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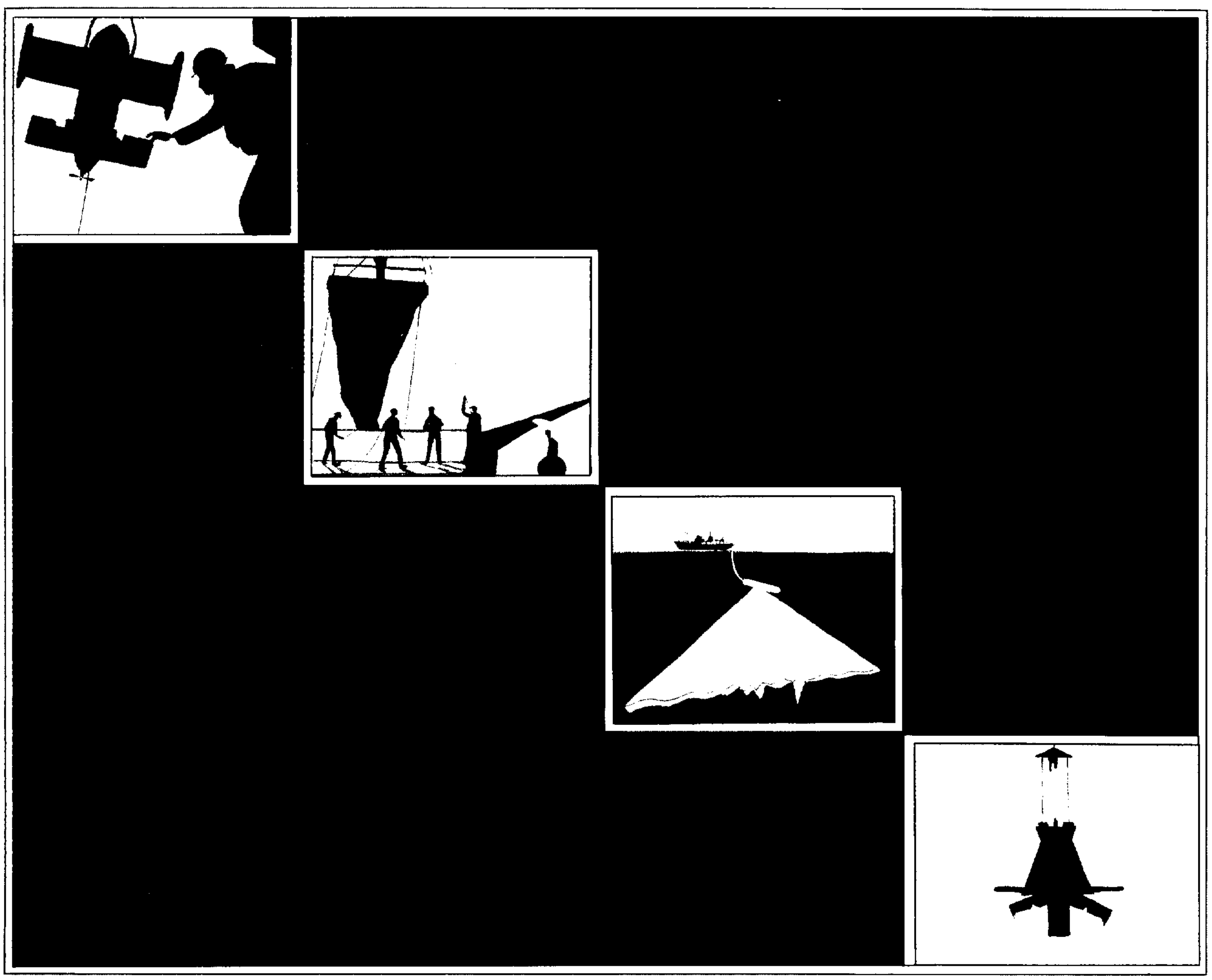
Chemical tracer studies at IOSDL - 1

D Smythe-Wright

Report No 274 1990



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The Design and Construction of Analytical Equipment for the measurement of chlorofluorocarbons in seawater and air

D Smythe-Wright

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ABSTRACT

The Institute of Oceanographic Sciences, Deacon Laboratory, has recently built specially designed equipment for the shipboard measurement of Chlorofluorocarbons in seawater and air. The analysis depends on a purge and trap technique followed by electron-capture gas chromatography. Details of the design and construction of the equipment are given together with information regarding the analytical principle.

IOSDL Report No 275, Chemical Tracer Studies at IOSDL, II. Method manual for the routine shipboard measurement of chlorofluorocarbons in seawater and air gives information about the use and maintenance of the equipment.

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1. INTRODUCTION

The Institute of Oceanographic Sciences, Deacon Laboratory (IOSDL) has recently become interested in using chemical substances with known histories of production or release into the environment as indicators of physical oceanographic processes. The use of such tracers has increased in popularity with physical oceanographers in recent years because unlike more conventional techniques the tracers provide a time frame on which the rates of processes can be estimated.

The tracers enter the ocean from the atmosphere in given temporal and areal patterns. From the surface they spread into the ocean's interior like a dye that follows oceanic circulation and mixing. Tracer information complements basic temperature and salinity data in a unique way, because a tracer survey gives a snapshot of the 'dye' and this represents the water flow and mixing integrated with time. It is the tracers' ability to provide a time dimension which makes them uniquely helpful in determining for example, large-scale integrated mean circulation on one hand to short-term transport and mixing on the other. Tracers are particularly important tools when defining the extent, rate and variability of water mass sources and modification processes.

The tracers fall into two categories: those which require in excess of 100 litres of sample for analysis and those which can be measured from small volume (i.e. 10 litre) samples. Sampling large volumes of water poses problems not only with logistics of handling but also because of the time required to collect such samples routinely. For this reason small volume sample tracers which can be measured using relatively modest cost analytical equipment are far more appealing. A number of compounds have been used for such studies; the most popular are the chlorofluorocarbons CFC-11 and CFC-12 because of the relative ease and low cost involved in carrying out the analysis.

Chlorofluorocarbons are totally man-made substances first manufactured in the 1930s for use in refrigeration, air conditioning and as industrial solvents and blowing agents. They are particularly volatile and have quickly spread into the atmosphere causing exponentially increasing concentrations throughout both hemispheres over the last 50 years. Because of different production rates CFC-12 concentrations increased more rapidly (see Figure 1). It is the ratio of one CFC concentration to the other which forms the basis of the CFC tracer technique.

When a water mass comes in contact with the atmosphere at the sea surface it takes about one month for it to reach equilibrium with the overlying atmospheric CFC concentration. Entry into the oceanic environment depends only on the CFC solubility. Once in the water mass the concentration is only altered by mixing. By measuring the concentrations of the CFCs in the ocean with depth and estimating the ratio of the two CFCs it is possible to estimate the last contact time with the atmosphere.

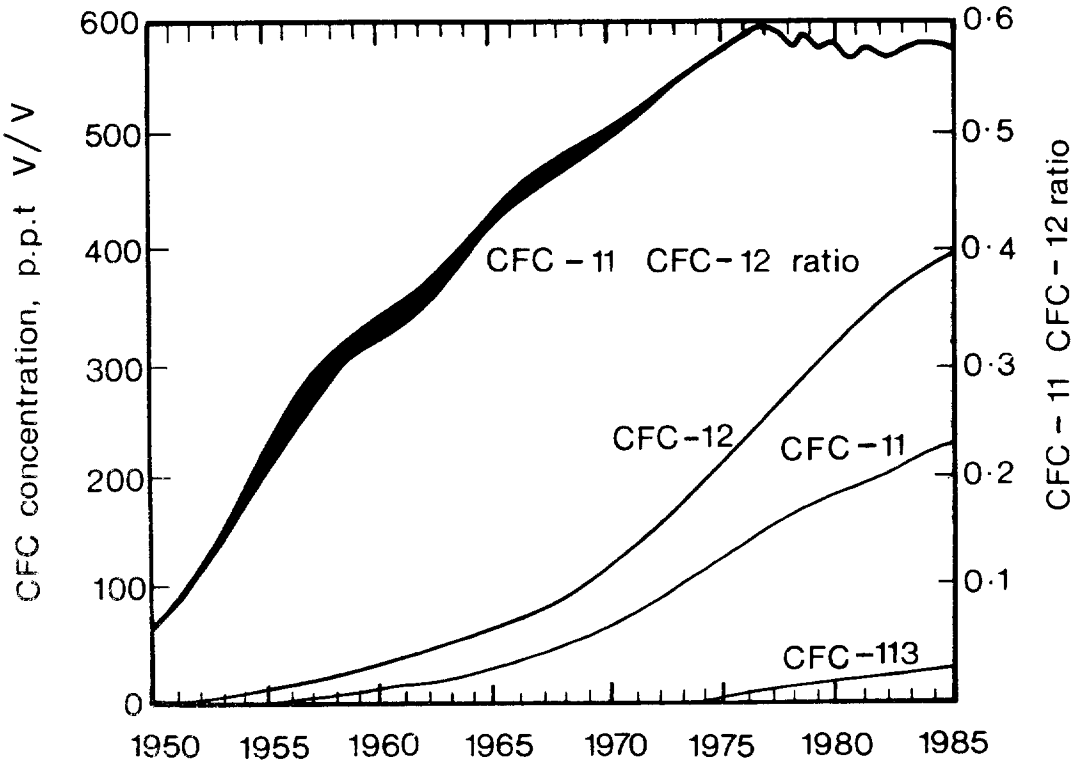


Figure 1 The increase of CFC concentrations in the atmosphere with time.

Knowing the path the water mass followed when it left the sea surface and spread into the ocean's interior, it is possible to estimate the distance it has travelled and calculate a transport time.

Figure 2 shows the increase, with time, of surface sea water CFC concentrations estimated from solubility data and the known time history of the two CFCs in the atmosphere. Probably the most striking feature of the figure is the fact that since 1975 the ratio has not changed substantially. This makes it impossible to 'age' waters that have been in contact with the atmosphere since 1975. But this is not important for the majority of the world's ocean since many of the water masses are in excess of 35 years old and the CFC signal is only just being observed. Scientists are now looking to use CFC-113 in order to extend the technique from 1975 to the present. The CFC analytical equipment described here will measure CFC-113, but this report does not go into the details.

Measuring CFCs to a precision of 1% at the part per trillion level found in sea water is not a trivial task. There are severe contamination problems. This is because atmospheric concentrations are orders of magnitude greater than those found at depth in the sea. This means that once a sample is brought to the surface it can very rapidly become contaminated. Analysis must be carried out at sea as quickly as possible. Specially designed equipment is required and sample handling and measurement has to be carefully carried out to avoid the ingress of the surrounding air. In addition non-metallic materials have the ability to absorb CFCs from the atmosphere and desorb them in a non-linear fashion. For this reason the amount of non-metallic material used in the construction of the equipment must be kept to a minimum. Even metallic compounds have to be thoroughly cleaned because often substances used during extrusion coat the surface and these are also able to adsorb CFCs.

The purpose of this document is to give details of the design and construction of the CFC Analytical System (CFCAS) recently constructed by IOSDL. The equipment was specially designed for the shipboard measurement of CFC-11 and CFC-12 in air and seawater samples and to compare them with reference standards and blanks. Sections 2 and 3 give, respectively, a summary of the analytical principle and an overview of the equipment, whilst section 4 gives a detailed stepwise account of the system. Individual components referred to in section 4 in bold italic type face will be further described in Section 5. Section 5 has been compiled so that anyone constructing a similar system can refer to the design of individual components quickly. Section 6 deals with the electrical/electronic and computer hardware aspects of the system. Figure 5 is a foldout to allow the reader to refer to it whilst studying the text. A list of all commercially-available components, with supplier is given in Appendix A. The total cost of these components is about £35,000 at the time of publication. Appendix B gives circuit diagrams and Appendices C and D give drawings of the components built in house. Detailed technical drawings are available on request.

The concept was based on similar equipment built by Bullister and Weiss at Scripps Institution of Oceanography and in the early stages of the IOS work Bullister's PhD thesis (Bullister,1984)

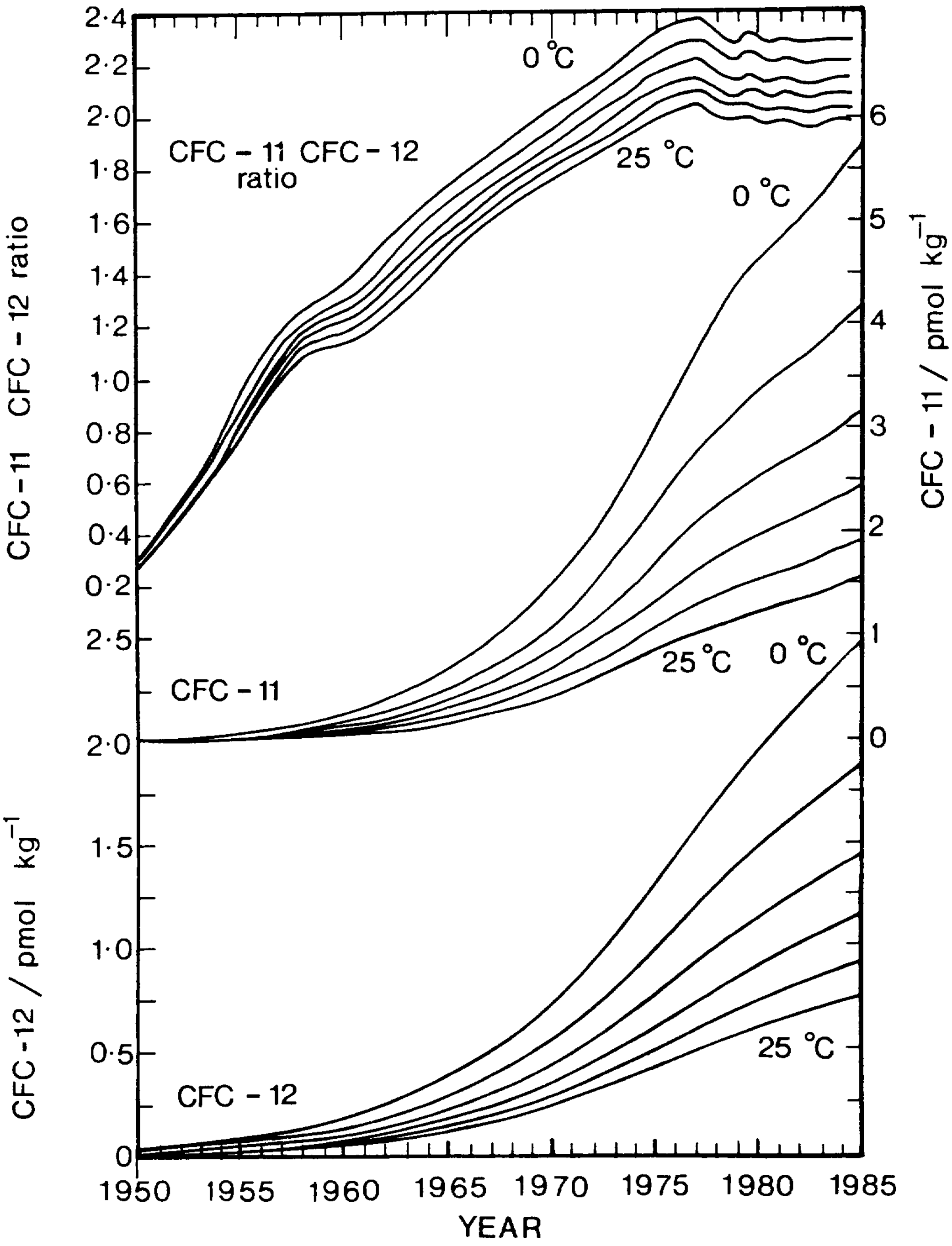


Figure 2 The increase of CFC concentration in surface seawater with time. (estimated from solubility data).

provided valuable documentation. However the IOS system is not a carbon copy of that used by Scripps. A number of major modifications have been designed and incorporated making the IOS system far more robust, transportable and easier to use. Smythe-Wright (1990) gives details of the use and maintenance of the equipment.

2. ANALYTICAL PRINCIPLE

The principle of the analytical technique is to use a purge and trap arrangement to preconcentrate and separate gaseous CFCs from other dissolved gases in the seawater and air samples and to inject them into a gas chromatograph for analysis. The analysis is dependent both qualitatively and quantitatively on comparison with standard gases. Air, standards and blank samples are introduced into the extraction system in gaseous form and pass directly into the trap. For sea water samples the dissolved gases have to be purged out in a stripping chamber using a mixture of 95% Argon and 5% Methane and then carried into the trap. To simplify the analytical procedure the purge gas is the same as that used as the carrier gas for the chromatographic analysis. A mixture of 95% Argon and 5% Methane was chosen as the carrier gas because it gives better resolution of the CFC-12 peak than nitrogen.

The two component trap, containing Porasil C and Porapak T, is cooled to -30°C during trapping using a propan-2-ol bath. Whilst it retains a number of compounds with the CFC-11 and CFC-12, it allows the stripping gas, oxygen and some dinitrogen oxide to pass through. After the CFCs have been trapped, the purge gas is diverted to by-pass the trap and the trap is heated to 100°C using a water bath. A separate stream of carrier gas is then directed into the trap in the reverse direction to the path followed by the purge gas when trapping. The CFC-11 and CFC-12 are eluted from the trap by this stream into a short precolumn, where they are separated from the more slowly eluting compounds and then pass into the separating column of the gas chromatograph (GC). Once the CFC-11 and CFC-12 have passed into the GC column the flow though the precolumn is reversed and the more slowly eluting compounds in the precolumn are backflushed and vented. Processing of the next seawater sample can begin while the CFCs pass though the gas chromatograph and the precolumn is backflushed.

