J. SCI. INSTRUM., 1967, VOL. 44

A glove-box and drying system for the manipulation of moisture sensitive materials

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MS. received 30*th March* 1967, *in revised form* 18*th May* 1967

Abstract. This note describes a system for the provision of a working 'atmosphere' in a commercially available glove-box. Air is pumped out of the box, chilled, passed through a column of cooled molecular sieve, and returned to the box. The air-lock of the box can be treated separately allowing the removal and introduction of equipment while maintaining dry conditions in the main compartment. Pressure in the box is controlled by foot switches operating electromagnetic valves. A device for the measurement of frost-point is described by means of which it has been shown that the frost-point of the air in the box is less than $-90°C$, corresponding to a moisture content of 10^{-4} mg l^{-1} (approximately 0·1 p.p.m.). Transfer of items from the laboratory to the working chamber is simple and rapid, the air-lock requiring about 15 minutes for operation.

1. Introduction

The system described was developed for work with compounds which are hygroscopic and decomposed by water but it should be applicable whenever manipulations or measurements have to be done in an intensively dried 'atmosphere'. In the present context we are concerned only with atmospheres having frost-points of less than $-60°C$ (moisture content 0·007 mg l^{-1} corresponding to 0·05% r.h. at room temperature).

The drying of the air in a large chamber is accomplished very slowly by the simple means so frequently adopted of imtroducing a quantity of desiccant and the procedure results in the occupation of working space by the desiccant container. The frequent removal or introduction of objects is quite inpracticable because of the time taken by the system to come to equilibrium by diffusion. Even when a stream of dry gas is introduced the process is slow and unsuited to work requiring frequent transfers. Williams and Park (1960) have described a glove-box system that uses a stream of dry nitrogen and they quote 10 weeks as the time taken to reach an estimated frost-point of $-60°C$. An evacuable glove-box of adequate size is the ideal solution but such a box is not available as a standard product. The best compromise is to pump out the air, dry it, and return it to the box in a continuous cycle. The equipment built by the author for carrying out work in dry conditions is based on a commercially available glove-box manufactured by the South London Electrical Company. It is a welded steel box with standard U.K.A.E.A. pattern glove ports. It is joined by a gas-tight sliding door to an air-lock fitted with an access door for the transfer of objects from the laboratory into the main chamber or vice versa. Because the box is of inadequate strength for evacuation, the air is dried by circulation through a drying system. The bulk of the water is removed from the air by being passed through a cooling device, the cooled air being then put through a drying column and returned to the box.

2. The drying agent

The qualities required of a drying agent are high capacity, low water-vapour pressure at equilibrium and chemical stability. Laboratory drying agents have been thoroughly discussed by Dodd and Robinson (1957) and all of them have some disadvantages. The agent selected for the present work was a molecular sieve (Union Carbide type 5A). The molecular sieves are probably the most useful of all drying agents and their uses and properties have been outlined in a handbook (British Drug Houses Ltd. 1965) containing many references. Adsorption and regeneration characteristics of molecular sieves have been investigated in more detail by Steinberg and Rohrbrough (1965). The ultimate frost-point obtainable by the use of molecular sieves at a bed temperature of $-20°C$ is about $-110°C$, where the vapour pressure of ice is approximately 10^{-6} torr.

3. The drying system

The circulating system is shown in figure 1. The extension C to the air-lock B was provided to allow the lock to be used with items of the full effective length of the main chamber A. The pump G used was a normal oil-immersed, rotary vacuum pump with a built-in non-return valve. It withdrew air from the main chamber A or the lock B depending on which of valves V_1 and V_2 was open. The air then passed through

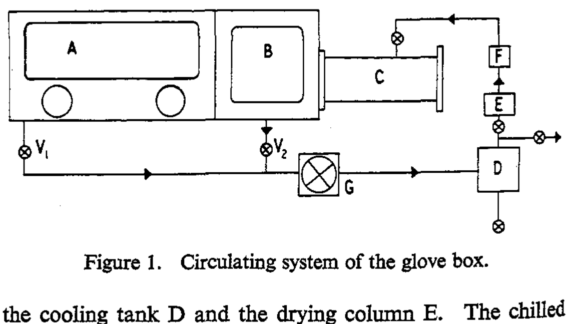

Figure 1. Circulating system of the glove box.

the cooling tank D and the drying column E. The chilled air was then warmed up to room temperature by the electric heater F and returned to the glove-box by way of the extension C. When the internal door was closed, V_1 closed and V_2 open, circulation was restricted to the air contained in the lock allowing rapid drying of freshly introduced air.

