continuous cooling runs up to 140 h were completed successfully. Both prolonged exposures with Mo $K\alpha$ radiation and complete sequences of equi-inclination photographs with Cu $K\alpha$ radiation were made, the latter by means of the split-cassette technique (Steinfink, Ladell, Post & Fankuchen, 1953). Weissenberg photographs of excellent quality were obtained. They were characterized by low background density, even on heavily exposed films (filtered Cu $K\alpha$ radiation), and by sharpness of the reflexions up to the edge of the films.

A few minor difficulties must be mentioned here. First, excessive cooling of the goniometer head may cause slight warping of metal parts with attendant misalignment of the crystal. This effect can be avoided by mounting the crystal specimen in the tip of a relatively long (>15 mm) capillary tube and by covering the exposed parts of the goniometer head with a piece of aluminum foil. Secondly, thin wafers of ice may accumulate around the outlet. Touching with a copper wire will remove these instantaneously.

Fitting the adaptor into its correct position on the Weissenberg goniometer takes only a minute or so. Within 10 min of starting operations the temperature drops below 90 °K. The siphon must be removed now and then for filling of the storage vessel; this takes a few minutes and does not interfere with the regular flow of cold vapour upon the specimen.

The adaptor functions equally well if the side arm is tilted to 45° from the horizontal plane. Therefore, a similar apparatus constructed with an angle of 45° between boiler and delivery tube can be used with the tube in the horizontal as well as in the vertical position. When the cold gas flows into the open air, *e.g.* when the apparatus is applied to some other diffraction techniques, an outer sheath of dry gas is necessary (Post, Schwarz & Fankuchen, 1951; Robertson, 1960).

With some modifications the adaptor can perhaps be used for X-ray diffraction at liquid-hydrogen temperatures. The leakage of heat into the boiler vessel (2·7 W) is less than half of that reported for a successful liquid-hydrogen cryostat (Robertson, 1960). Immersion of the entire reservoir in liquid nitrogen is perfectly feasible and would minimize the heat leakage. Some experiments in this direction are being planned.

This project was carried out under the supervision of Dr C. Romers. I wish to thank Prof. E. Havinga for his constant interest. I am indebted to Prof. J. J. M. Beenakker, Kamerlingh Onnes Laboratory, and to Dr J. H. Robertson, University of Leeds, for stimulating discussions. Dr G. A. Wiegers, University of Groningen, kindly supplied valuable information concerning level-sensitive devices. Parts of the apparatus were constructed by Messrs. C. J. van der Poel and L. Kroone of this laboratory.

* Philips Bedrijfsapparatuur Nederland N.V.

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