3. OVERVIEW OF THE CFC ANALYTICAL SYSTEM

The Chlorofluorocarbon Analytical System is shown in Figure 3. It comprises an extraction board which houses the purge and trap apparatus to extract the CFCs from the air and seawater samples, and a gas chromatograph fitted with a ^{63}Ni electron capture detector (ECD) for analysis. Ancillary components include a integrator with integral chart recorder, a cryocool and two vacuum flasks.

The extraction board can be subdivided (see figure 4) into three main sections:

- a selection valve and two sample loops for the injection of air, standards and clean carrier gas, as a blank,
- a glass stripping chamber and two associated switching valves used for purging the seawater sample of dissolved gases,
- a two component trap, to quantitatively collect and preconcentrate the CFCs, coupled to two electronically actuated valves which control the flow through the trap and divert the gas stream through a precolumn and into the gas chromatograph for analysis.

The system has a backflush facility to stop unwanted compounds entering the GC column with the CFC-11 and CFC-12.

The components which make up the extraction board are mounted on an aluminium framework. A second aluminium framework with an elevated flat surface is bolted to the rear of the first to provide a stand to which the gas chromatograph is bolted. The entire construction occupies a bench area of 0.585 m width, 0.62 m depth and a maximum height of 0.615 m. It has been constructed so that the gas lines coupling the GC to the extraction board can be disconnected and the two sections unbolted and packed separately for transportation if necessary. An aluminium box cover with handles has been constructed for the extraction board and the GC is packed in a separate carton.

Alternatively, the whole construction may be bolted to a wooden base and enclosed by a wooden box. This is preferable, and where possible the system is transported in this way. It allows the gas lines from the extraction board to the GC to remain intact. This stops the ingress of air to the system and maintains the system gas tight. Continual opening and closing of the Swagelok fittings which make up most of the connections in the CFCAS will deteriorate the seating and should be kept to a minimum. Obviously during routine use some fittings do need to be opened in order to change drying agents and external sources of gas.

The integrator is positioned to the left hand side of the extraction board and the cryocool and two vacuum flasks, one containing propan-2-ol (cooled to -30°C) and the other water (heated to 100°C), to the right. Figure 3 shows the entire system in its working position.

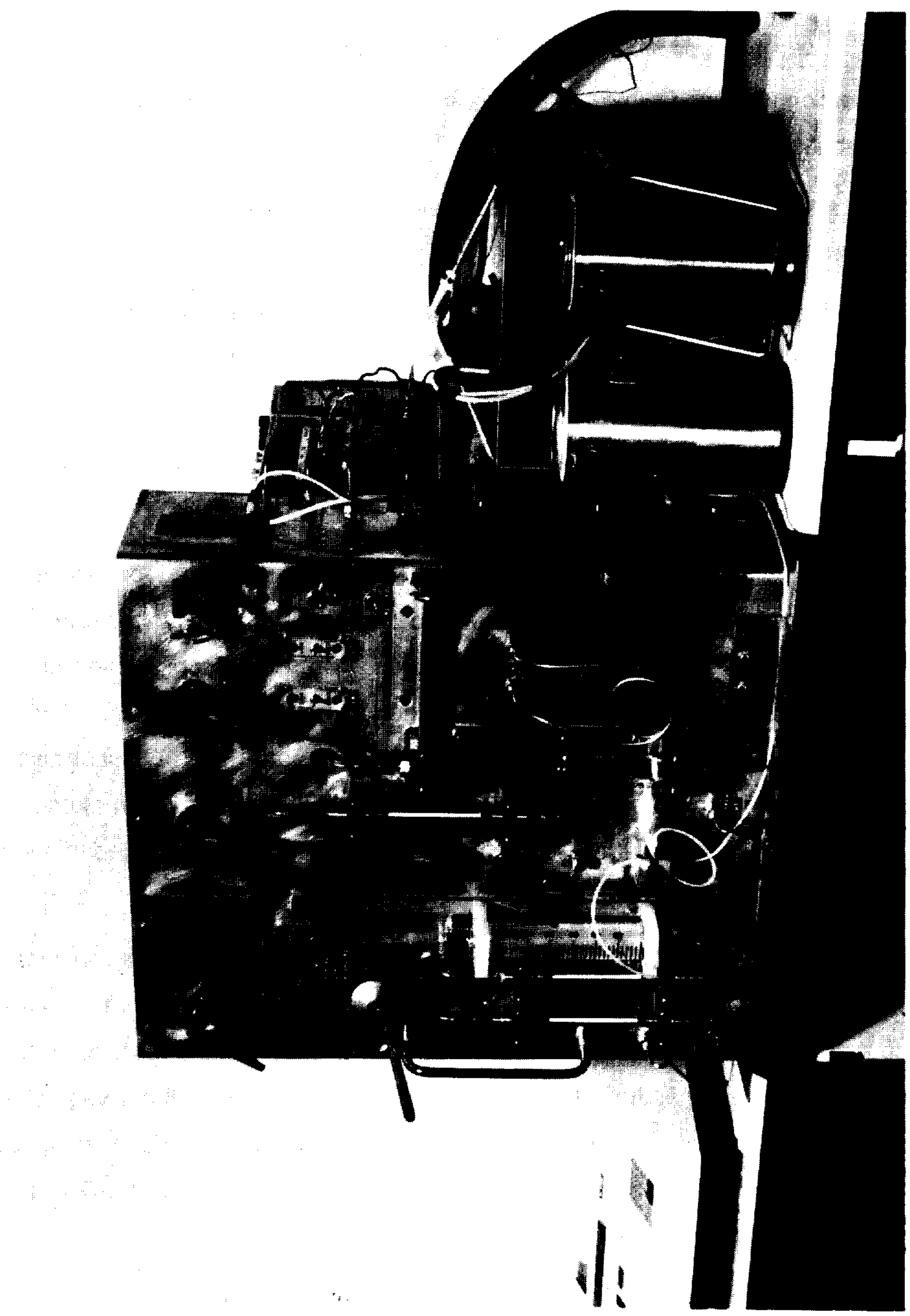


Figure 3 The CFC Analytical System in its working position.

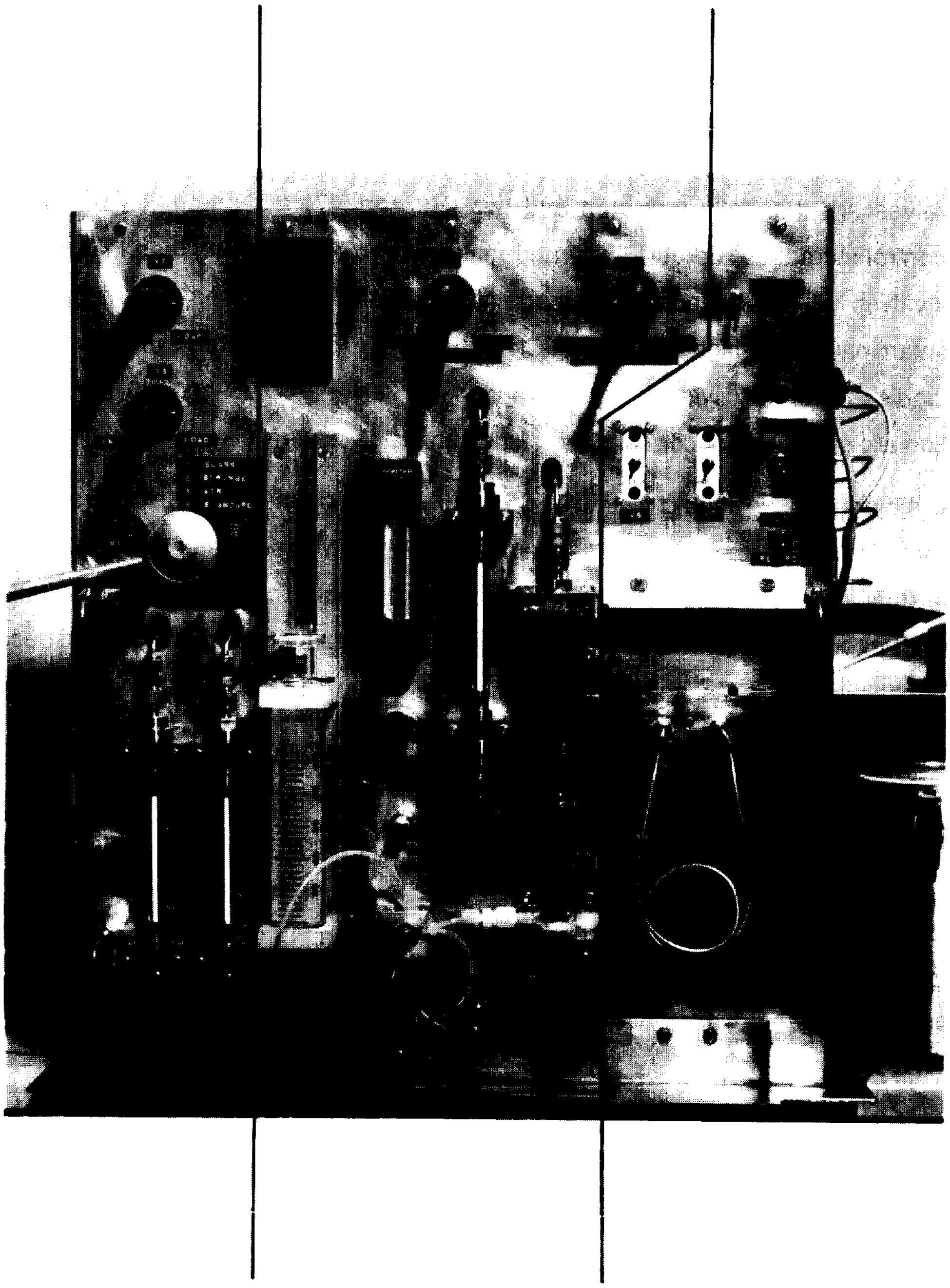


Figure 4 The three sections of the CFC Extraction Board.

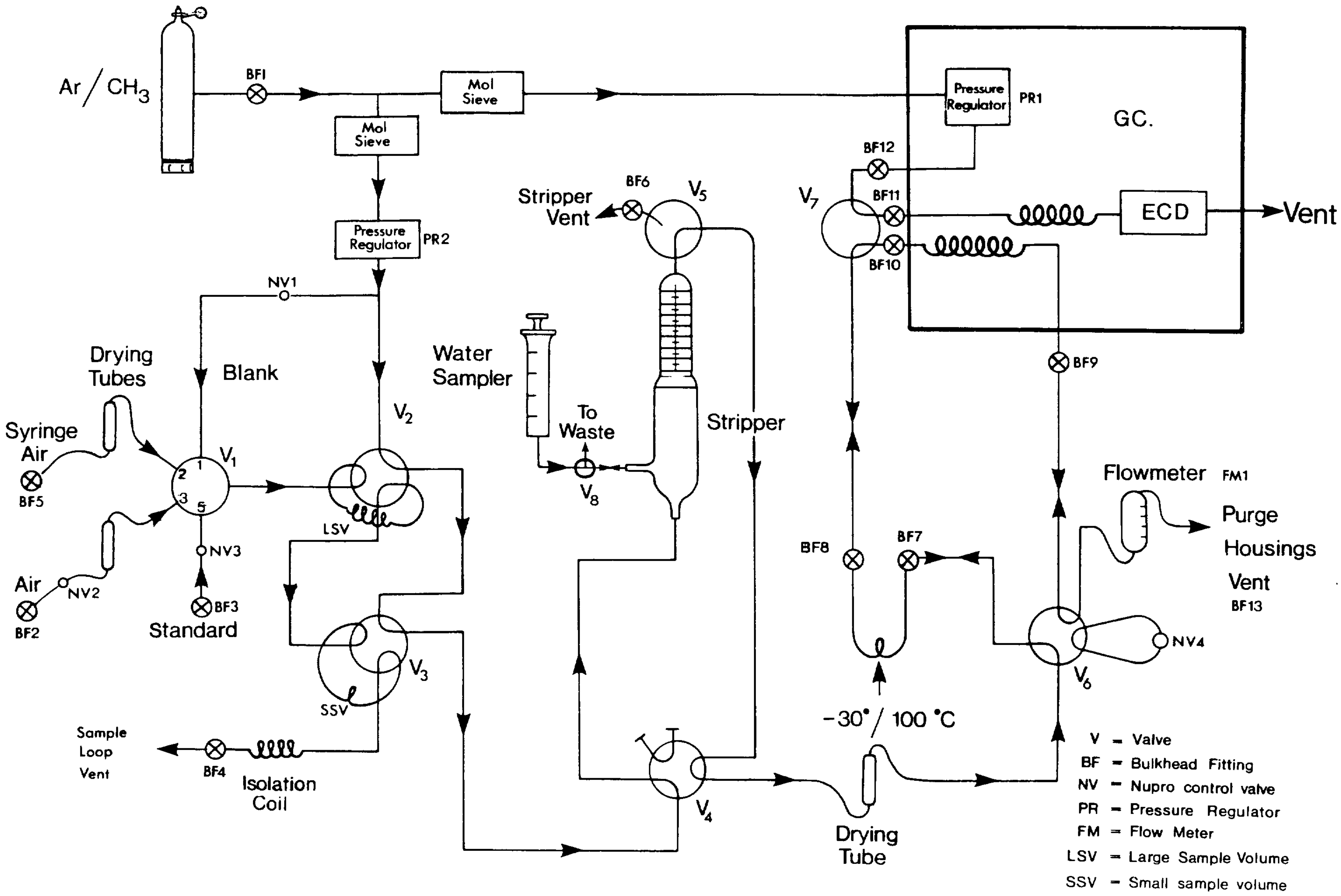
Carrier gas and standards are piped to the equipment from cylinders; clean air, from an exterior source, is supplied using a metal bellows pump and an air line. A copper tube allows the gases exhausted from the ECD to vent to an area well away from the working environment (manufacturers recommend at least 1 m from where personnel are allowed). On board ship this usually means up a mast or stay. In the laboratory the ECD vents to the roof.

There are a total of seven Valco valves in the system; one is a manually operated selection valve (V1) and the other six (V2-V7) are switching valves (see Figure 5). Four (V2-V5) of the six switching valves are manually operated and two (V6 and V7) are controlled by the integrator. Automatic control increases reproducibility and makes sample processing less tedious. To reduce blank levels valves V2-V7 are enclosed in purge housings. This minimises the amount of laboratory air, often contaminated with high levels of CFCs on board ship, entering the system during switching. The valve bodies in contact with seawater vapour i.e. valves V4, V5 and V6 are constructed of Hastelloy C an alloy that is more corrosion resistant than stainless steel.

The majority of the tubing in the CFCAS is 1/8 inch diameter chromatography grade 316 stainless steel. However where the gas stream is in contact with seawater or seawater vapour, i.e between the stripping chamber and the trap, the tubing is 1/8 inch diameter Inconel 600, an extremely corrosion resistant material. Stainless steel 316 cannot be used throughout the system because it will corrode in the anoxic conditions which prevail.

Prior to assembly, all components i.e. valves, metal tubing, glassware, etc are thoroughly washed with hexane (60-80°C) and methanol (technical grade) and then rinsed with water and dried with carrier gas. Elastomers in the Valco valves and other 'O' rings and seals are cleaned by heating overnight to 70°C in an oven purged with Nitrogen. Gas is simultaneously passed through the valves by joining all ports with small lengths of tubing. The flow is configured to eliminate the need for switching the valves during heating.

Figure 5 Schematic flow diagram of the CFC Analytical System


Ar / CH3
BFI
Mol Sieve
Mol Sieve
Pressure Regulator
PR2
NV1
Pressure Regulator
PR1
GC.
BF12
BF11
BF10
V7
ECD
Vent
Stripper Vent
BF6
V5
Water Sampler
To Waste
V8
Stripper
Drying Tubes
Blank
Syringe Air
BF5
V1
V2
LSV
Air
NV2
BF2
NV3
BF3
Standard
SSV
V3
Sample Loop Vent
BF4
Isolation Coil
V4
BF9
Flowmeter FM1
Purge Housings Vent
BF13
BF8
BF7
NV4
V6
-30° / 100 °C
Drying Tube
V - Valve
BF - Bulkhead Fitting
NV - Nupro control valve
PR - Pressure Regulator
FM - Flow Meter
LSV - Large Sample Volume
SSV - Small sample volume

4. DETAILS OF THE CFC ANALYTICAL SYSTEM

4.1. Carrier and Stripper Gas

A two stage BOC Spectrol pressure regulator is used to reduce the 95% argon / 5% methane gas supply to 60 psi. It is important that the regulator does not have Teflon or other non-metallic parts in contact with the gas stream. Gas is piped from the cylinder to BF1 on the left hand side of the extraction board (see Figure 6). It is then divided into two streams, the carrier gas stream and the stripping gas stream using an 1/8 inch Swagelok straight 'T' fitting. To remove traces of CFC-11 and CFC-12 in the gas mixture each stream passes through a ***molecular sieve trap***. Under continual use the molecular sieve adsorbant lasts about a week before it needs to be regenerated (see section 5.1).

The carrier gas enters the GC at a gas inlet to the rear. The flow rate through the GC column is adjusted to 30 cc per minute (measured at the ECD vent) using the pressure regulator PR1 in the GC. The stripper gas flow passes through the Porter Instrument pressure regulator (PR2) and is adjusted to about 50 cc/minute as measured at the purge housing vent (BF13). Both the pressure regulator and the purge housing vent are on the front of the extraction board. The carrier and stripper gas flow rates are fine tuned during normal usage to minimise surging of the gas through the system when V6 and V7 are switched.