Figure 2 shows the construction of the cooling apparatus. The requirements were for a device having low resistance, large active area, freedom from blockage by ice and ease of

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removal of trapped water. A number of designs were tried and rejected before a satisfactory one was developed. The inner container held a mixture of alcohol and crushed, solid carbon dioxide. The air passed through the space between the inner and outer containers. After a few weeks of use, the accumulated water and any oil carried over from the pump were drained off. The whole unit was lagged and mounted in a wooden chest fitted with a sliding lid.

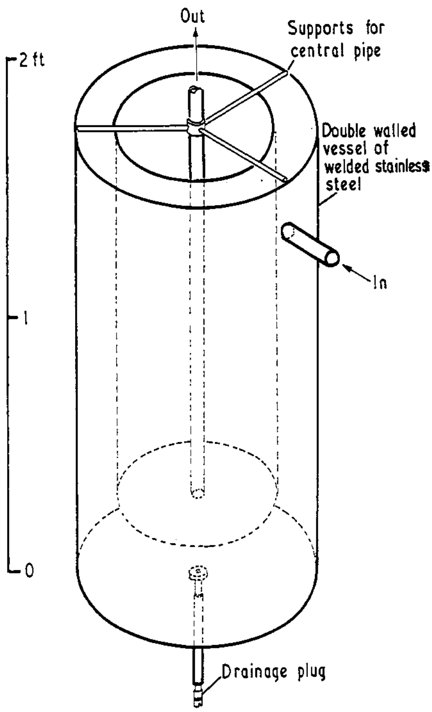

Figure 2. Cooling tank.

The drying column E, a brass tube two feet long and three inches in diameter, contained the molecular sieve pellets packed between circular pieces of cotton cloth supported on wire gauze to guard against the movement of dust arising from the molecular sieve. The column was lagged to allow the air stream to cool it, and normally reached a temperature of about −25°c at its top flange. To prevent the rest of the equipment being cooled, the air was warmed on emerging from the drying column, the heater F consisting of an electric heater mounted inside a brass canister. All the components were fitted with screwed vacuum unions and joined by copper pipes.

The pressure in the box was kept at slightly above atmospheric to minimize the effects of any undetected leaks. Pressure was maintained by the passage of argon purified by being passed through a column of molecular sieve M (figure 3) followed by a column of titanium sponge L heated to 850°c (Mallet 1950). The effluent gas was discharged through glass bubblers K_1 and K_2 containing di-butyl phthalate. These sealed the outlets against back-diffusion and acted as sensitive pressure indicators.

A pair of full-length, sleeved, glove-box gloves has considerable volume and the insertion or removal of the hands is accompanied by changes in pressure sufficiently great to hinder either operation. To enable the hands to be inserted or removed quickly, the glove-box was fitted with two electromagnetic valves H_1 and H_2 operated by conveniently placed footswitches. H_1 allowed the rapid introduction of gas to aid withdrawal of the hands and H_2 was a pressure release valve to assist their insertion. These two valves make a considerable contribution to the convenience of the system. The gas introduced was purified argon which was stored at 15 lb in^{-2} in an evacuable tank T of about 10 l. capacity provided with a manometer. This gas supply was provided for general experimental work and was used with other equipment but the purification system and storage tank described were incorporated in the dry-box system for convenience.

4. The performance of the drying system

The measurement of low humidities is extremely difficult and the treatise by Gregory and Rourke (1957) on hygrometry suggested no method suitable for routine measurements. Nevertheless, the two most important properties of the system have been evaluated. These are the normal equilibrium humidity in the glove-box and the time taken for the air in the lock to reach an acceptable humidity. For assessment purposes a frost-point of −60°c was adopted as being acceptable after the outer door has been open. Humidity was estimated by the observation of frost-point; the apparatus used is shown in figure 4. The horizontal copper part was brazed into the vertical copper rod and into the stainless-steel tube. The thin-walled tube acted as a thermal insulator between the copper and the mounting flange which was fitted with a Neoprene gasket and bolted on to the rear wall of the glove-box. The thermocouple inlet hole was drilled to within 0·01 in. of the front surface which was highly polished.

