

A Glove Box System for the Manipulation of Air Sensitive Compounds

The growth of organometallic chemistry over the past ten years and the subsequent necessity of handling air sensitive compounds has resulted in a need for the development of new handling techniques. While some manipulations of air sensitive compounds can be successfully carried out on the bench top using Schlenk tube techniques or on a vacuum line, numerous manipulations (e.g., preparation of mulls for ir spectra, filling of X-ray capillary tubes, filtration of extreme air sensitive compounds, etc.) require the use of an inert atmosphere glove box.

Glove boxes are available on the open market today that are considerably better than the home-made plywood and Plexiglas boxes that were in general use until about ten years ago. More recently, recirculating systems have become available from glove box manufacturers; however, these systems are quite expensive (in some cases more than 200% greater than the cost of the glove box). After considerable experimentation over a number of years with several glove boxes and recirculating systems, we have arrived at what we believe to be an excellent glove box system for handling air sensitive compounds¹. Our conclusions are based on cost of construction of the system, ease of operation, maintenance, and efficiency of oxygen removal. Since we have been asked so many times to provide details of parts of the system, we have now taken the time to provide details of the entire system so that anyone might take advantage of some hard won experience.

Pioneering work on glove box recirculating systems was carried out by T. L. Brown and coworkers^{1,2}. They coated vermiculite with manganese oxalate ($MnC_2O_4 \cdot 2H_2O$) and packed the dry material in a glass column. The glass column was then heated to 350°C in a H_2 atmosphere to generate green manganese oxide (MnO). Green MnO is very active toward oxygen turning brown (Mn_2O_3) as an indication of its reaction. The Mn_2O_3 is then regenerated to the green MnO by reaction with H_2 at 350°C. A molecular sieve was used to remove H_2O and any organic vapors recirculating through the system in order to prolong the life of the manganese oxide columns. The system to be discussed in this paper is somewhat similar to that used by Brown, but with a number of modifications and changes. The following are the details of the assembly and maintenance of the glove box and attendant recirculating system which we have found most effective in our work.

Glove Box and Recirculating System

A general schematic drawing of the glove box and recirculating system can be seen in Figure 1. The important features of the system which shall be discussed separately are: glove box (A) and entry port (B); Dry Ice-acetone traps (C); recirculating pump (D); oxygen scrubber (E); entry port evacuation system (H, G, and F).

It is important to notice the sequence of the Dry Ice-acetone traps, recirculating pump, and oxygen scrubber. The Dry Ice traps, if placed after the recirculating pump, can become plugged with frozen solvent resulting in evacuation of the glove box. If the Dry Ice traps are placed after the oxygen scrubber, the scrubber will become pressurized resulting in a violent release of the ground glass joint at the top of the scrubber. When the stopper is re-

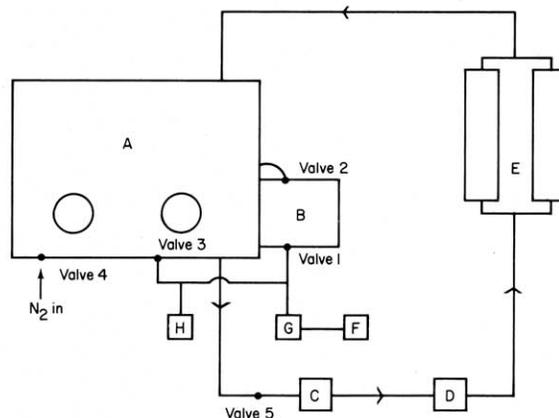


Figure 1. Schematic of recirculating system. A. Glove box, B. Entry port. C. Dry Ice-acetone traps. D. Recirculating pump. E. Oxygen scrubber. F. Vacuum pump. G. Liquid nitrogen traps. H. McCleod gauge.

leased so also are the contents of the scrubber. For this reason the Dry Ice-acetone traps (C) are placed between the glove box (A) and the recirculating pump (D).

Connections between the various parts of the system are made with $\frac{3}{8}$ -in. copper tubing using flair fittings. Glass to metal connections are made using heavy wall rubber tubing as a sleeve.

Glove Box and Entry Port

There are a number of glove boxes on the market today. Our own experience is that we have found the Vacuum Atmospheres glove box (model H3-43) to be excellent³. This glove box is superbly engineered and it is easy to maintain a good atmosphere. Unlike other glove boxes which develop leaks in the gasket system used to interface the six sides of the box, the Vacuum Atmospheres glove box is free of such problems. An important feature in maintaining a good atmosphere is the entry port. The entry port on the Vacuum Atmospheres glove box is rounded with autoclave type doors and "O" ring gaskets. This type entry port minimizes leaks through the doors. Connection to the nitrogen source, the recirculating system, and the vacuum system are made through threaded openings in the rear of the box. The connection is made with a $\frac{1}{2}$ -in. brass fitting using a flair connection to the copper tubing. Butasol Rubber gloves⁴ (\$30 per pair) should be used to minimize diffusion of air and water through the gloves. These are special high sulfur impreg-

¹ For a detailed discussion of glove boxes see, Shriver, D. F., "The Manipulation of Air Sensitive Compounds," McGraw-Hill Book Co., New York, 1969, p. 164.