4.2 Gaseous samples

Supplies of air, standard and blank carrier gas pass into the extraction board through the six port selection valve V1. Each port is connected as follows.

* Port 1: to a supply of clean carrier gas which is used as a blank. This gas is taken from the stripper gas flow using a Swagelok straight 'T' placed immediately after the pressure regulator PR2. It passes through Nupro needle valve NV1 on the left side of the extraction board before entering the selection valve. The flow rate is about 100 cc per minute.
* Port 2: to a supply of 'syringe air'. This is air collected in ground glass syringes at various locations around the ship to check for contamination. The inlet for syringe air is BF5 positioned at the bottom left front corner of the extraction board.
* Port 3: to a supply of clean air pumped from an inlet positioned as far forward and as high as possible above the deck of the ship using a length of 10 mm diameter Decabon tubing and a metal bellows pump. Such a system flushes several litres of marine air per minute. In the laboratory, the air flow is split. Approximately 100 cc per minute, pass into the extraction

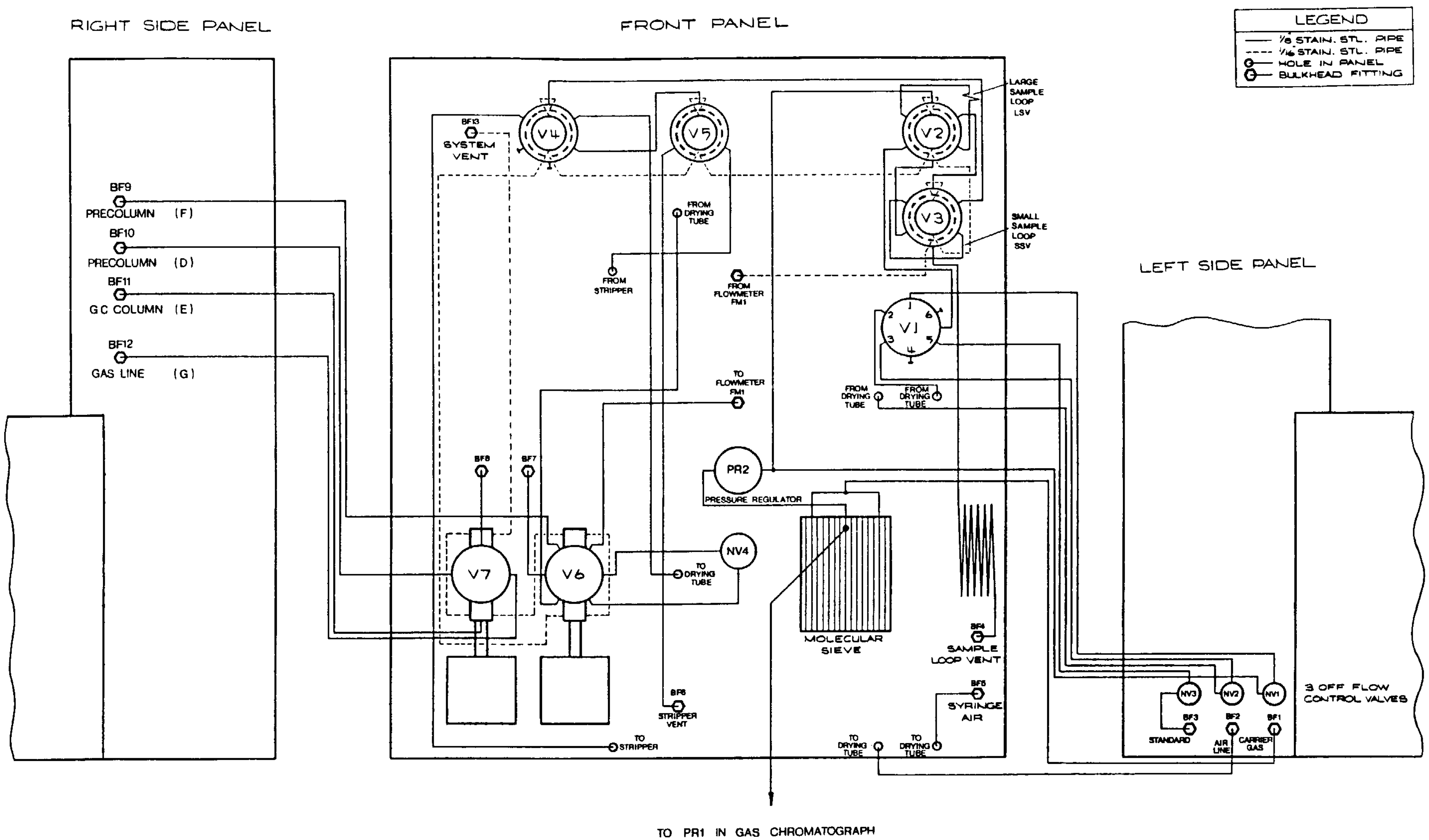


Figure 6 Schematic of the pipework and fittings to the rear of the CFC Extraction Board.

board at BF2. The flow rate is controlled by Nupro needle valve NV2. The remaining air flow is vented around the metal bellows pump and into the laboratory. This is to prevent any local contamination entering the air line through the pump housing. During normal usage at sea, syringe air samples collected from the bows of the ship and samples from the air line should show no difference. On land the air line intake is positioned high up on the exterior of the building in the direction of the prevailing wind.

* Port 4: this is blanked off.

* Port 5: to a gas cylinder containing calibrated standard gas. This is usually clean marine air or nitrogen spiked with CFCs. It enters the system at BF3 and passes via Nupro valve NV3 to position 5 on the selection valve. It is important that the pressure regulator controlling the gas supply does not contaminate or remove CFC concentrations in the standard. A BOC two stage Spectrol pressure regulator with stainless steel diaphragm is used to reduce the cylinder pressure to 30 psi. The flow rate through the selection valve is about 100 cc per minute.

  CFC concentrations in the gas standards are usually at a level close to that of modern air.

* Port 6: this is blanked off.

Because of the mode of operation of the selection valve it is preferable to have the sources at alternate ports i.e. 1, 3 and 5. Ports 4 and 6 are blanked off to give an 'off' position between each source. Port 2, the inlet for syringe air, is only used intermittently and can easily be blanked off during routine work.

Purpose built ***drying tubes*** containing magnesium perchlorate are placed in both the air and syringe air lines. The tubes are located on the front of the extraction board and the gases pass through them before entering the selection valve.

The outlet from the selection valve is connected to two Valco, 6 port valves (V2 and V3) joined in series. Each valve controls the flow through a calibrated ***sample loop*** fitted across two ports. Two sample loops of different sizes are incorporated into the system to allow for multiple injections from one or both loops. By injecting varying aliquots of standard gas into the system a calibration curve can be constructed. Gas from the selection valve passes through both loops before venting to the atmosphere through an ***isolation coil*** and BF4.

The sample is injected into the system by switching either valve V2 or V3 (or both) from the load to the inject position. This directs the stripper gas into the sample loop and drives the calibrated volume into the trap. If multiple volumes are required the sample loop valve is switched back to the load position after 30 seconds. It is flushed for a further 30 seconds before the second aliquot is injected. When gas samples are being analysed the stripper column is isolated from the system by switching the stripper valve, V4 to bypass. The gas stream passes through a second drying tube (primarily for drying gases purged from seawater samples) before entering the trap via V6.

During routine analysis the exact volume of gas injected into the extraction system must be known. This is dependent on ambient pressure and temperature. A ship's aneoroid barometer, kindly loaned by the UK Meteorological Office is used to measure pressure. The temperature of each gas sample loop is individually measured to +/- 0.1°C using platinum resistance thermometry. See Section 6.4.

4.3 Seawater samples

Seawater samples are collected directly into 100 cc ground glass Rocket syringes fitted with Luer Lock tips and two way Pharmaseal K71B stopcocks. Each syringe is positioned in turn on the extraction board and a short flexible Nylon tube connects the Pharmaseal fitting to the inlet of a 3-way Hamilton valve, V8. One outlet of the valve is connected to waste and the other via a nylon Swagelok reducing adaptor (1/4-1/8 inch) to the side arm of the ***glass stripper column***. All glass terminations in the system are 1/4 inch so fitments from the stripper column and the drying tubes require 1/4 to 1/8 inch adaptors.

The nylon tubing and the adaptor are the only non-metallic connections in the system. They do not cause a major contamination problem but will adsorb CFCs with time. Experience has shown that it is good practice to heat the Hamilton valve and the nylon fittings in a ***vacuum oven*** purged with nitrogen every few weeks.

Prior to filling the stripper a small quantity of water is flushed through the Hamilton valve to waste. The sea water sample is transferred to the stripping chamber by opening the Pharmaseal valve and slowly depressing the syringe plunger. Valve V5 has been incorporated in the extraction board to vent gas displaced during the filling process. It is opened as soon as filling commences. In order to stop the ingress of air during the venting procedure a length of stainless steel tubing is run from V5 to BF6 on the lower front of the extraction board to provide a buffer. The volume of water in the stripper is determined from the calibrated lines on the stripping column. A small quantity of water is retained in the side arm connecting the stripper to the Hamilton valve which is not stripped of dissolved gases during the analytical procedure. This volume has to be determined mathematically and subtracted from the volume of water stripped.

Immediately the stripper is filled both the Hamilton valve and V5 are closed. The purge gas is directed into the bottom of the stripping column via V6 and passes through a course glass sintered disc into the water sample. The coarse disc breaks up the gas stream to give an even flow of bubbles and consequently even purging. Gases dissolved in the sample are removed by purging and are directed back through V4, dried with magnesium perchlorate and pass through V6 into the trap. After

4 minutes purging the water can be drained from the column to waste via the Hamilton valve. Purge gas flow is maintained through the stripper during the draining process to keep it free of CFC contaminated air. Once empty the stripper can then be prepared for another sample. Verification of complete stripping can be confirmed by restripping the sample. The volume of water normally stripped is 35 cc.

4.4 Trapping and analysis

The gas stream enters the ***trap*** via the six port valve V6. A Nupro needle valve (NV4) is fitted across two of the ports to maintain a constant stripper gas flow during switching of V6. This also prevents surges of flow when the trap is bypassed and the stripper gas is directed through the flowmeter FM1 and the purge housings. During the trapping process the trap is immersed for four minutes in a stainless steel vacuum flask containing propan-2-ol cooled by a ***Cryocool*** to -30°C. The stripper gas stream containing the sample enters the Porasil C side of the trap first. CFC-11 is held on the Porasil C at -30°C. During the trapping period the CFC-12 in the stripper gas slowly migrates through the Porasil C but is quantitatively held on the Porapak T section. Most of the oxygen and dinitrogen oxide in the sample passes through the cold trap and V7 and into the ***precolumn*** housed in the ***gas chromatograph*** oven at 70°C. After 4 minutes trapping V6 is switched electronically by the ***integrator*** and the cold trap vacuum flask is manually replaced by a hot vacuum flask containing water at 100°C. Thirty seconds is allowed to elapse for the trap to heat before V7 is switched automatically. The carrier gas stream enters the trap in the reverse direction to the stripper gas stream. It flushes the gases, which have eluted from the packing material by the heating process, out of the trap through the precolumn and into the ***GC column***. The chromatographic run begins as V7 is switched. Plotting and integration of the signal from the ECD then commences. The trap is backflushed for forty seconds. This is sufficient time for the CFCs to elute from the trap and pass through the precolumn into the GC column. The unwanted more slowly eluting compounds are held in the precolumn. Valves V6 and V7 are then returned to the trapping positions. The stripper gas stream backflushes the unwanted compounds from the precolumn whilst the CFC-11 and CFC-12 from the sample continue through the GC column. Once V6 and V7 have been returned to the trapping position preparations for the next sample can begin.

5. COMPONENTS OF THE CFC ANALYTICAL SYSTEM

5.1 Molecular Sieve traps

The carrier/stripper gas is not commercially available to the required purity. Molecular sieves are necessary to clean the gas immediately it enters the extraction board. The sieves are made from two three metre lengths of clean 1/4 inch stainless steel tubing packed with 60-80 mesh MX13X adsorbant. The adsorbant is retained in the tubes with small quantities of silanised glass wool. When packed the tubes are carefully coiled to a diameter of approximately 0.125 m. Care must be taken when coiling to make sure that the curvature is shallow so that the packing remains uniform. Using 1/4 to 1/8 inch adaptors, the coils are suspended from an alloy framework attached to the rear of the extraction board. They are wound with a 400 watt, 1.2 m long heating tape and wrapped in a multi-layer insulation material. A thermocouple is placed between the coils under the insulation as a sensor for the temperature controller (see section 6.4 for further details).

The MX13X adsorbant requires initial conditioning to remove water and other compounds which have been adsorbed since manufacture. This is achieved by heating the sieves to 300°C for approximately 20 hours. During this time the flow of gas through the sieves is adjusted to 300-400 cc per minute and vented to atmosphere. The gas must not be allowed to pass into the remainder of the extraction system because it will contaminate. Once the initial conditioning is complete the sieves are coupled to the purge and trap flow paths via the 1/4 to 1/8 inch adaptors.

During normal use the traps will remove trace concentrations of contaminating gases for about a week. Once the sieves become saturated the contaminating gases begin to break through and the analytical signal becomes noisy. The sieves must then be regenerated by heating to 250°C for between 8-12 hours. There is no need to disconnect the sieves from the system during this process: the retained compounds are quickly eluted from the heated traps and vent through the extraction board.

5.2 Drying tubes

Glass tubes containing chemical drying agent are fitted in the air and syringe air inlets so that concentrations can be reported directly in terms of units of mole fraction of CFC in dry air. This avoids the need to make corrections due to the varying water vapour content. It also allows for the comparison of like with like since standards and blanks are prepared from dry gases. Magnesium perchlorate was chosen as the drying agent because it has the best water retention properties of chemical dryers.

It is preferable to have the dryer in glass tubes in order to observe quickly the need for replacement. However, early trials showed that direct linkage between metal and glass tubing could only be made gas tight by very careful tightening of the Swagelok fittings. Often it was impossible to obtain a seal before crushing the top of the glass tube. A casing, which had metal to metal unions and was easy to dismantle for the frequent change of drying agent, was designed and constructed for the glass drying tube.

The casing is made from a 15 cm length of stainless steel tubing into which an elongated window has been cut (see Figure 7). A stainless steel collar is fitted to each end. The collar is machined so that a Viton seal can be inserted between it and the glass tube. The larger diameter of the collar has an internal thread into which is screwed a mating piece. A seal is made by a Viton 'O' ring fitted into a groove machined in the mating piece. The assembly is connected into the system with Swagelok 1/4 to 1/8 inch adaptors fitted to the tails of the mating pieces.

The glass drying tubes are 16.5 cm lengths of 1/4 inch tubing. They are 3/4 filled with the magnesium perchlorate drying agent which is retained by plugs of silanised glass wool. Normally the drying agent lasts about 2-3 days: it is then replaced. Drawings of the casing and the drying tubes are given in Appendix D.

5.3 Sample loops

Gas sample loops are incorporated into the CFCAS to allow for the analysis of standards and air. Two sample loops of different sizes are required because multiple injections of either one or both loops are needed to construct a calibration curve. The volume of the larger sample loop is nominally 3 cc. This volume was chosen so that the amount of CFC-12 injected in one aliquot of standard was the same as that for a 30 cc seawater sample. The smaller loop represents a CFC-12 concentration approximately equal to that found in deeper waters.

The largest sample loop is made from an 85 cm length of 1/8 inch stainless steel tubing: the smaller from a 20 cm length. The largest loop is connected to opposite sides of valve V2: the smaller loop to opposite sides of V3 (see Figure 5 for port configuration). The exact volume of each loop is calibrated gravimetrically with water. This is a tedious process and is carried out before the valves are positioned in the extraction board. It requires each valve to be clamped in a convenient position and filled with water in such a way that no air bubbles are trapped. The valve is then switched from the load to the inject position and the water blown out into an accurately preweighed container. The container is then reweighed. Knowing the temperature when the valve was switched it is possible to calculate the volume of the sample loop from density tables. Obviously for this technique to be accurate the procedure needs to be repeated many times and a mean calculated: a total of 50 calibrations were made for each of the sample loops in the IOSDL CFCAS.