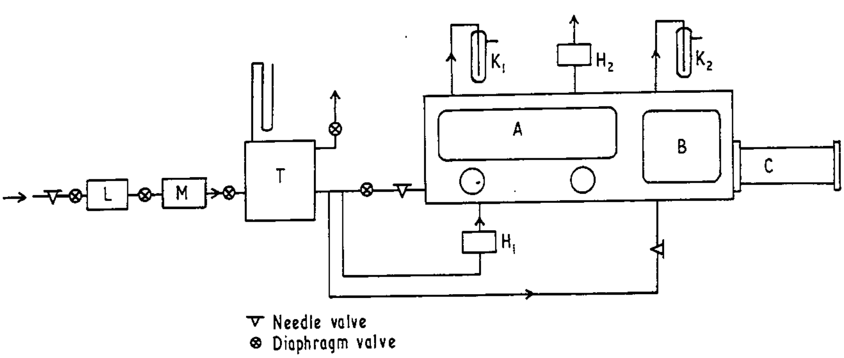

Figure 3. Gas flow and pressure control system.

When a measurement was to be made the copper rod was immersed repeatedly in liquid nitrogen and the polished face watched through the glove-box window for the formation of frost or dew. The temperature of the copper face was measured to ±1 degc by means of a copper–constantan thermocouple, whose cold junction was in the liquid nitrogen, and a potentiometer. Visual observation proved to be unreliable presumably because of the formation of glassy ice which is difficult to observe, so an automatic indicator was arranged using a cadmium sulphide photocell. The light from a galvanometer projector was reflected from the copper on to the photocell and a minute reduction in light intensity caused a sensitive relay to switch on an indicator light. The temperature was then read. Results were rarely reproducible within 10 degc.

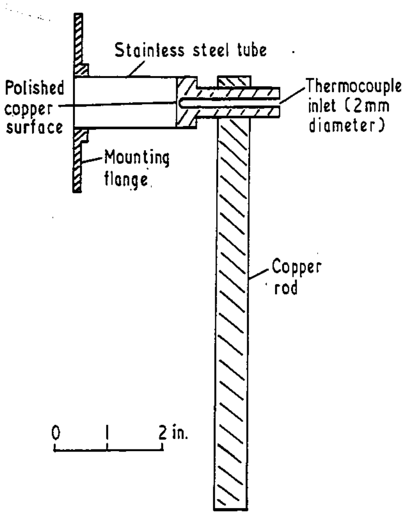

Figure 4. Device for the observation of frost-point.

The thermocouple wires were only of 0·005 in. diameter and they passed through a twin-bore, recrystallized-alumina sheath of outside diameter 2 mm in the centre of a thick copper rod (figure 4). The temperature at any point on the wire enclosed in the copper would correspond very closely with that of the surrounding copper and this would be true of the wires at the junction. The arrangement tends to eliminate errors arising from thermal conduction along the wires. The difference between the temperature of the thermocouple junction and that of the polished copper face could not have been greater than 0·1 degc. Poor reproducibility was caused by lack of sharpness in the formation of visible frost under the conditions used.

After the air in the box had been re-circulated for 3 days, the frost-point was below −90°c corresponding to a moisture content of 10^{-4} mg l^{-1}. (approximately 0·1 p.p.m.).

15 minutes was found to be a reasonable period for operation of the air-lock. The observations served to show that the system worked well and they acted as a guide to the permissible speed of operation of the air-lock but were not pursued because of their obvious lack of accuracy and the unreasonable time required to make them.

After this work had been completed King (1965) described an accurate and simple method of humidity measurement based on the change of resonant frequency of a quartz oscillator crystal when a film of moisture is adsorbed on to it. The minimum detectable moisture content is 0·1 p.p.m. and a measurement can be made in a few minutes The simplicity of the method, its speed, and the convenience of remote reading make King's piezoelectric hygrometer an obvious choice for inclusion in a dry-box system for routine measurements.

Thanks are due to the University of Glasgow for a Research Studentship held during this work.

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