² Brown, T. L., Dickerhof, D. W., Bafus, D. A., and Morgan, G. L., *Rev. Sci. Inst.*, **33**, 491 (1962); Private Communication ECA to T. L. Brown.

³ Vacuum Atmospheres Corp., 7356 Greenbush Ave., North Hollywood, California 91605.

⁴ Charleston Rubber Co., 158 Stark Industrial Park, Charleston, South Carolina.

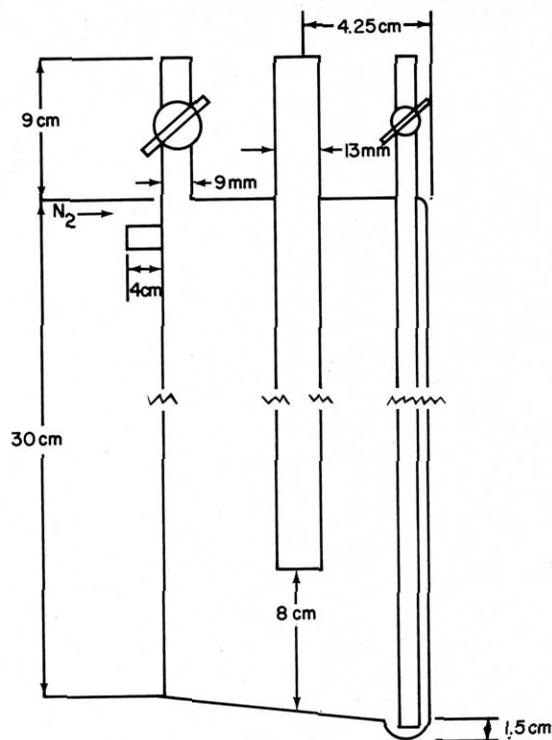


Figure 2. Dry Ice-acetone trap. Stopcocks are 4 mm glass bore.

nated gloves designed for low permeability. If broken, the windows on the box can be replaced by auto safety glass. The cost of the basic Vacuum Atmospheres box is approximately \$2300 (includes basic box, gloves, shelves, and light).

Dry Ice-Acetone Traps

The Dry Ice-acetone traps used in this system are shown in Figure 2. The traps are immersed in a 4-qt Dewar flask filled with Dry Ice-acetone. The purpose of these traps is to remove solvent and water vapor from the box atmosphere. The box atmosphere flows into the upper left hand side of the trap. It then exits through the tube in the center of the trap. Since water and solvent are frozen out in the trap a reverse flow could cause the center tube to become blocked. The solvents which collect in the trap are removed by allowing the trap to warm to room temperature and then flushing out the liquid with nitrogen. This is done by running a nitrogen line to the stopcock in the upper left hand corner of the trap and an exit line (Tygon tubing) from the stopcock in the upper right hand corner of the trap to an Erlenmeyer flask. Valve 5 (see Figure 1) is then closed and the two stopcocks opened. The nitrogen is then turned on and the liquid flushed into the Erlenmeyer flask. The nitrogen is then turned off, both stopcocks closed and then valve 5 opened. In order to provide more efficient solvent removal two traps are used in series. These traps should be flushed once a week.

Recirculating Pump

The atmosphere next flows to the recirculating pump shown in Figure 3. The atmosphere flows through the Hoke valve, a gas filter, and flow gauge. The gas then goes through the tubing to the pump (Little Giant Pump⁵, model 13152; cost \$89). The pump forces the gas into the can and out. The Hoke valve is used to adjust the flow rate. The gas filter and flow gauge come with the pump. The can is a 5-gal Fisher solvent can with top removed.

Figure 4 shows a drawing of the pump can lid. The plate can be made of steel or aluminum and is $\frac{5}{16}$ in.

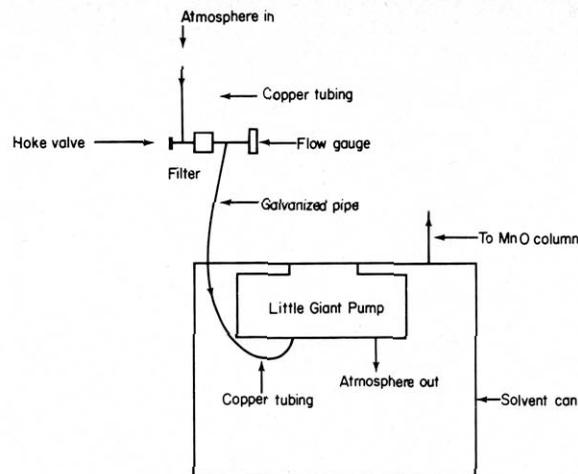


Figure 3. Recirculating pump assembly.