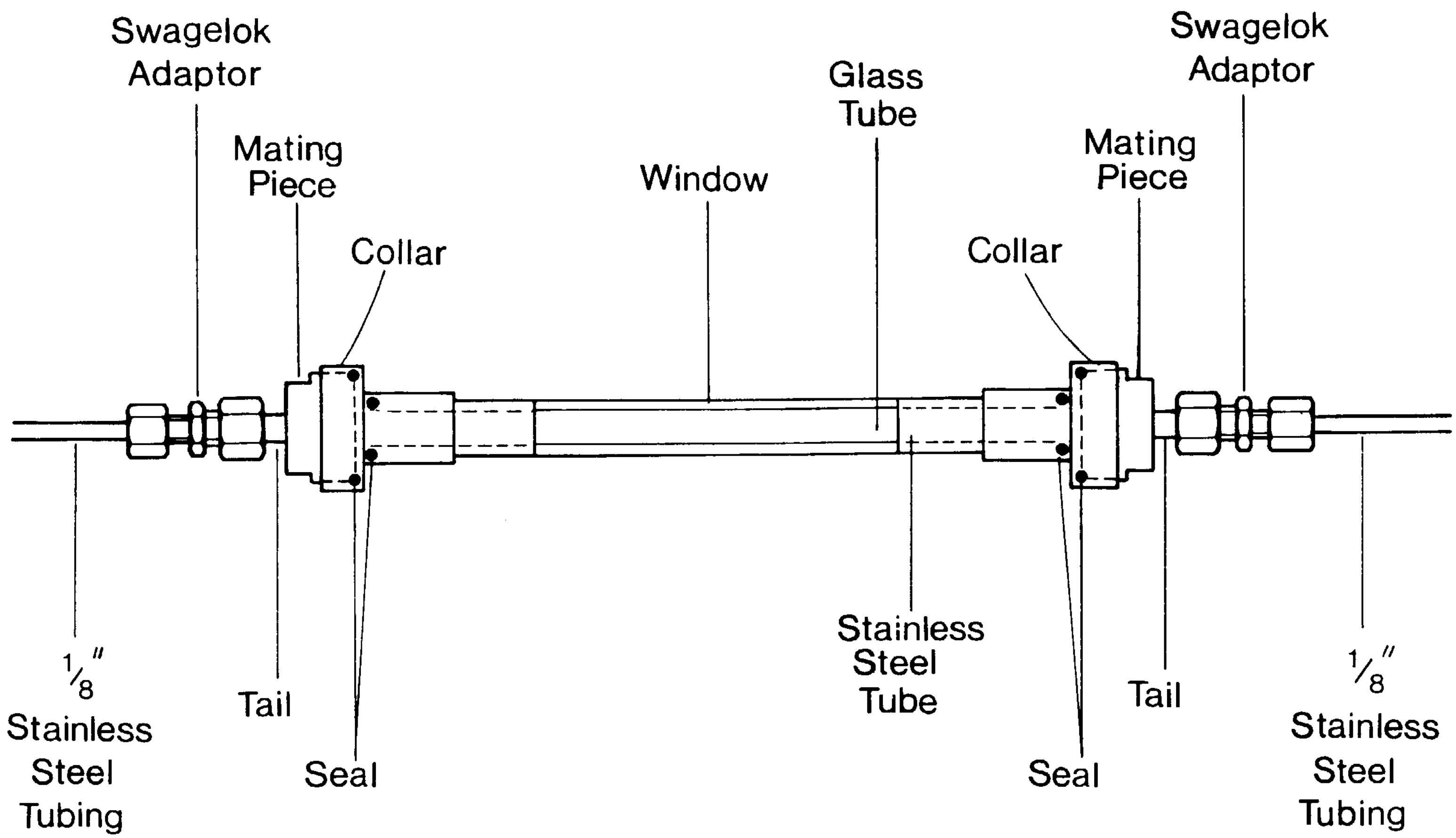


Figure 7 The drying tube casing.

5.4 Isolation coil

The isolation coil is made from a 3 m length of 1/8 inch stainless steel tubing, coiled to a diameter of about 0.08 m. Its function is to stop air being sucked into the system when the selection valve V1 is switched. It is fitted between valve V3 (see figure 5 for the port configuration) and BF5.

5.5 Glass stripping column

The glass stripping column is an elongated pear shape with a 2.6 cm diameter lower section and a 1.3 cm wide upper section. Both sections terminate with 1/4 inch tails. A sintered disc of porosity 3 is fitted inside the lower section. Its primary function is to disperse the gas as it enters the stripper and give a uniform bubble path through the water sample. It also helps to retain the water in the stripper. There is a short 1/4 inch glass side arm protruding from the lower section just above the sintered disc: this is the water sample inlet.

The narrow top section has a series of calibrated lines on the outer wall. This allows the volume of water in the stripper to be measured.

The overall length of the stripper is 25.0 cm. It is held in place on the extraction board by two end caps which are similar in design to the drying tube collar assembly. With this arrangement it can easily be removed from the board for transportation. Drawings of the stripper are given in Appendix D.

5.6 Vacuum Oven

A vacuum oven is an essential piece of equipment during the building of the CFCAS and for routine CFC measurements. It is used to condition the Valco valves, 'O' rings and seals, syringe tips, and the Hamilton valve and it's associated fittings. It is invaluable when dealing with contamination problems which almost certainly will transpire. A Towson and Mercer Vacuum Oven was chosen because it has a second vacuum tap on the door to allow control gas (usually nitrogen) to pass through the chamber during heating.

5.7 Trap

A two component trap has been specially designed to quantitatively collect the CFC-11 and CFC-12 at -30°C rather than at the more usual -70°C temperature. The ability to trap the CFCs at the higher temperature allows the use of a cryocool to cool a propan-2-ol bath. This removes the logistic problems of using dry ice or liquid nitrogen at sea. The trap is made from a 60 cm length of 1/8 inch stainless steel tubing. It is packed with five cm of glass beads, followed by five cm of Porasil C

(80-100 mesh), five cm of Porapak T (80-100 mesh) and five cm of glass beads. The packing material is retained by small wads of silanised glass wool.

To pack the trap a short length of polythene tubing and a filter funnel is attached to one end of the 60 cm length of stainless steel tubing. With the aid of a metal rod calibrated at 5 cm intervals a small piece of glass wool is inserted at 40 cm from the filter funnel end. The rod is removed and small quantities of glass beads are shaken into the tube. Throughout the packing procedure the tube is run up and down a glass engraving tool in order to vibrate the contents and facilitate even packing. The calibrated rod is inserted periodically until only 35 cm enters. The same procedure is used to insert the Porasil C, the Porapak T and the second length of beads. When all the packing material is inserted, the polythene tube and filter funnel are removed and using the rod, the distance of the packing material from each end is checked to be 20 cm. The tube is then bent to make a loop in the central section with two lengths of approximately 15 cm extending at each side. The trap is fitted to the extraction board at positions BF7 and BF8. It is important to fit the Porasil C side of the trap to the bulkhead fitting leading to V6.

5.8 Cryocool

A Neslab Cryocool CC 60 II refrigeration unit is used to cool the propan-2-ol cold bath. It operates by pumping the coolant into a probe at the end of a flexible hose. The probe is inserted into the propan-2-ol bath and the temperature is maintained at -30°C by the use of a controller (see section 6.3). If a controller is not fitted the system will cool to -60°C and maintain that temperature.

5.9 Precolumn

The function of the precolumn is to hold back slowly eluting compounds while the more volatile components pass into the GC column. Once the CFCs have passed through, the flow through the precolumn is diverted and the unrequired substances in the sample backflushed to waste. The precolumn is made from a 15 cm length of 1/8 inch stainless steel tube packed with 80-100 mesh Porasil C and gently bent to form a 'U'. It is completely filled to reduce dead volume space and the packing material is retained by small quantities of glass wool firmly wedged in both ends. It is positioned between V6 and V7 in the flow stream and located in the GC oven which maintains it at a temperature of 70°C.

5.10 Gas Chromatograph

A Shimadzu Mini 2 E fitted with a ^{63}Ni ECD is used in the CFCAS because it is the smallest GC available and is easily transported. It is a basic instrument which can easily be adapted for direct on column injection. It is also reasonably priced. A number of changes have been made, but in such a way that the instrument can easily be returned to its original state.

The Shimadzu Mini 2E is designed to take dual column, dual detector systems, but it can be supplied as a single system. This is all that is required for CFC analysis. By removing the blanking panels for the second system, it is possible to pierce the glass fibre packing material. This gives direct access to the GC oven from the front of the equipment.

Figure 8 shows a schematic diagram of the front of the gas chromatograph. The IOSDL GC has the injection port fitted at A, the ECD at B and the ECD vent at C. These features have been left entirely as supplied by the manufacturers. The blanking panels at D, E and F have been removed and short lengths of pipe to which Swagelok unions are fitted are inserted through the packing material and into the GC oven. A second set of Swagelok fittings are attached to the tubes inside the oven. Two unions on each line are fitted so that the columns in the oven can easily be removed and so that the GC can be disconnected for transportation. The use of one union is not really practicable, as dismantling would require re-insertion of the tubing through the packing material and the latter's consequent degradation.

In the IOSDL system the GC column is fitted between B and E and the precolumn between D and F. The gas lines from the extraction board into the GC follow the routes BF9 to F, BF10 to D and BF11 to E (see Figure 9).

The standard fitments on the Shimadzu Mini 2E is for glass columns. It is, therefore, necessary to purchase metal column adaptors for insertion into the ECD port.

Modifications are also necessary to the flow line within the GC. The electronic section hinges out from the main body of the GC to expose the flow lines underneath (see Figure 8). A schematic of the flow line is given in Figure 10. The line emerging from the pressure gauge at the rear splits into two: one line purges the ECD and this is left as supplied by the manufacturers, the other is the carrier gas line which goes through the injection port to the column. By dismantling the carrier gas line at the pressure gauge, it is possible to remove the molecular sieve (labelled I on Figure 10). A new length of 1/8 inch tubing is attached to the pressure regulator outlet, and exits the GC via a Swagelok union at position G (see Figure 8). This union, in turn, is attached to BF12 on the extraction board. If this modification is done carefully, without removing any of the components J-L on Figure 10, it is possible to reinstate the use of the injection port at any time.

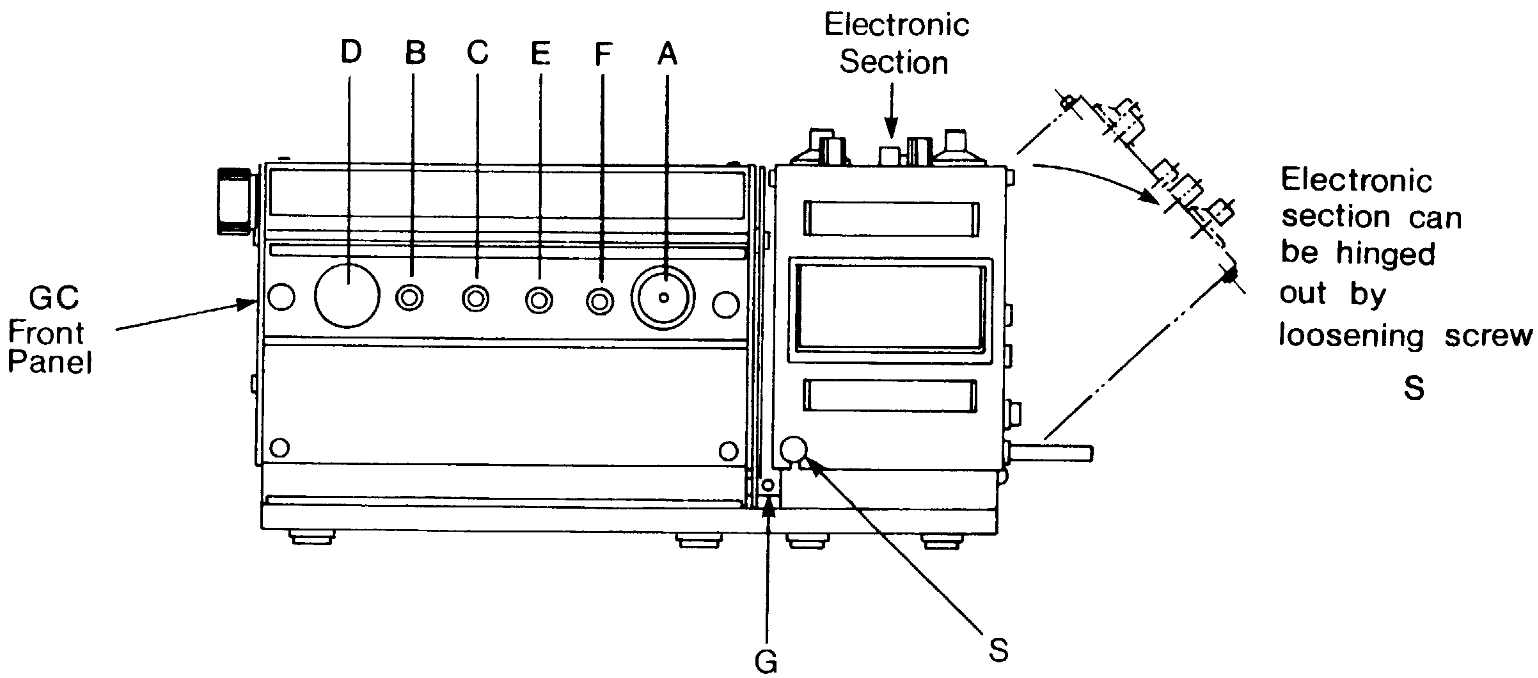


Figure 8 Schematic diagram of the front panel of the GC.

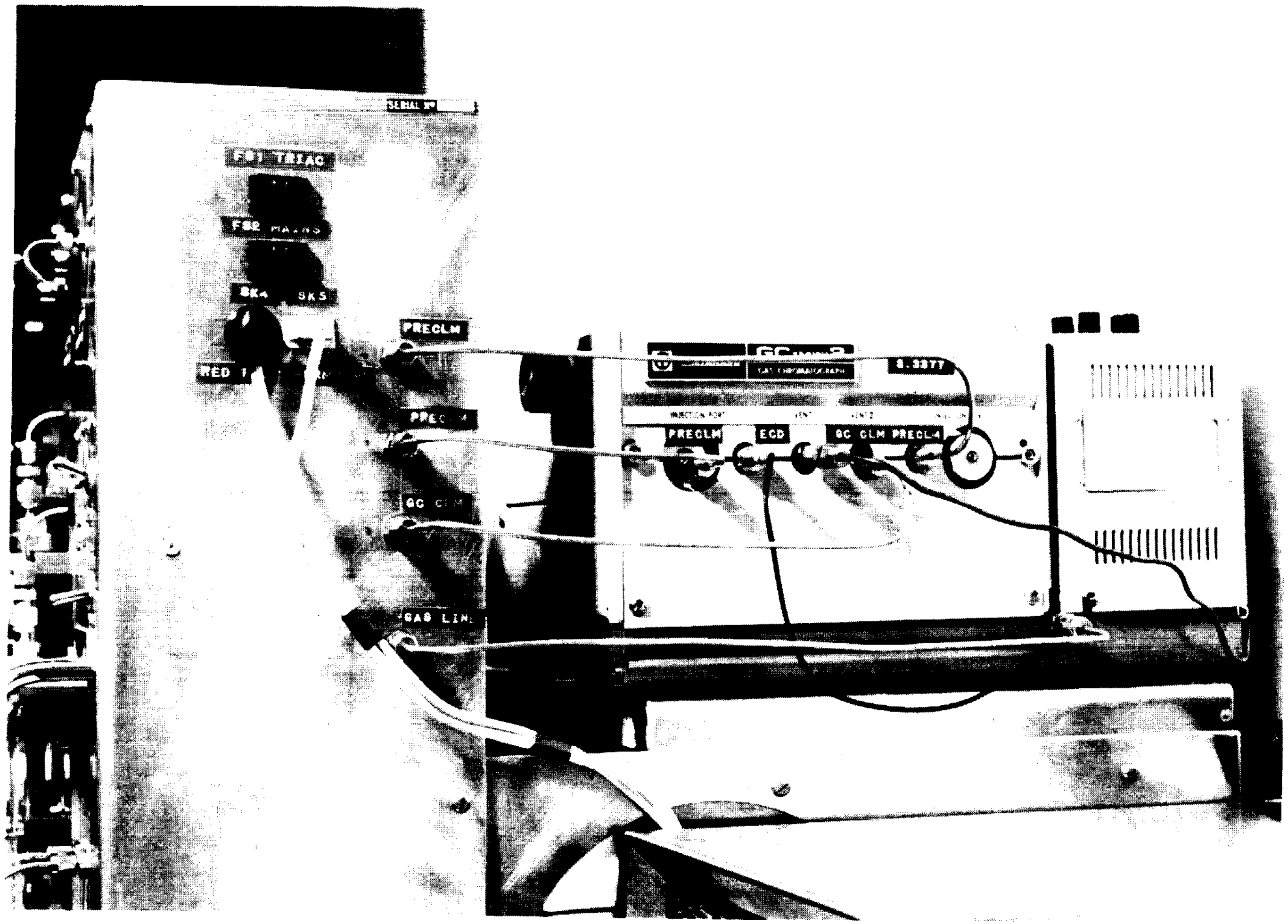
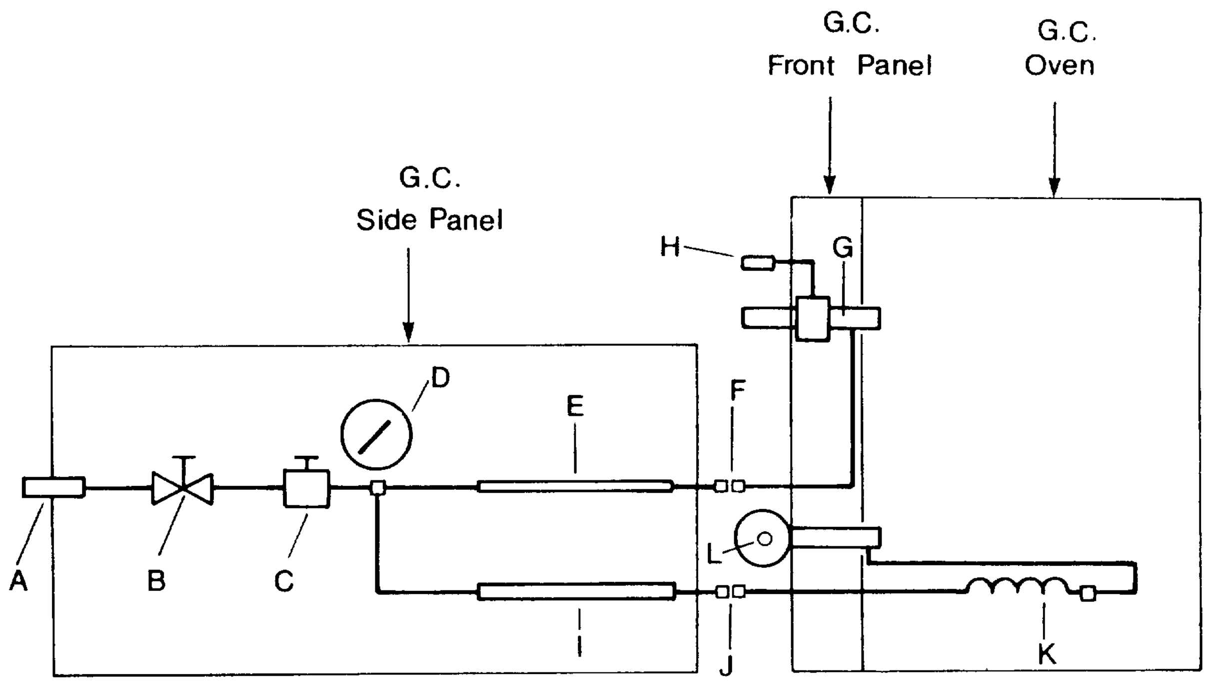


Figure 9 The right hand side of the CFC Extraction Board showing the connections to the GC.



