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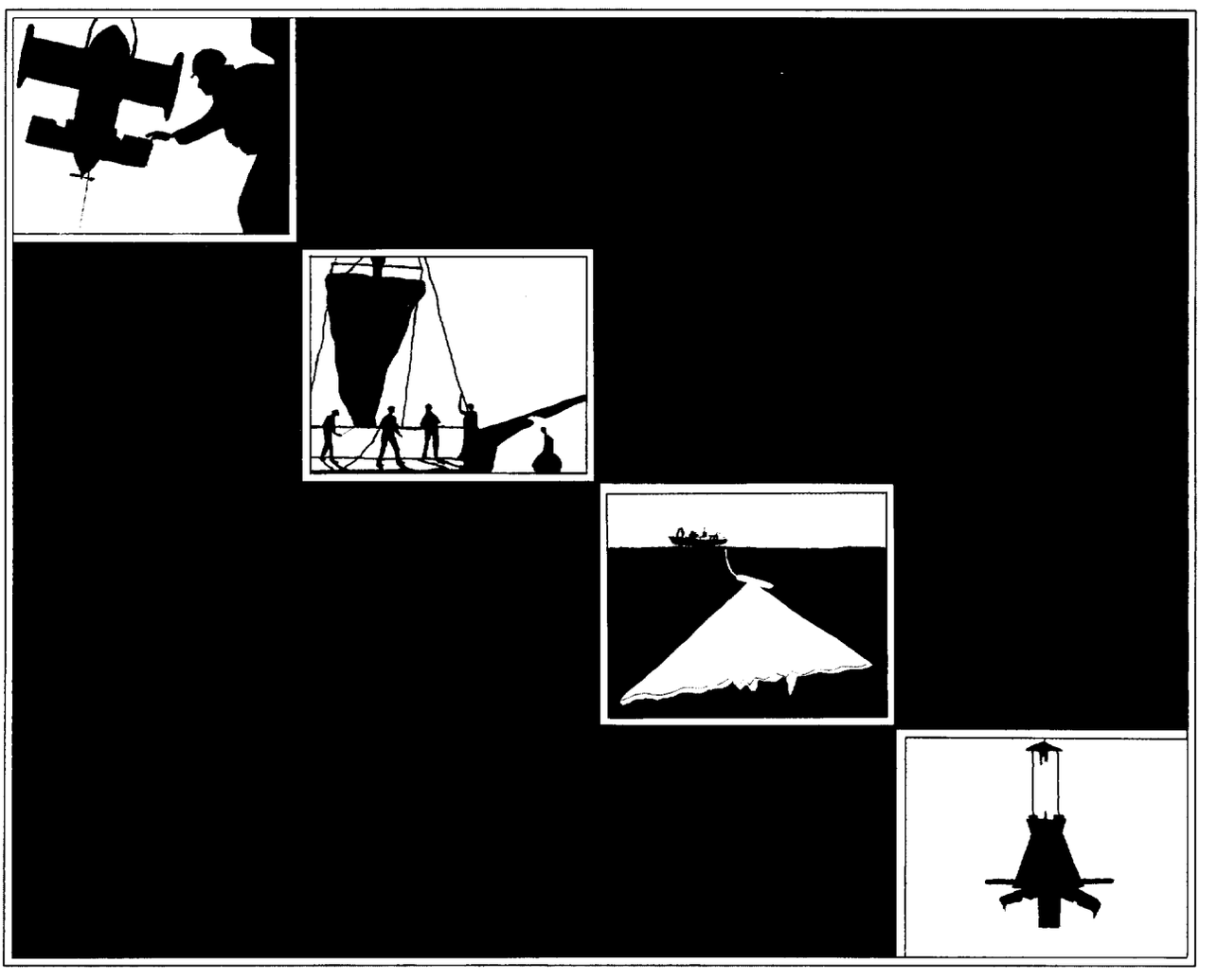
Chemical tracer studies at IOSDL - 2

D Smythe-Wright

Report No 275 1990



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Method manual for the routine measurement of chlorofluorocarbons in seawater and air

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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. This document explains the use of this equipment and the necessary precautions for the collection and analysis of samples. The analysis depends on a purge and trap technique followed by electron-capture gas chromatography. For details of the design and construction of the equipment the reader is referred to IOS Report No 274 (Chemical Tracer Studies at IOSDL, 1. The design and construction of equipment for the routine measurement of chlorofluorocarbons in seawater and air).

KEYWORDS

AGE OF SEAWATER
ANALYTICAL TECHNIQUES
CHLOROFLUOROCARBONS
CHLOROFLUOROMETHANES
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MEASUREMENT
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CONTENTS

1. INTRODUCTION

The value of Chlorofluorocarbons as time dependent tracers of ocean circulation and mixing is now well recognised. Over the past decade a number of investigations into the vertical distribution of the dissolved CFCs, CFC-11 and CFC-12 in the ocean have been carried out. There are a number of characteristics which make CFCs especially promising as tracers in the ocean. The Electron Capture gas chromatographic technique used for analysis is extraordinarily sensitive to these compounds and concentrations at the parts per trillion level found in sea water can be measured routinely at sea using specially constructed equipment. Preliminary profiles of CFC concentrations in the water column can be obtained within eight hours from the completion of the station. Such rapid sample analysis allows interesting features in the water column to be studied quickly and facilitates sampling strategies at subsequent stations. In addition CFC data is useful in chosing depths to collect samples for other tracer measurements such as ^{14}C and ^{3}H, which require land based laboratories.