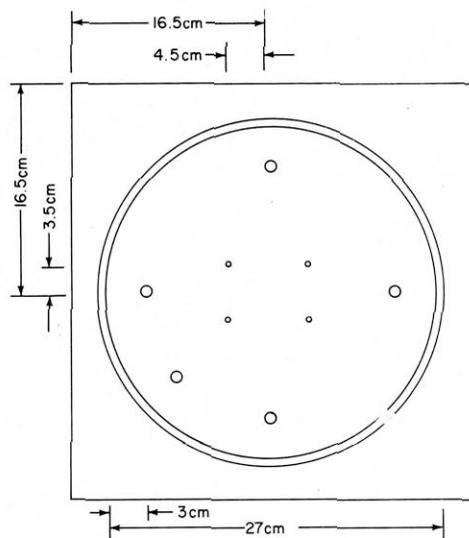


Figure 4. Pump can lid.

thick. The outer groove shown in the drawing is $\frac{1}{4}$ in. across and $\frac{3}{16}$ in. deep. It is approximately 27 cm in diameter but this diameter will have to be fitted to the individual can used. The can is sealed to the lid by filling the groove with epoxy cement and forcing the rim of the can into the groove. The four circles in the middle are for attaching the pump to the lid. The five outer circles are for the atmosphere inlet and outlet, the wiring to the pump, a pressure gauge, and a pressure release valve. The atmosphere inlet is the $\frac{1}{2}$ -in. galvanized pipe in Figure 3. This is screwed through the lid and a brass fitting for $\frac{3}{8}$ -in. copper tubing attached to it. Copper tubing can then be used to connect the pipe with the pump itself. The exit hole for the wiring should not be threaded. The pressure release valve could be a simple needle valve. These connections to the lid should be covered with epoxy cement to prevent the pump assembly from leaking.

Oxygen Scrubber

The atmosphere now flows to the oxygen scrubbing columns shown in Figure 5. These columns are basically those described by T. L. Brown and coworkers² with some modification. There are two columns arranged in parallel so that one column can be regenerated while the other is being used.

The atmosphere should flow in through the T-bore stop-

⁵ Gelman Instrument Co., Ann Arbor, Michigan.

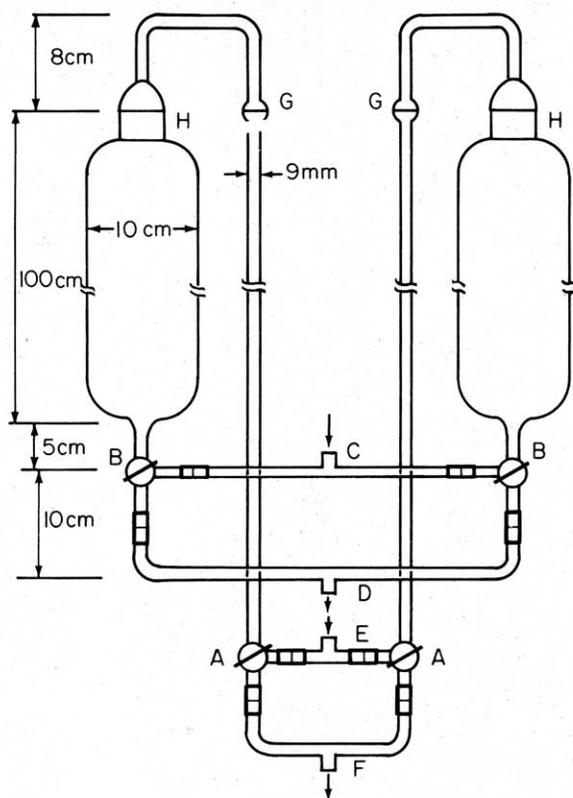


Figure 5. A. Stopcock A, 4 mm bore. B. Stopcock B, 4 mm bore. C. Atmosphere in. D. H₂ out. E. H₂ in. F. Atmosphere out. G. Ball joint 20 mm diameter. H. $\frac{5}{16}$ 55/50 Joint.

cock B and out through T-bore stopcock A. When the columns are regenerated the hydrogen should flow in through stopcock A and out through stopcock B. This is so that the water formed during regeneration of the column will not condense in the upper parts of the column.