Inlet

A Carrier Gas inlet
B Stop valve
C Pressure controller
D Pressure gauge

Purge line

E Restrictor
F One touch connectors
G ECD cell
H Vent

Carrier gas line

I Molecular sieve
J One touch connector
K Carrier gas preheater pipe
L Injection port

Figure 10 Schematic diagram of the gas flow lines in the GC.

5.11 Integrator

A Shimadzu CR3A Chromatopac is used for recording and analyzing the chromatographic peaks. It is attached to the GC via the integrator socket at the rear. When using the integrator without a chart recorder, the manufacturers suggest that the integrator is plugged into the recorder socket. Experience has shown this is not satisfactory and it is best to put the integrator in the correct socket to avoid confusion. The GC electronics are such that the integrator socket takes the signal prior to attenuation whilst the recorder socket takes it afterwards. When using the recorder terminal for the integrator the attenuation on the GC must be set to 1 otherwise the signal will be attenuated twice and this can result in errors when comparing data.

The CR3A language is a version of BASIC. Software for manipulating results is held in a ROM. In order to drive the electronic valves and an audible alarm a Shimadzu PC 16N digital input/output board was purchased. A detailed account of the electronics is given in Section 6.1, and a listing of the program in Appendix B.

5.12 GC column

The GC column is a 3 m length of 1/8 inch stainless steel tube completely packed with 80-100 mesh Porasil C. It is coiled to a diameter of 0.125 m so that it fits neatly inside the GC oven. It can be packed as a 3 m straight length, the packing material being retained by small quantities of silanised glass wool fitted in both ends, and then gently coiled making sure that the curvature is shallow so the packing material remains uniform. Alternatively the tubing can be coiled and subsequently filled using a vacuum pump to suck the packing material into place. Both methods have drawbacks so it is a matter of preference. There are commercial firms who will pack columns to specification. Obviously this is more expensive but commercially packed columns are often more satisfactory.

6. ELECTRICAL/ELECTRONIC CONTROLS AND COMPUTER HARDWARE

The electrical system of the CFCAS is based on commercial components. Additional circuitry has been designed to provide an integrated operating system.

6.1 Automatic valve and audible alarm Control

The Chromatopac integrator is used to drive the two electrically actuated motorised valves, V6 and V7. It also operates an audible alarm which is used as a timing device. A simple CR3A BASIC program controls these functions and governs the chromatographic run. A listing of the program is given in Appendix B.

The hardware consists of

* an expansion case with a Shimadzu PC16N digital input output board fitted,
* an interconnecting cable,
* a two tone buzzer mounted on the side of the extraction panel.

Control of the valves is achieved by connecting, in a changeover configuration, the relays of the PC16N board to the load and inject command lines of the electrically actuated valves V6 and V7. Two relays are connected to each valve and programmed to switch alternately.

A feed back is provided to the integrator via opto-electric couplers on the PC 16 N board. Plus 5 volts is taken via a 200 ohm resistor (current limiting) from pin 1 of the PC16N board to the motorised valve contact closure terminal. When the valve closes the +5 volts is applied to the LED anode causing it to illuminate and present a logical 1 to the integrator. Zero volts on pin 12 is connected to the cathodes of the LEDs.

The audible alarm is driven by switching +5 volts via a 500 ohm resistor to either the high note or low note supply lines. The alarm common is connected to pin 12 of the PC16N board.

The interface between the PC16N and the extraction panel is a 1.5 m screened multicore cable fitted with a Shimadzu supplied connector at one end and a 37 way 'D' connector at the other. The audible alarm, valves and resistors are all on the CFCAS extraction board. Command of the relays is in hexidecimal format and is called up by the CR3A BASIC programe. Figure B1, in Appendix B, is a circuit diagram of the control network; it gives the relay reference numbers and the hexidecimal number used to close the contacts.

6.2 Heating Control

The heating control is dual function. It is controlled by a Eurotherm 103 temperature controller with 'K' type thermocouple sensors. The heating tape wrapped around the molecular sieve traps is connected with its thermocouple to one side of a four pole changeover switch. The other side of the switch is connected to the Hot Rod immersion heating element used to heat the water bath. The sensor for the immersion heater is a 'K' type thermocouple probe mounted in tandem with the Hot Rod. The wipers of the four pole switch are connected to the Eurotherm controller (see Figure B2 in Appendix B). Connection of the Hot Rod and its thermocouple is made via connectors in the side of the CFCAS extraction board. The Eurotherm controller is mounted on the front of the CFCAS extraction board.

6.3 Cooling Control

The Cryocool is controlled by a platinum resistance probe PT 100 coupled to an on/off temperature control. The probe is inserted in the propan-2-ol bath with the Cryocool probe. When the required temperature is reached the controller switches a solenoid in the body of the Cryocool stopping the flow of coolant.

The Cryocool and the PT 100 probe are connected to the controller using an 11 pin socket. Connection to the Cryocool is by a matching plug inserted into its controller socket. The 240 volt mains supply for the controller is derived from the Cryocool (see Figure B3 in Appendix B).

6.4 Temperature Monitoring

The temperatures of the gas sample loops are monitored by two digital PT 100 temperature indicators mounted side by side in an alloy box attached to the top of the extraction board. A small platinum film detector is fastened in close contact with each sample loop and the loop wrapped in multi-layer insulation. The detectors are connected to the indicators using 15 way 'D' type plugs and sockets; four wire resistance measurement techniques are used to minimise errors. The indicators are connected to the mains via a 100 milliamp fuse and a double pole on/off switch. See Figure B4, in Appendix B, for circuit diagram.

The alloy box containing the two temperature indicators is removed from the top of the extraction board and fixed to the framework supporting the gas chromatograph when the system is in transit.

6.5 Power Supply

The heating and cooling components are plugged directly into the 240 volt mains supply. All other equipment is connected to the mains via a filtered multiconnector. A filtered power supply is used as a precaution against electrical spikes which would interfere with the smooth running of the equipment.

7. PUTTING THE CFC ANALYTICAL SYSTEM TOGETHER

At the outset building a CFC Analytical System seems to be a daunting task. It need not be. The following gives some 'do's and don'ts' and helpful hints on how to go about it. The tasks listed below are in priority order, but there is scope for overlap. The gas chromatograph, integrator, and valves may take some time to arrive so it is possible to carry on with the extraction board at this stage.

1. Order the gas chromatograph, integrator, Valco and other valves, stainless steel tubing and all Swagelok fittings. It is advisable to purchase a surplus of Swagelok ferrules, nuts and straight unions as these will be needed throughout construction.
2. Build the aluminium framework.
3. Cut the stainless steel tubing to manageable lengths (at least 3 m; remember the GC column and the molecular sieve traps) and wash thoroughly with hexane, methanol and water and make sure they are completely dry.
4. Soak all the needle valves and Swagelok fittings in hexane (for 3-4 hours), methanol (for 3-4 hours) and water (to well rinse). Take them apart to make sure they are thoroughly clean. Dry and put back together.
5. Make the molecular sieves, but do not condition them; just seal the ends gas tight.
6. Make the trap, precolumn and GC column. Seal them gas tight. Do not condition the packing material in these components by heating to elevated temperatures; this practise is often recommended by commercial manufacturers but it can lead to permanent damage (particularly of the Porasil C which, for CFC work, does not like being heated above 120°C). It is preferable to link all the components together and place them in an oven with carrier gas flowing through and venting to waste. They should be heated to no more than 115°C for approximately 12-16 hours. It is essential that the oven does not overheat at any time. This technique should remove any water vapour and contaminants held on the packing material. Such conditioning should be left until you are finally ready to fit these components in the system.
7. Order all remaining components.
8. Decontaminate the Valco valves by washing through with hexane, methanol and water. Do not soak but wash well. Join all the valves together so that gas can flow through each port and heat the valves to 70°C in an oven purged with nitrogen for about 24 hours.
9. Commission a glass blower to make the stripper column and the drying tubes.
10. Make the gas sample loops. Join them to the relevant valve in the correct position and calibrate them.

11. Make the drying tube casings and the stripper cap assemblies.

12. You are now ready to start putting the components on the extraction board.

13. Fit the selection valve V1.

14. Fit the carrier gas supply to the extraction board.

15. From now on check all joints are gas tight as you go along. This can be done relatively inexpensively using the carrier gas and Snoop leak detector. Make sure the Snoop does not get inside any of the system. Wipe all surfaces as soon as the check is made. Snoop can cause severe interference problems when you get to the chromatography. Alternatively, it is possible to use a commercially available gas leak instrument with, for example, helium gas, but this can be expensive.

16. Fit the drying tube casings to the front of the extraction board.

17. Fit the bulkhead fittings and the Nupro valves to the left hand side of the extraction board and join to the appropriate ports of V1. Start at position 3. (ie nearest to the front of the extraction board) and work outwards. It gets very cramped in there after a while. Remember to join the drying tubes where necessary.

18. Fit the Porter Instrument flow meter and the pressure regulator PR2

19. Fit the molecular sieves and join up the gas supply. The sieves should be complete with heating tapes sensors and insulation and mounted on the framework.

20. Fit and join up valves V2-V4.

21. Fit the glass stripper column assembly.

22. Fit the Hamilton valve.

23. Fit the trap.

24. Fit valves V5-V7 and join up. Don't worry about the electrical connections at this stage.

25. Fit the bulkhead connectors to the right hand side of extraction board.

26. Modify the gas chromatograph, fitting all new unions etc.

27. Fit the column and the precolumn.

28. Bolt the gas chromatograph to its stand.

29. Join all the pipework from the gas chromatograph to the extraction board.

30. Join V6 to the flow meter. Join all the valve purge housings and connect to the purge housing vent. Remember the purge housings have 1/16 inch fittings so you will need an 1/8 to 1/16 inch reducing adaptor after the flow meter.

31. You should now have all the valves and pipework fitted. Make sure it is gas tight.

32. Now you can begin the electrical installation. Wire as shown in circuit diagrams given in Appendix B as you go.

33. Fit the Eurotherm controller, the connectors for the Hot Rod and its sensor and all other associated electrical components.

34. Connect the molecular sieve heating tape and thermocouple.

35. Fit the Integrator interface connector and wire to the valves and audible alarm, not forgetting to include resistors where required.

36. Fit the expansion box and PC16N board to the integrator following the manufacturers instructions explicitly.

37. Install the CR3A BASIC program.

38. Fit the controller to the cryocool.

39. Fit the temperature sensors to the gas sample loops and insulate.

40. Fix the temperature indicator box to the top of the extraction board and make the connections.

41. Consult Smythe-Wright (1990) for instructions on how to use the equipment.

REFERENCES

BULLISTER, J. 1984. Atmospheric chlorofluoromethanes as tracers of ocean circulation and mixing: measurement and calibration techniques and studies in the Greenland and Norwegian Seas. University of California, San Diego, PhD Thesis, 172 pp.

SMYTHE-WRIGHT, D. 1990. Chemical Tracer Studies at IOSDL, II. Method Manual for the routine shipboard measurement of chlorofluorocarbons in sea water and air. Institute of Oceanographic Sciences Deacon Laboratory Report 275, 55 pp.

APPENDIX A

A LISTING OF THE COMPONENTS REQUIRED TO BUILD A CFC ANALYTICAL SYSTEM

THE COMPONENTS REQUIRED TO BUILD A CFC SYSTEM

The following is a comprehensive list of the components required to build a CFC Analytical System and for routine CFC measurement. It is divided into sections to facilitate the identification of individual items. Sundry items such as grommets, cable clips, cable ties, cable markers, screws and fixings have not been included: they are left to the discretion of the individual.

1. Major Capital Items

1.1 Gas chromatograph

* Shimadzu Mini 2 E fitted with a single ^{63}Ni Electron Capture detector.
* Shimadzu SUS adapters for using 1/8 inch stainless steel columns in the Mini 2E. [2 off].
* Graphite ferrules for SUS adaptors. [1 pack].
* Adaptor to connect 1/8 inch tubing to Shimadzu ECD vent.

Available from Dyson Instruments Limited, Hetton Lyons Industrial Estate, Hetton, Houghton-le-Spring, Tyne and Wear DH5 0RH. Tel 091 526 0452. Fax 091 517 0844. Telex 53689.

* GC quality 1/8 inch copper tubing (for ECD vent). Cat No COT001. [20 m].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

1.2 Integrator

* Shimadzu CR3A integrator.
* Shimadzu PC16N digital input/output board. Part No 221-21193-91.
* Shimadzu 3 slot expansion case. Part No 221-26850-90.

Available from Dyson Instruments Limited, Hetton Lyons Industrial Estate, Hetton, Houghton-le-Spring, Tyne and Wear DH5 0RH. Tel 091 526 0452. Fax 091 517 0844. Telex 53689.

1.3 Cryocool and associated controller

* Neslab Cryocool CC 60 II Immersion cooler with flexible probe.
* Cryocool auxiliary connector for temperature controller.

Available from Neslab Instruments, Parkway Court, Glaisdale Parkway, Bilborough, Nottingham NG8 4GN. Tel 0602 280834. Fax 0602 280835.

* Series 2 on-off temperature controller for use with PT 100 sensor covering -50°C to +150°C temperature range. Stock No.344-596.
* Platinum resistance probe (PT 100) PTFE insulated. Stock No.158-985.
* Relay free socket 11 pin for above controller. Stock No.402-721.

* 3 core cable, PVC insulated 0.75 mm^2. Stock No 378-117. [as required].

Available from RS Components Limited, PO Box 99 Corby, Northants NN17 9RS. Tel 0536 201234. Fax 0536 201501. Telex 342512.

1.4 Vacuum oven and pump

* Townson and Mercer vacuum oven Size 2 with excess temperature cut out. Cat No O22-125.
* NGN single stage vacuum pump PRS-1. Cat No V10-300.
* Heavy wall red rubber pressure tubing 6.5 mm bore diameter. Cat No T77-310. [10 metres].

Available from Orme Scientific and Technology, PO Box 3, Stakehill Industrial Park, Middleton, Manchester M24 2RH. Tel 061 653 4589. Fax 061 655 3011. Telex 669846.

1.5 Syringes

* Rocket of London 100 cc ground glass interchangeable syringes fitted with Luer-Lock tips. [30 off].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

* Pharmaseal K71 B stopcocks. [Box of 100].

Available from Arnold Horwell Limited, 73 Maygrove Road, West Hampstead, London NW6 2BP.

1.6 Gas cylinder pressure regulators

* Spectrol regulator 602-GG-BS3 (for nitrogen or calibrated gas standard) without Teflon diaphragm.
* Spectrol regulator 602-GG-BS4 (for argon methane carrier gas) without Teflon diaphragm.

Available from BOC Special Gases Limited, 24 Deer Park Road, London SW19 3UF. Tel 081 542 6677. Fax 081 543 7268. Telex 928154. These regulators are specials they do not contain any material which could be a potential contamination threat to the CFC measurements. Discuss with manufacturer before purchase.

2. Extraction Board (Mechanical)

2.1 Valves

* V1: Valco MSD6P manual 6 position SD type stream selector valve with 1/8 inch connections.
* V2: Valco 6UWP-PHA-2 manual 2 position 6 port inline valve with 2 inch stand-off, 1/8 inch connections and purge housing.
* V3: as valve V2.

* V4: Valco 6UWP-HC-PHA-2 manual 2 position 6 port inline valve in Hastelloy C with 2 inch standoff, 1/8 inch connections and purge housing.
* V5: Valco 3UWP-HC-PHA-2 manual 2 position 3 port valve in Hastelloy C with 2 inch standoff 1/8 inch connections and purge housing.
* V6: Valco E-6UWP-HC-PHA-2 electric actuated 2 position 6 port inline valve in Hastelloy C with 2 inch standoff, 1/8 inch connections and purge housing.
* V7: Valco E-4UWP-HC-PHA-2 electric actuated 2 position 4 port valve in Hastelloy C with 2 inch standoff, 1/8 inch connections and purge housing.
* V8: Hamilton HV 626777 for HVP, 3 port 3, 'T' plug valve.

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

2.2 Pressure regulator PR2

* Porter Instruments 8286 SMVS 30 pressure regulator 0-30 psi.

Available from Scientific Glass Engineering, Potters Lane, Kiln Farm, Milton Keynes MK11 3LA. Tel 0908 568844. Fax 0908 566790. Telex 825017 SGE G.

2.3 Flow meter

* Porter Instruments F65 BO-A125-5SS flow meter.

Available from Scientific Glass Engineering, Potters Lane, Kiln Farm, Milton Keynes MK11 3LA. Tel 0908 568844. Fax 0908 566790. Telex 825017 SGE G.

2.4 Glassware

* Glass stripping column.
* Glass drying tubes.