Nevertheless measuring CFCs at sea is not easy. There are presently only 12 laboratories in the world carrying out such measurements routinely. There are severe contamination problems which need to be overcome. Analysis must be carried out as quickly as possible using specially designed equipment and careful sample handling. Whilst the technique used for measuring the CFCs by all laboratories is based on purge and trap gas chromatography, individual systems and the procedures used for sample collection, measurement and data handling all differ.

IOSDL has recently constructed equipment for the shipboard measurement of CFC-11 and CFC-12 in air and seawater samples. The purpose of this document is to give details of the use and maintenance of the IOSDL system. Details of the system's construction are given in SMYTHE-WRIGHT (1990). Section 2 gives an overview of the analytical principle. Section 3 deals with contamination problems and Section 4 the preparations required for seagoing and transportation. Section 5 describes how to set up the equipment on board ship and Section 6 how to collect and store seawater samples. Section 7 gives detailed stepwise accounts of the analytical methods. Section 8 gives details of routine working practises at sea and Section 9 covers results and quality control.

In order to understand this document it is important that the reader is totally familiar with the flow diagram of the system given in Figure 1 and it is recommended that they read SMYTHE-WRIGHT (1990) detailing the construction of the equipment.

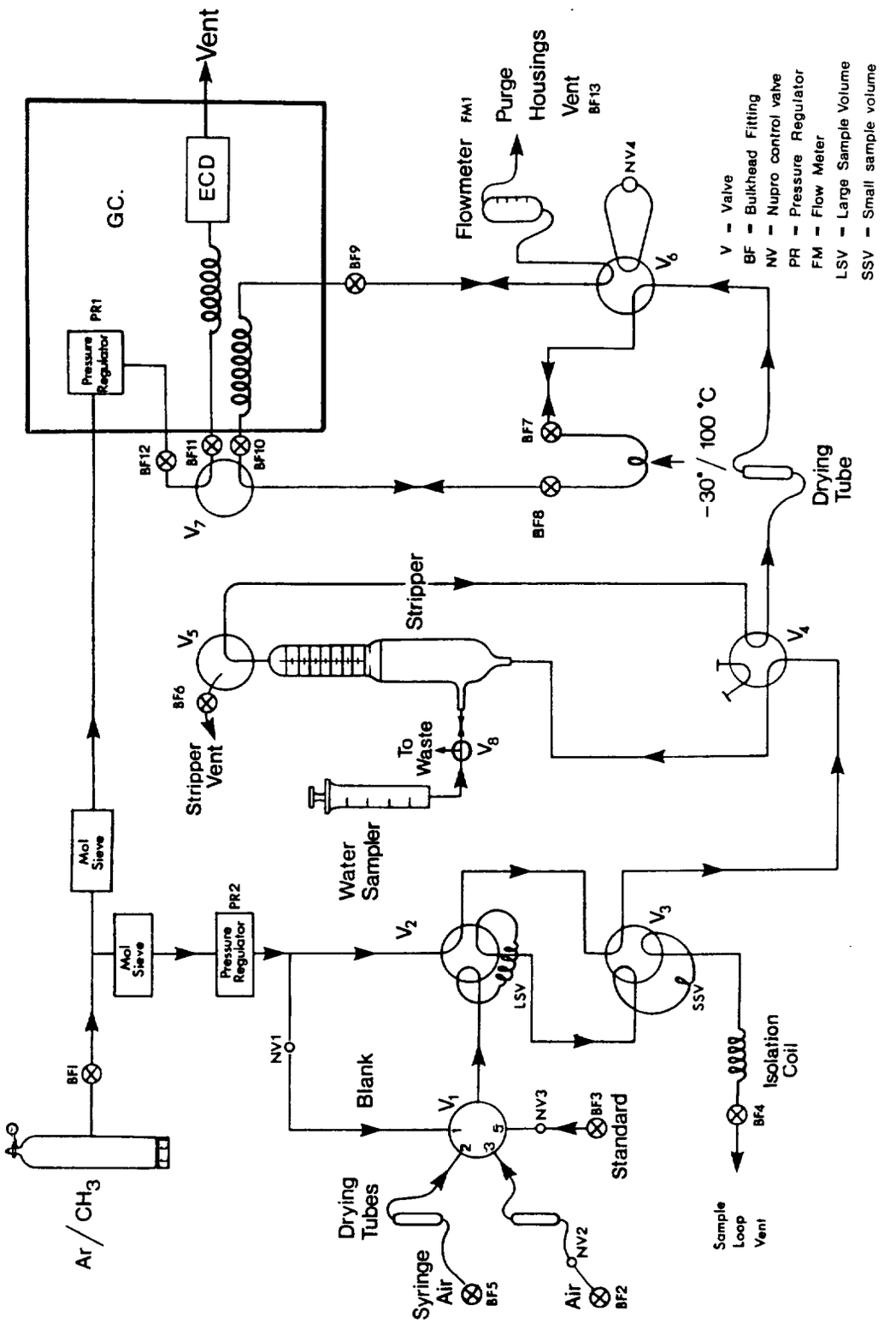


Figure 1 Schematic flow diagram of the CFC Analytical System

2. ANALYTICAL PRINCIPLE

The principle of the analysis is to use a purge and trap technique to preconcentrate and separate gaseous CFCs from other dissolved gases in the seawater and air samples and to inject them into a gas chromatograph (GC) for further separation and measurement by a ^{63}Ni electron capture detector. CFCs in air, standards and blank samples are introduced into the extraction system in gaseous form. Two calibrated sample loops are built into the system to allow known aliquots of gas sample to be injected into the trap. In contrast the dissolved gases in sea water are purged out in a graduated glass stripping chamber using a mixture of 95% Argon and 5% Methane and then flushed into the trap. The volume of water stripped is accurately measured; it is usually about 35 cc. 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 because it gives better resolution of the CFC-12 peak than nitrogen.

A two component trap, containing Porasil C and Porapak T cooled to -30°C during trapping, is used to retain the CFCs. The trap is positioned in the system so that the stripping gas stream enters the Porasil C side of the trap first. CFC-11 is held on the Porasil C while the CFC12 slowly migrates through and is quantitatively held on the Porapak T section. Most of the oxygen and dinitrogen oxide in the sample is not held on the trap but passes to waste. After a 4 minute trapping period, valve, V6 is switched electronically by a signal from the integrator and the audible alarm sounds. This is the signal to replace the cold bath of propan-2-ol surrounding the trap with a water bath at 100°C. Thirty seconds elapses to enable the trap to warm up and the gases to elute from the packing material. Valve, V7 is switched electronically and the carrier gas stream enters the trap in the reverse direction to the stripping gas and flushes the eluted gases out of the trap into the precolumn. In the precolumn the CFC-11 and CFC-12 are separated from the more slowly eluting compounds before they pass into the main GC column for further separation.