The actual scrubbing agent is MnO deposited on vermiculite as the solid support. The packing material is prepared in the following way. A volume of vermiculite equal to 2½ volumes of a column is sifted to remove any excess dust which may clog the lines. The extra ½ volume of a column is for any settling that may occur during mixing. The vermiculite is then dampened with water, and 1200 g of MnCO₃ (600 g/column) is added slowly to the wet vermiculite with thorough mixing. A piece of glass wool is then placed in the bottom of each column, and the column is filled with the coated vermiculite. This packing is then covered with glass wool. The column is then regenerated by heating slowly under N₂ purge to remove the water and CO₂. The voltage is then stepped up periodically to 100 V, and then the purge gas is changed to H₂ to generate the column. The packing will turn green when MnO is generated. When the column has turned brown from oxygen exposure, it is regenerated by passing H₂ through the column heated to 350°C until the packing has turned green again. If the box atmosphere is good, the columns should need regenerating only once every 1-2 weeks. The column packing should be changed about once a year.

In order to fabricate the column so that it can be heated, the column is wrapped with asbestos cord in a right hand helix and then with 22 gauge Chromel A wire (Curtin Scientific; ¼ lb; \$6.95) in a left hand helix allowing 1.5 in. between each spiral. The wire should not touch the glass since this will cause the glass to crack after a few regenerations. The column is then wrapped with successive layers of asbestos paper, glass wool, another layer of asbestos paper, and finally aluminum foil. The wrapping may then be held in place by wire or asbestos cord. The Chromel wire is then connected via a crimp and eyelet

connection to normal electrical wire. This can then be plugged into a Variac. The bare Chromel wire can be covered with small sections of glass capillary tubing. Two holes, 1 in. in diameter, should be made near the ends of the column through the layers of wrapping to observe the color change in the packing. The Variac setting to get a temperature of 350°C then can be determined by simply inserting a thermometer into the wrapping.

Entry Port Evacuation System

The entry port evacuation system consists of a liquid nitrogen trap and a mechanical vacuum pump. A Welch-Duo Seal Vacuum pump model 1405 is satisfactory. The liquid nitrogen trap is connected to the pump via a heavy wall vacuum tubing connection to a 25-mm side arm. The trap is then connected to the entry port via a 25-mm tube at the top of the trap. A 9-mm side arm is used to connect the trap to a McCleod gauge (H) and a vacuum outlet in the drybox itself. All connections should be securely clamped with ring clamps.

Operation of the Glove Box

After the glove box and recirculating system have been assembled it is necessary to purge the system before use. The glove box itself can be purged by simply opening the nitrogen source (Valve 4, Figure 1) and the vacuum source, Valve 1. The purge can then be regulated with Valve 4 to insure that the box is neither evacuated nor overly pressurized. This can be easily monitored by simply watching the gloves. The box should be purged for approximately eight hours. The recirculating system itself can be purged by turning it on as the box is being purged. The atmosphere in the traps and pump can be vented through the hydrogen exit lines by adjusting the T-bore stopcock B (Figure 5) (in order to avoid regeneration of the column until the system has been thoroughly purged). To assure the maintenance of a good box atmosphere, the recirculating system should be run continuously.

The day to day operation of the glove box consists mainly of bringing glassware and solutions into the glove box via the entry port. If glassware alone is to be taken into the box the following procedure is recommended. The glassware should be dried either by placing in a drying oven or by heating with a burner. When the glassware is dry it is placed in the entry port and the outer door closed. Valve 1 (Figure 1) is then opened and the port is evacuated to a pressure of 25 μ. This generally takes approximately 15-20 min. When the port has been evacuated, Valve 1 is closed. The port is repressurized with box atmosphere by opening Valve 2. To maintain atmospheric pressure in the box, nitrogen is bled into the system through Valve 4. When the port is repressurized the inner door may be opened and the glassware brought into the box.

If solvents are to be brought into the box the following procedure should be followed. The solutions are placed in the entry port and the outer door is closed. The port is then flushed with box atmosphere by opening Valves 1 and 2. The pressure in the box is then maintained with nitrogen via Valve 4. The nitrogen flow from Valve 4 should be adjusted so that the gloves hold steady. The port should then be flushed for 10-15 min. When the flushing is complete the valves should be closed in the order of 4-1-2.

Conclusion

The system described has been found to be excellent for carrying out studies involving extremely air sensitive compounds. If the system is properly maintained a working atmosphere of 5-10 ppm of oxygen and water can be maintained.⁶

Acknowledgment

We would like to express our gratitude to Dr. Roy Duke (Marathon Oil Co., Littleton, Colorado) and Dr. J. R. Sanders (Celenese Corp., Charlotte, N. C.), two former students, for their contribution in the early development of the present glove box system. Also we would like to thank the National Science Foundation for support of all

of our organometallic work for which this glove box system was developed.

⁶ When the glove box atmosphere was allowed to recirculate for 24 hr without using the box, the atmosphere was 1–2 ppm oxygen as determined by an oxygen detector. Triethylaluminum does not fume on pouring from one beaker to another and an exposed light bulb filament lasted 8 da without burning out.