Both manufactured to specification by Hampshire Glassware, 77-79 Dukes Road, Southampton, Hampshire SO2 0ST. Tel 0703 553755/6. Telex 477812 RDGLAS G.

2.5 Fittings

* Swagelok 1/8 x 1/8 inch stainless steel union. Cat No -200-6. [4 off].
* Swagelok 1/8 x 1/8 inch stainless steel bulkhead union. Cat No -200-61. [12 off].
* Swagelok 1/16 x 1/16 inch stainless steel bulkhead union. Cat No -200-6. [1 off].
* Swagelok 1/4 x 1/8 inch stainless steel reducing union. Cat No -400-6-2. [12 off].
* Swagelok 1/8 x 1/16 inch stainless steel reducing union. Cat No -200-6-1. [1 off].
* Swagelok 1/8 x 1/8 inch stainless steel union 'T'. Cat No -200-3. [2 off].

* Swagelok stainless steel male connector 1/8 inch tube to connect to 1/8 inch female NPT thread. [4 off].
* White acetal 1/8 inch nut for Hamilton valve. Cat No OL-500W. [3 off].
* Natural tefzel 1/8 inch ferrule. Cat No OL-051. [3 off].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.
Or from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

2.6 Needle valves

*NV1-NV3 Nupro fine metering valve 1/8 x 1/8 inch angle brass. Cat No B-SS2-A. [3.off].
*NV4 Nupro fine metering valve 1/8 x 1/8 inch angle stainless steel. Cat No SS-SS2-A. [1 off].

Available from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

2.7 Tubing

* Premium grade 1/8 inch stainless steel tubing for GC. Cat No SST006. [approx 30 m].
* Premium grade 1/4 inch stainless steel tubing for GC. Cat No SST008. [10 m].
* Premium grade 1/16 inch stainless steel tubing for GC. Cat No SST004. [10 m].
* 1/8 inch Inconel 600 tubing supplied by Valco. [2 m].
* Natural coloured 1/8 inch Nylon tubing. Cat No NT001. [30 m].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

2.8 Chromatography packing material

* Porasil C 80-100 mesh. Cat No SS154. [100 g].
* Poropak T 80-100 mesh. Cat No SS091. [75 g].
* MS13X 60-80 mesh. [100 g].
* Glass beads fine mesh. [250 g].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

2.9 'O' rings and seals

* Gaco 'O' ring, Viton VC75 IRHD. Cat No RM0161-16 VC 75 IRHD. [8 off].
* Gaco seal, Viton VC75 IRHD. Cat No D1025 VC75 IRHD. [8 off].

Available from Barnwell Services, 16 Spring Road, Bournemouth, Hants BH1 4PX. Tel 0202 37334.

3. Extraction Board (Electrical)

3.1 Heating

* Eurotherm Type 103 triac time proportioning controller for 'K' type thermocouple input with scale range 0-400°C, supply voltage 250 V, 50 hz and screw terminals. Cat No 103-142-03-020-19-09.
* Electrothermal HT5 series heating tape, 400 W, 240 V, 1.2 m length. Cat No HT 551.
* Electrothermal type 'K' glass insulator thermocouple, 0-400°C, 2 metre wires. Cat No 151-192.
* Electrothermal Red Rod BD series immersion heater, 300 W, 120 mm long. Cat No BD-6931.

Available from Electrothermal Engineering Limited, 419 Sutton Road, Southend on Sea, Essex SS2 5PH. Tel 0702 612211. Telex 995387 THERMO G.

* General purpose type 'K' probe. Stock No 151-186
* HBC super quick fuse, 2 A, 20 mm. Stock No 414-235.
* Fuse holder. Stock No 413-254. [2 off].
* DPST switch 250 V 15 A. Stock No 316-838.
* Neon indicator (including resistor). Stock No 576-052.
* Miniature mains socket (panel mounted), 3 pin. Stock No 488-573.
* Miniature mains plug, 3 pin. Stock No 488-567.
* Type 'K' thermocouple miniature panel socket. Stock No 473-105.
* Type 'K' thermocouple miniature line plug. Stock No 473-111.
* Equipment wire 24/0.2 mm, red. Stock No 356-690. [as required].
* Equipment wire 24/0.2 mm, black. Stock No 356-656. [as required].
* Equipment wire 24/0.2 mm, yellow/green. Stock No 357-148. [as required].

Available from RS Components Limited, PO Box 99 Corby, Northants NN17 9RS. Tel 0536 201234. Fax 0536 201501. Telex 342512.

* Four pole changeover switch. Part No 93A420B.

Available from Arrow Hart (Europe) Limited. Plymbridge Road, Estover, Plymouth PL6 7PN. Tel 0752 701155. Telex 45340.

3.2 Valve control and interface cable

* Two tone low voltage audible alarm. Stock No 249-851.
* Resistor 0.25 watt metal film, 200 Ω. Stock No 148-332. [2 off].
* Resistor 0.25 watt metal film, 510 Ω. Stock No 148-433.
* Standard 'D' connector socket, 37 way. Stock No 469-465.
* Standard 'D' connector plug, 37 way. Stock No 469-415.

* Socket crimp contact. Stock No 469-493. [37 off].
* Pin crimp contact, Stock No 469-487. [37 off].
* Screwdown hood for 37 way 'D' connector. Stock No 469-594.
* Multicore cable (screened) 7/0.1 mm, 25 core. Stock No 367-640. [as required].
* Equipment wire 7/0.02 mm, white. Stock No 357-249. [as required].

Available from RS Components Limited, PO Box 99 Corby, Northants NN17 9RS. Tel 0536 201234. Fax 0536 201501. Telex 342512.

* Shimadzu 25 way connector for interface with the PC16N digital input/output board.

Available from Dyson Instruments Limited, Hetton Lyons Industrial Estate, Hetton, Houghton-le-Spring, Tyne and Wear DH5 0RH. Tel 091 526 0452. Fax 091 517 0844. Telex 53689.

3.3 Temperature monitoring

* Panel mounted temperature indicator (PT 100). Stock No 258-192.
* Die cast aluminium case, 222 mm x 146 mm x 106 mm. Stock No 509-260.
* DPST switch 250 V, 6 A. Stock No 316-989.
* Neon indicator (including resistor). Stock No 576-052.
* Fuse holder. Stock No 413-254.
* Quick acting fuse 100 mA, 20 mm. Stock No 412-920.
* Standard 'D' connector socket, 15 way. Stock No 469-443. [2 off].
* Standard 'D' connector plug, 15 way. Stock No 469-392. [2 off].
* Socket crimp contact. Stock No 469-493. [30 off].
* Pin crimp contact, Stock No 469-487. [30 off].
* Screwdown hood for 15 way 'D' connector. Stock No 469-572.
* Platinum film detector (standard element). Stock No 158-238. [2 off].
* Equipment wire 24/0.2 mm, red. Stock No 356-690. [as required].
* Equipment wire 24/0.2 mm, black. Stock No 356-656. [as required].
* Equipment wire 24/0.2 mm, yellow/green. Stock No 357-148. [as required].
* Multicore cable 7/0.2 mm, 4 core. Stock No 358-141. [as required].
* Multicore cable , 4 core. Stock No 358-141. [as required].
* 3 core cable, PVC insulated 0.75 mm^2. Stock No 378-117. [as required].

Available from RS Components Limited, PO Box 99 Corby, Northants NN17 9RS. Tel 0536 201234. Fax 0536 201501. Telex 342512.

3.4 Power supply

* Rewireable plug. Stock No. 489-655. [5 off].
* IEC, plug inlet, filtered mains lead. Stock No. 487-609.

* Rewireable integral lead. Stock No. 488-185.

Available from RS Components Limited, PO Box 99 Corby, Northants NN17 9RS. Tel 0536 201234. Fax 0536 201501. Telex 342512.

4. Air line

4.1 Metal Bellows pump

* Metal Bellows MB-151 pump 230/115 V 50/60 Hz fitted with Viton seals.

Available from Richard Oliver Limited, 4a Bramhall Technology Park, Pepper Road, Hazel Grove, Stockport, Cheshire SK7 5BW. Tel 061 483 1415. Fax 061 456 0543. Telex 669249.

4.2 Swagelok fittings

* Swagelok 10 mm tube to 1/4 inch male NPT Straight Union. Cat No -10MO-1-4RT.
* Swagelok 1/8 inch tube to 1/4 male NPT 'T' union. Cat No -200-3-4TMT.
* Swagelok front and back ferrule sets 10 mm. Cat Nos -10M41, -10M31. [5 off].

Available from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

4.3 Tubing

* Decabon type 1300 aluminium layered, polythene jacketed tubing, 10 mm OD.
  Part No 1300-1000X. [100 m].

Available from Samuel Moore (Europe), Crusader House, High Street, Maxey, Peterborough PE6 69HQ. Tel 0778 348162. Fax 0778 342934. Telex 32559.

4.4 Chemical dryer

* 'DRY-PERM' portable Nafion drier. Model DP3.

Available from Quadrex Scientific, PO Box 79, Weybridge Surrey KT13 9RA. Tel 09323 47648. Telex 8813487 LCLAD.G.

* Molecular sieve 13X 1/16 inch pellets. Cat No 540164A. [500 g].

Available from BDH Limited, Parham Drive, Boyatt Wood Industrial Estate, Eastleigh, Hampshire SO2 4NU. Tel 0703 619171. Fax 0703 643702. Telex 477916 TETRA G.

5. Gas lines

* Spectrol control valve DV 20 B series fitted with 1/4 inch in-1/8 inch out compression fittings. [2 off].
* Spectrol control valve DV 20 B series fitted with 1/4 in-1/4 out compression fittings. [2 off].
* Pressure gauge, 0-100 psi brass. Cat No 842341. [2 off].

Available from BOC Special Gases Limited, 24 Deer Park Road, London SW19 3UF. Tel 081 542 6677. Fax 081 543 7268. Telex 928154.

* 1/4 inch copper tubing. Cat No COT003. [2, 25 m lengths+ 5 m].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

* Cajon 1/4 inch straight 'T', brass. Cat No 4-ST. [2 off].

Available from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

6. Hot and cold baths

6.1 Flasks

* Dewar flask, 1 litre capacity with carrying handle. Cat No 236-1924-00. [2 off].

Available from BDH Limited, Parham Drive, Boyatt Wood Industrial Estate, Eastleigh, Hampshire SO2 4NU. Tel 0703 619171. Fax 0703 643702. Telex 477916 TETRA G.

6.2 Thermometers

* Low temperature thermometer, -80 to +30 ^{o}C. Cat No 268-0185-04.
* General purpose thermometer, -10 to +110^{o}C. Cat No 268-0220-02.

Available from BDH Limited, Parham Drive, Boyatt Wood Industrial Estate, Eastleigh, Hampshire SO2 4NU. Tel 0703 619171. Fax 0703 643702. Telex 477916 TETRA G

7. Consumables and spares

7.1 Fittings and tubing

* GC quality 1/8 inch copper tubing. Cat No COT001. [as required].
* Premium grade 1/8 inch stainless steel tubing for GC. Cat No SST006. [as required].
* Swagelok 1/8 inch front and back ferrules. Cat No -203-1/-204-1. [50 pairs as required].
* Swagelok 1/4 inch front and back ferrules. Cat No -403-1/-404-1. [20 pairs as required].

* Swagelok 1/8 inch stainless steel nut. Cat No -202-1. [10 off as required].
* Swagelok 1/4 inch stainless steel nut. Cat No -402-1. [10 off as required].
* Valco valve 1/8 inch ferrules. Cat No ZF2. [30 off].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

Or from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

7.2 'O' rings and seals

* Gaco 'O' ring, Viton VC75 IRHD. Cat No RM0161-16 VC 75 IRHD. [20 off].
* Gaco seal, Viton VC75 IRHD. Cat No D1025 VC75 IRHD. [20 off].

Available from Barnwell Services, 16 Spring Road, Bournemouth, Hants BH1 4PX. Tel 0202 37334.

7.3 Gases and chemicals

* 'J' size 95% Argon /5% Methane gas mixture. [as required].
* 'L' size Nitrogen gas, white spot purity. [as required].

Available from BOC Special Gases Limited, 24 Deer Park Road, London SW19 3UF. Tel 081 542 6677. Fax 081 543 7268. Telex 928154.

* Methanol technical grade, 2.5 l. Cat No 26129 6H. [as required].
* Hexane 60-80^oC fraction GPR, 2.5 l. Cat No 284846X. [as required].
* Propan-2-ol GPR, 2.5 l. Cat No 29694 6H. [as required].
* Magnesium Perchlorate dried GPR, 100 g. Cat No 29114 2F. [as required].

Available from BDH Limited, Parham Drive, Boyatt Wood Industrial Estate, Eastleigh, Hampshire SO2 4NU. Tel 0703 619171. Fax 0703 643702. Telex 477916 TETRA G.

* Snoop Leak detector, 8 oz. [as required].

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

7.4 Integrator

* Shimadzu CR-3A chart paper. Part No 221-25412. [as required].
* Shimadzu thermal pen head. Part No 221-25362-91.

Available from Dyson Instruments Limited, Hetton Lyons Industrial Estate, Hetton, Houghton-le-Spring, Tyne and Wear DH5 0RH. Tel 091 526 0452. Fax 091 517 0844. Telex 53689.

7.5 Replacement valve rotors

* Valco SSA-6UWP rotor for 6UPW valve.
* Valco SSA-4UWP rotor for 4UWP valve.
* Valco SSA-3UWP rotor for 3UWP valve.

Available from Thames Chromatography,16 Raymead Court, Maidenhead, Berkshire, SL6 8TN. Tel 0628 39504. Fax 0628 26652. Telex 848067 MUSIC G.

7.6 Dewar Flasks

* Inner vacuum vessel for 1 litre Dewar flask. Cat No 236-1924-10. [as required].

Available from BDH Limited, Parham Drive, Boyatt Wood Industrial Estate, Eastleigh, Hampshire SO2 4NU. Tel 0703 619171. Fax 0703 643702. Telex 477916 TETRA G.

8. Gas standard cylinders

* Whitey cylinders 1 gal, double ended, with 1/4 inch female NPT threads and electropolished interior. Cat No 304-L-HDF4. [3 off].
* Nupro H series valves with copper tips and 1/4 inch fittings. Cat No B4HG2. [6 off].
* 1/8 inch tube to 1/4 inch NPT female 200-7-4 stainless steel connector. [6 off].

Available from South London Valve and Fitting Co Ltd, 2 Wellington Town Road, East Grinstead, West Sussex RH19 2ES. Tel 0342 313877. Fax 0342 312312. Telex 957300.

APPENDIX B

THE CFCAS COMPUTER SOFTWARE AND CIRCUIT DIAGRAMS

THE SHIMADZU BASIC PROGRAM.

```
10   LET A=7
20   WAIT 40
30   OUT 1,10H
40   WAIT 1
50   OUT 1,0H
60   INPUT A
70   IF A=8 THEN GO TO 20
80   WAIT 240
90   OUT 1,30H
100  WAIT 1
110  OUT 1,0H
120  OUT 1,1H
130  PRINT LEVEL
140  ZERO
150  WAIT START
160  WAIT 40
170  OUT 1,4H
180  OUT 1,4H
190  WAIT 80
200  OUT 1,4H
210  OUT 1,2H
220  WAIT 1
230  OUT 1,2H
240  OUT 1,8H
250  WAIT 1
260  OUT 1,8H
270  WAIT 360
280  STOP
290  END
```

CIRCUIT DIAGRAMS

The following figures give circuit diagrams of

* the automatic valve and audible alarm control network,
* the heating control network,
* the cooling control network,
* the temperature monitoring network.

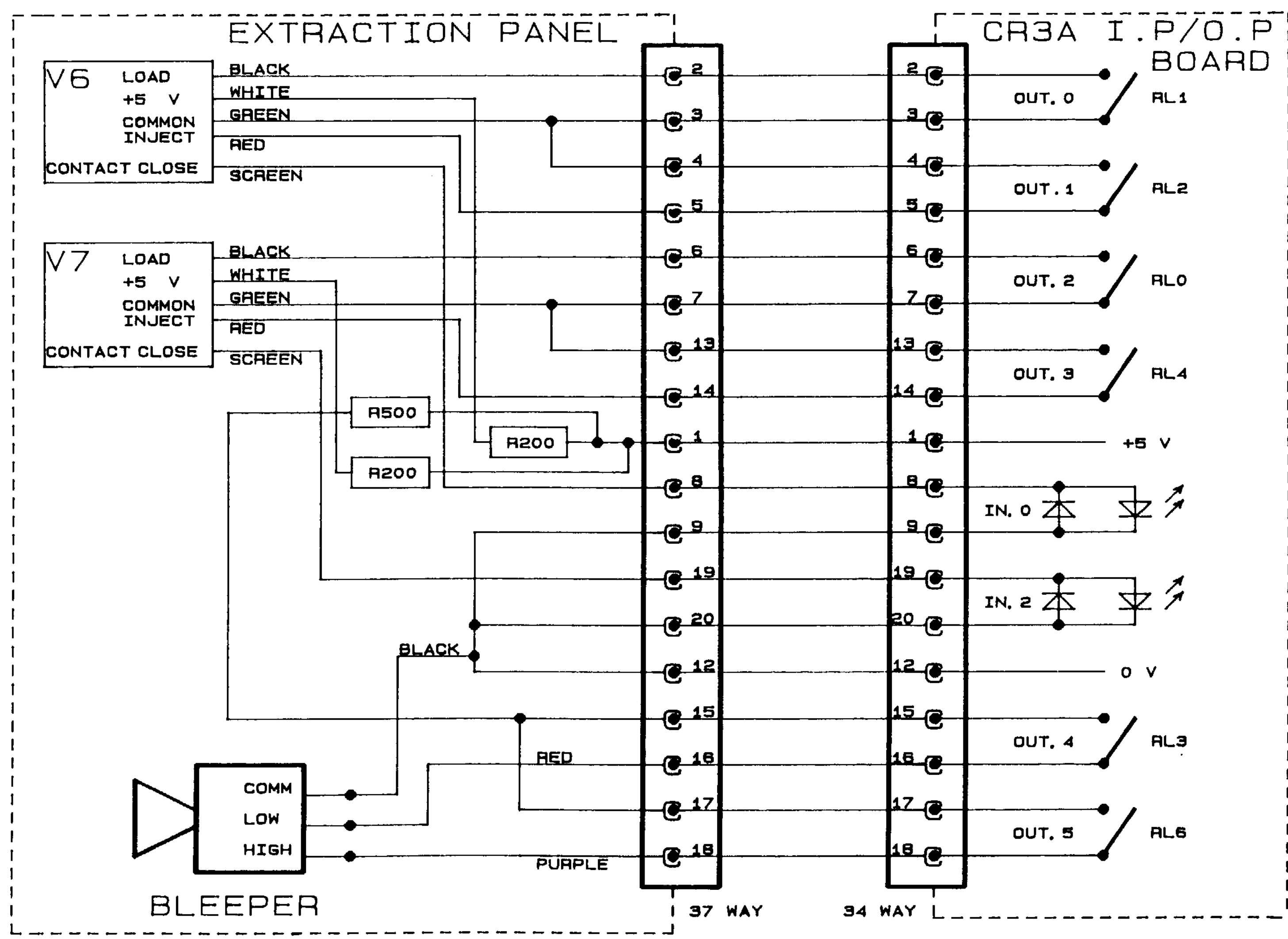


Figure B1 Circuit diagram of the automatic valve and audible alarm control network.

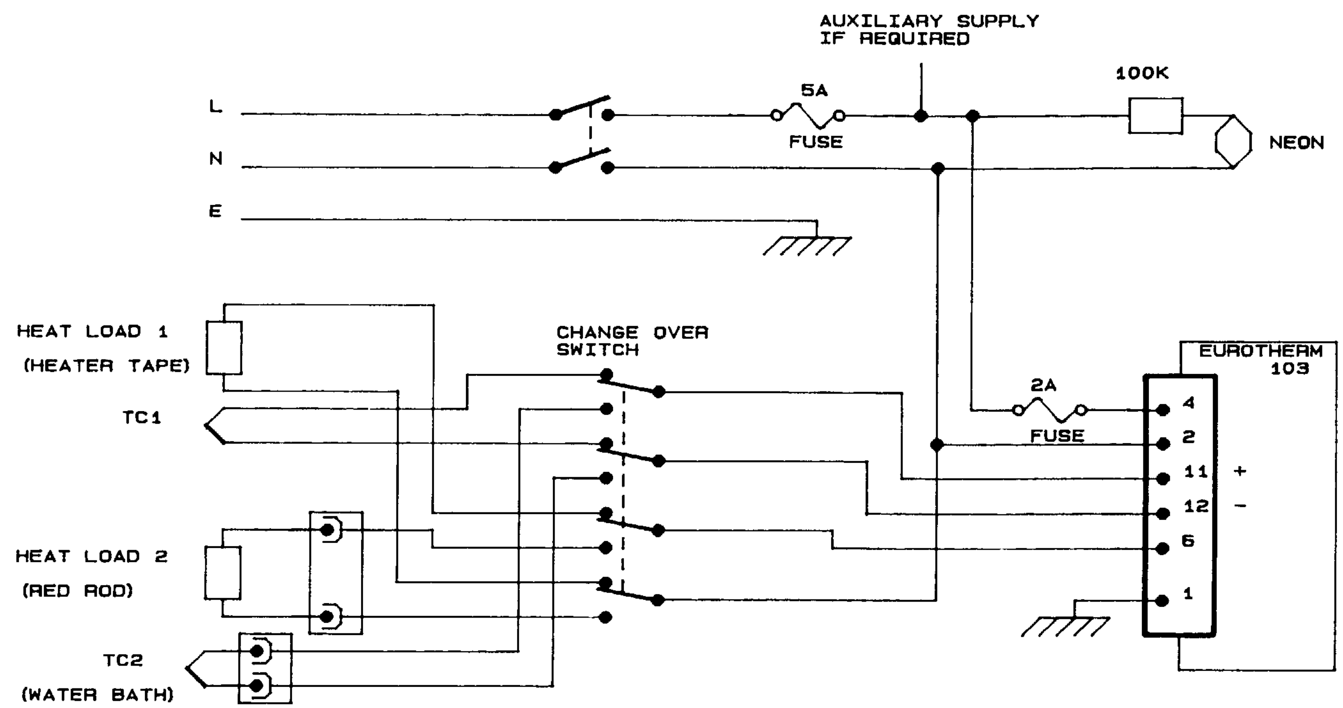


Figure B2 Circuit diagram of the heating control network.

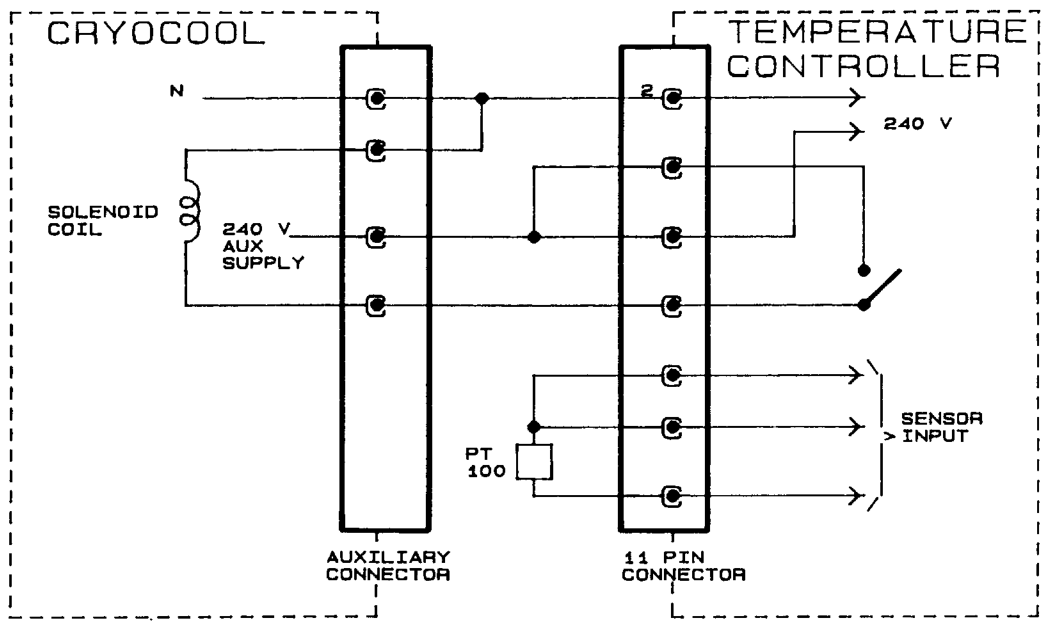


Figure B3 Circuit diagram of the cooling control network.

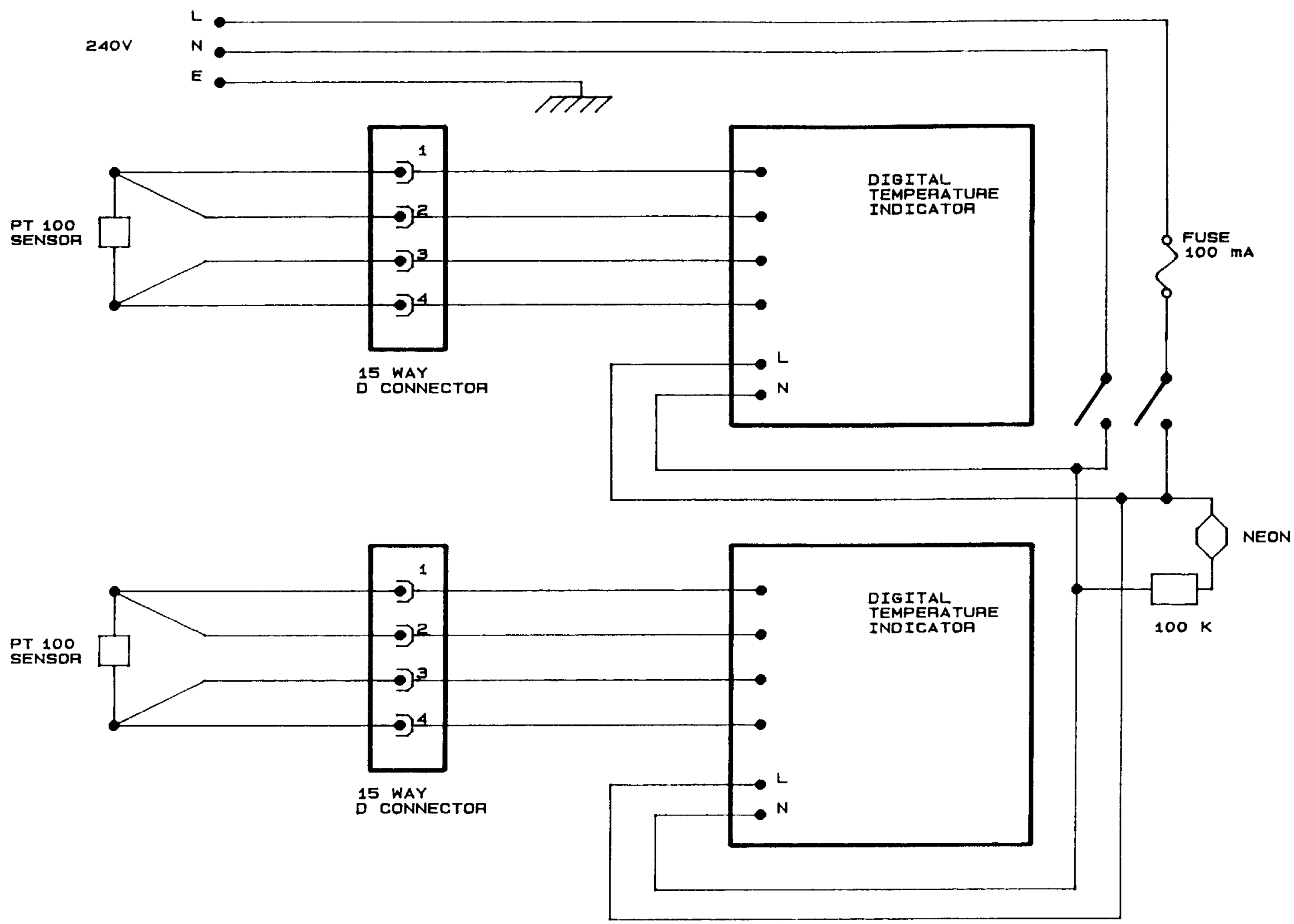


Figure B4 Circuit diagram of the temperature monitoring network.

APPENDIX C

DRAWINGS OF THE CFCAS EXTRACTION BOARD

THE CFC EXTRACTION BOARD

The following figures give the general assembly of

* the front of the CFC Extraction Board,
* the left hand side of the CFC Extraction Board,
* the right hand side of the CFC Extraction Board.

Full technical drawings are available on request.

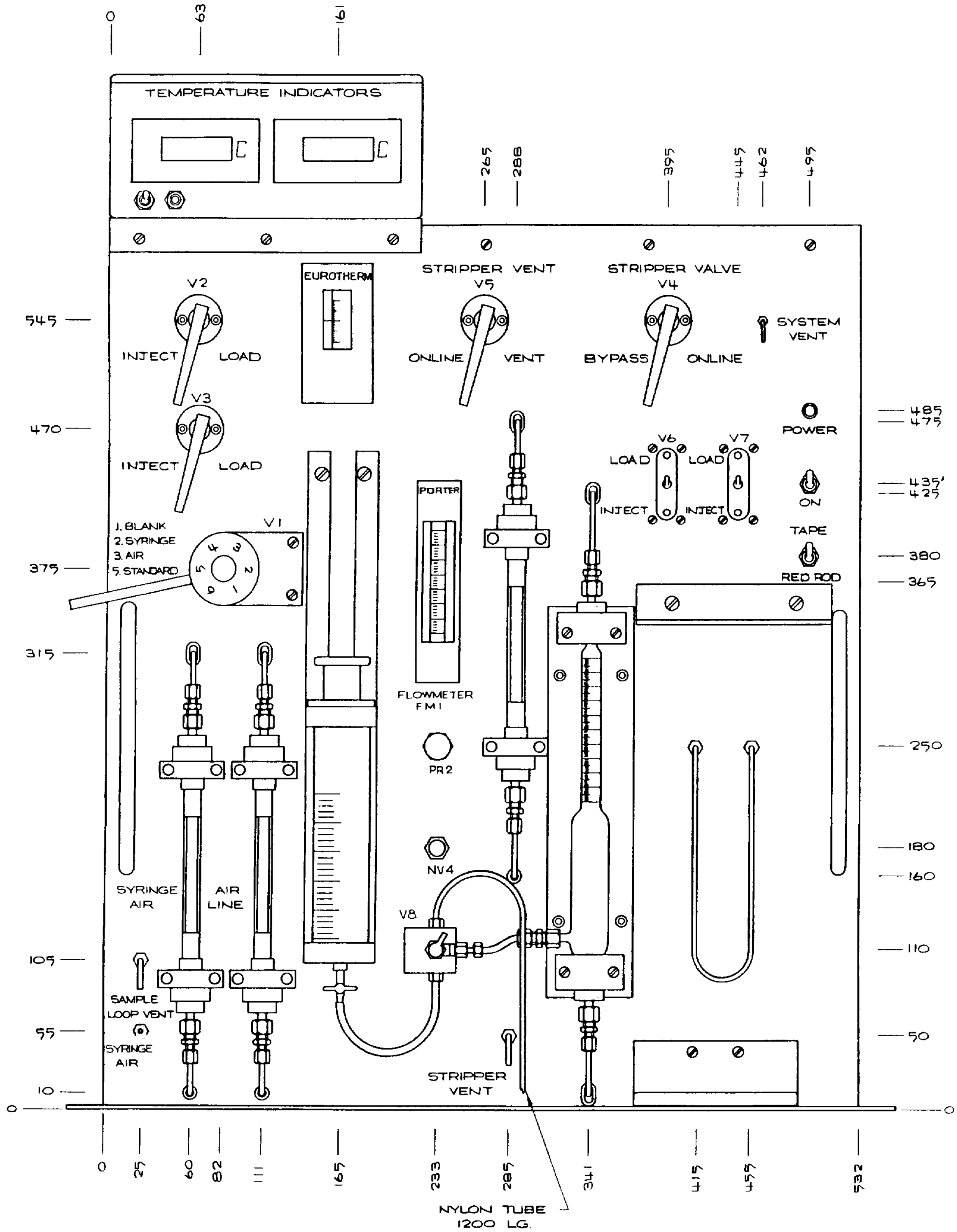


Figure C1 The front of the CFC Extraction Board.

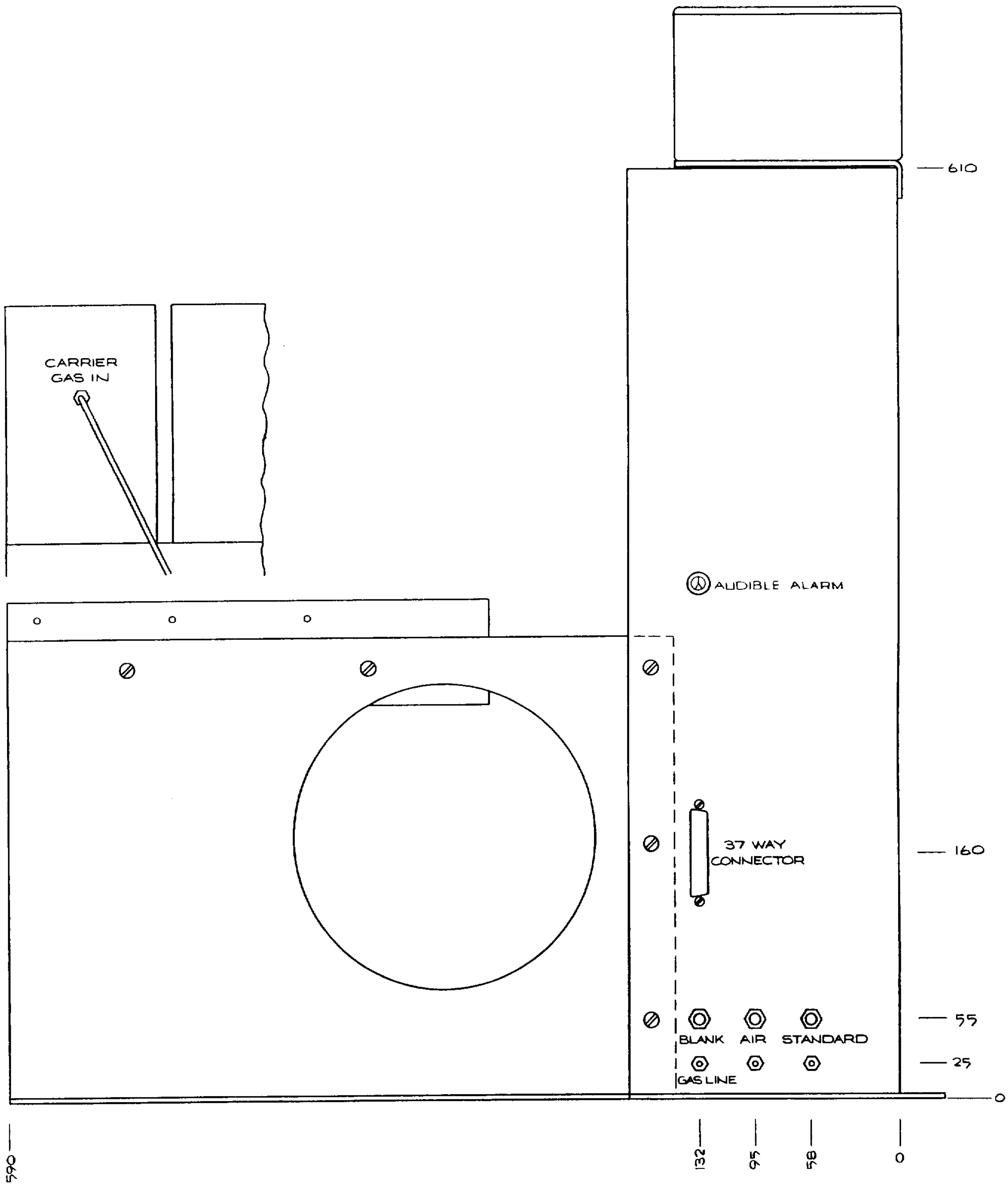


Figure C2 The left hand side of the CFC Extraction Board.

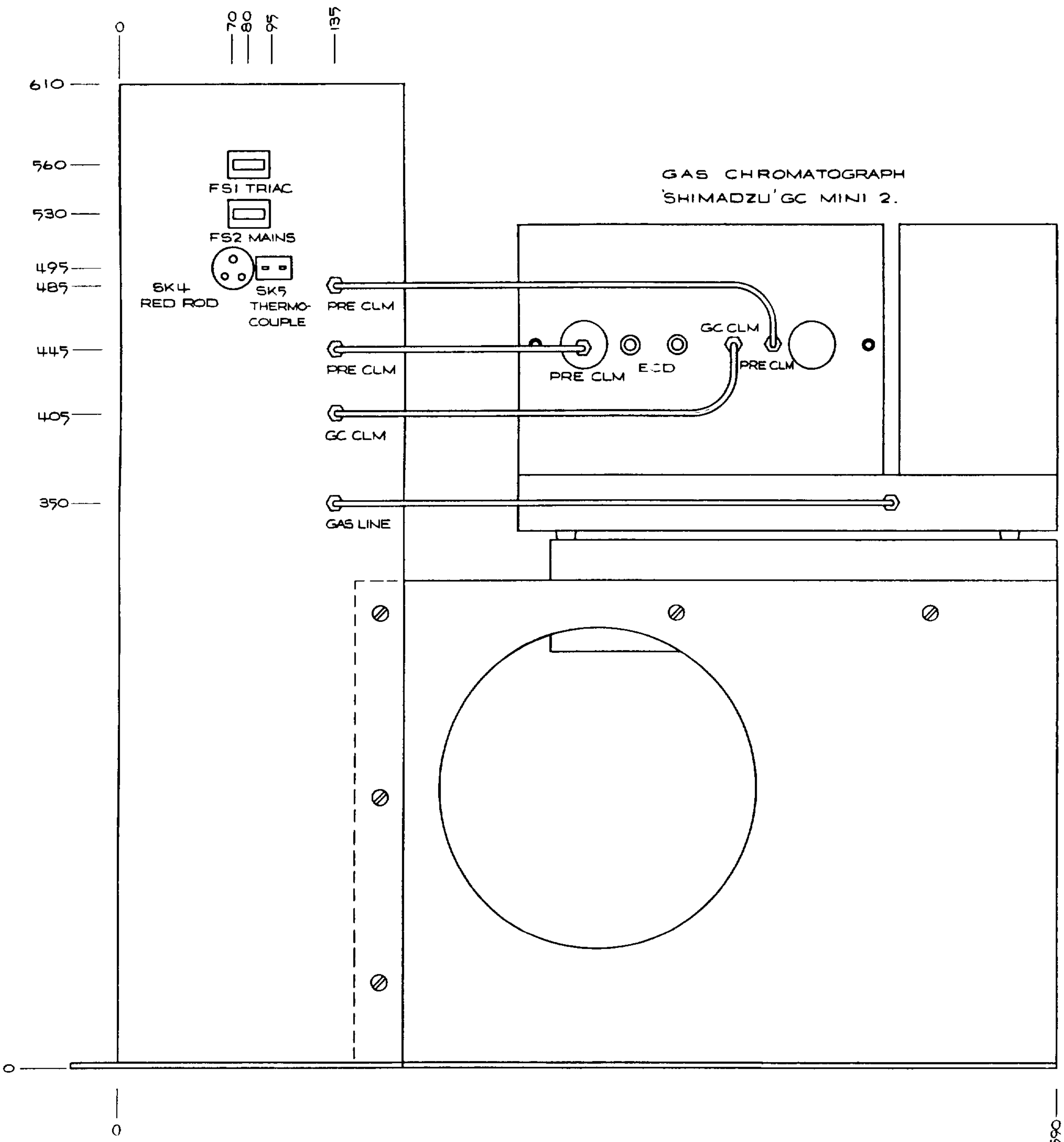


Figure C3 The right hand side of the CFC Extraction Board.

APPENDIX D

DRAWINGS OF THE CFCAS GLASS STRIPPING COLUMN

AND

DRYING TUBES

THE GLASS STRIPPER COLUMN AND DRYING TUBES

The following figures give the general assembly of

* the glass stripping column,
* the glass drying tubes,
* the drying tube casing,
* the glass stripping column mounting.

Full technical drawings are available on request.

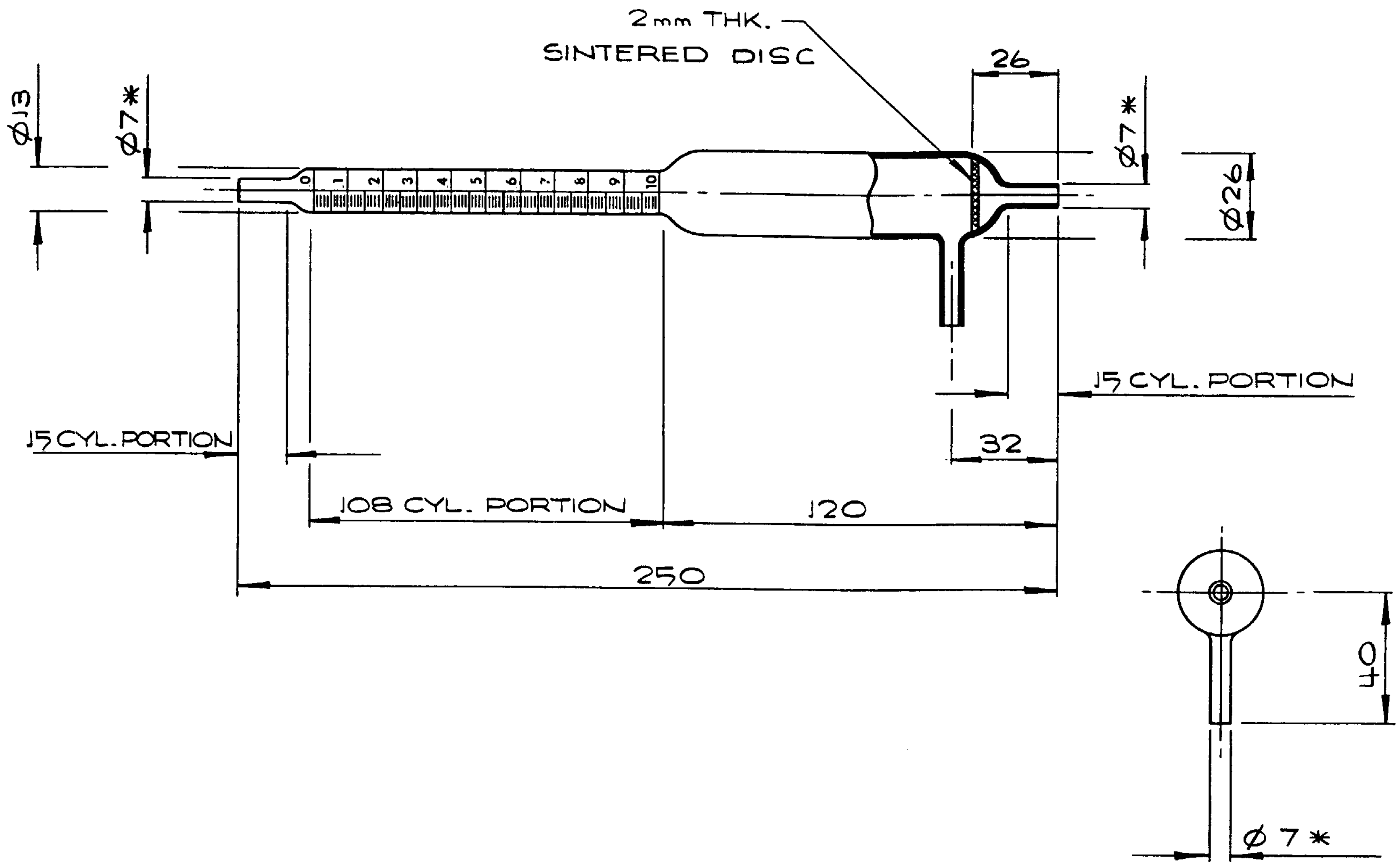


Figure D1 The glass stripping column.

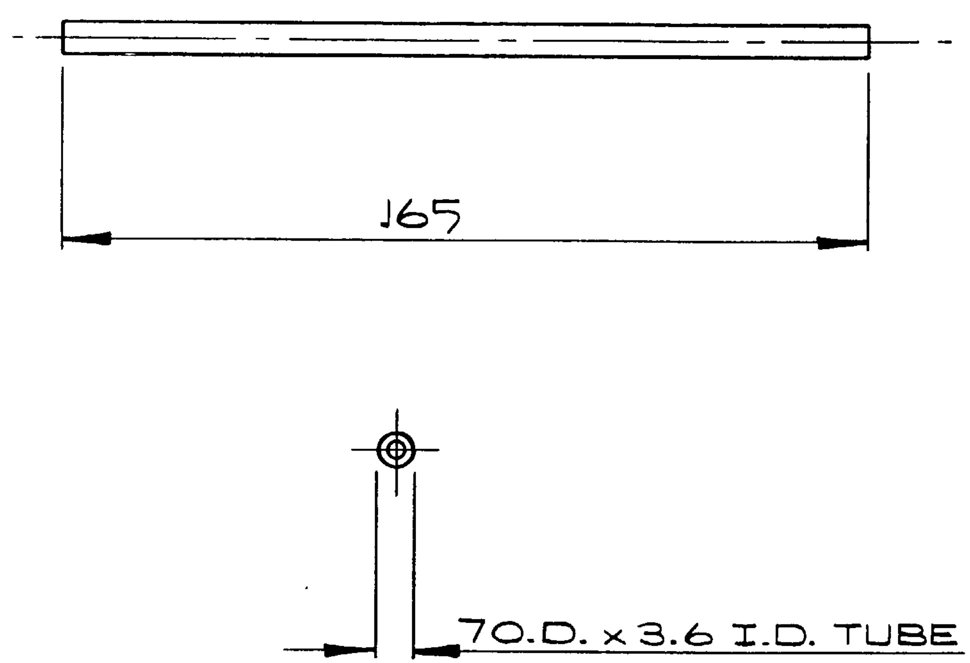


Figure D2 The glass drying tubes.

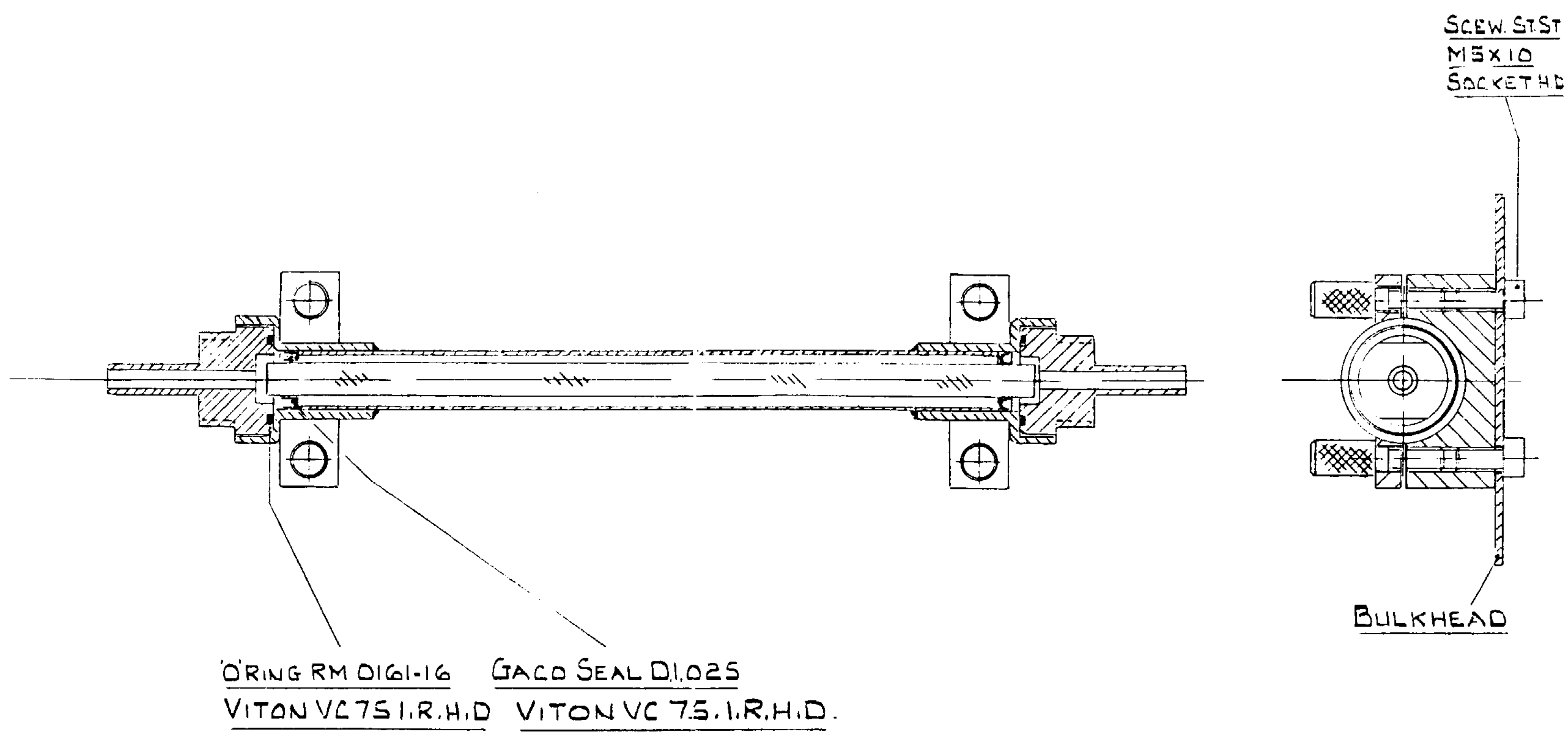


Figure D3 The drying tube casing.

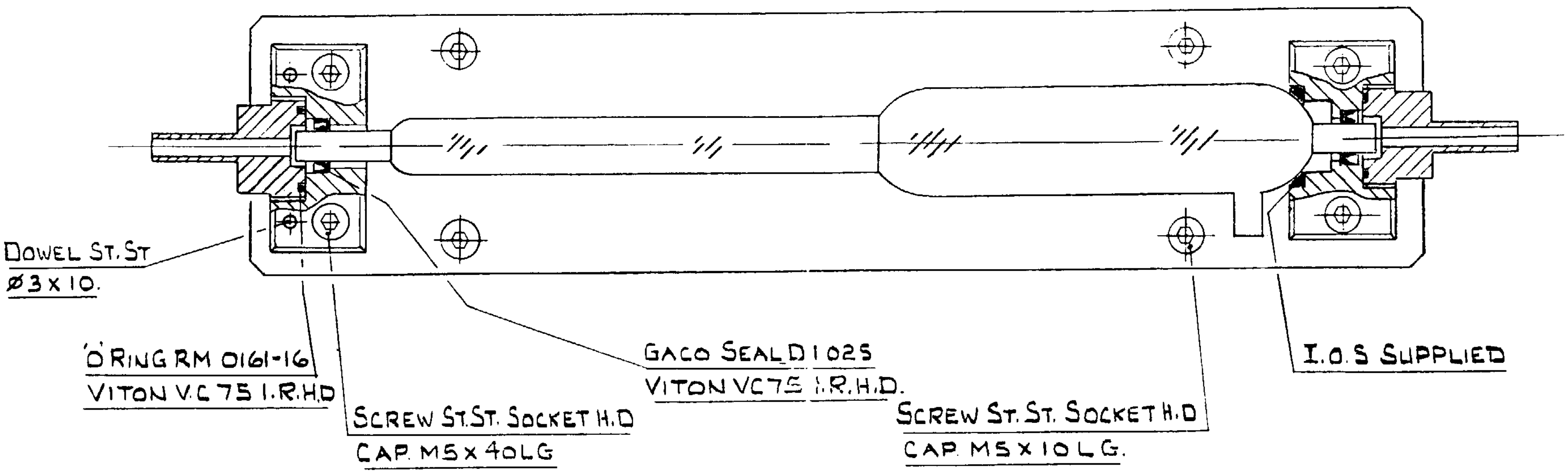


Figure D4 The glass stripping column mounting.