The chromatographic run begins as V7 is switched and plotting and integration of the signal from the ECD commences. The trap is flushed for forty seconds which is sufficient time for the CFCs to elute from the trap and pass through the precolumn into the GC column. Valves V6 and V7 return automatically to the trapping positions and the stripping gas stream backflushes, to waste, the slowly eluting compounds that have left the trap but are held in the precolumn. Whilst the CFC-11 and CFC-12 from the sample continue through the GC column preparations for the next sample can begin.

3. CONTAMINATION PROBLEMS

The concentrations of the CFCs in sea water are 10^{-12} moles per litre. Because of the very low levels samples can easily become contaminated from a variety of sources and care must be taken to avoid such contamination.

3.1 Atmospheric contamination

CFCs enter the ocean from the atmosphere. Consequently atmospheric CFC concentrations are often 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 prevent the ingress of the surrounding air. Details of sample handling and storage will be covered in Section 6.

3.2 Ship's environment

The ambient air aboard research vessels is often heavily concentrated with CFCs, to orders of magnitude higher than atmospheric levels, because of leakage from the large number of refrigeration and air conditioning units on board. On older vessels the coolants used in such units are mainly CFC-11 and CFC-12. Generally, if this is the case, it is almost impossible to make CFC measurements of any merit on the vessel. In contrast modern ships are usually fitted with units containing the coolant CFC-22. This contains, albeit very small amounts of, CFC-11 and CFC-12, and if there is excessive leakage from these units the concentrations of CFC-11 and CFC-12 can build up to cause contamination problems. For this reason it is important to regularly take syringe samples of laboratory and general ship air to check for potential sources of contamination. The IOS CFC analytical system has been designed to allow for the injection of such samples.

The main threat of ship air contamination is to the hydrographic bottles and during sample collection. These problems are further discussed in Sections 3.5, 4.2 and 6.

3.3 Insulation and packing materials

Many insulation and packing materials, particularly polystyrene foams, are manufactured using CFCs as the blowing agent. Such materials may be a hazard to CFC measurement because they desorb the CFCs with age.

Container laboratories on board research vessel should be used with caution for CFC measurements because experience has shown that the insulation material in commercially-available containers is likely to give off CFCs with time. Container laboratories can be used provided they are purchased as a shell without insulation. Non-contaminating materials such as, glass fibre held in place by wood cladding, can then be added as insulation.

Polystyrene or polyether foam packing materials are also a potential hazard and should be avoided. Where possible, paper towel, cotton wadding or course hair packing material should be used.

3.4 Non-metallic materials

Plastics (particularly teflon), natural rubbers and silicon rubber have the ability to adsorb CFCs from the atmosphere and subsequently desorb them in a non-linear fashion. For this reason the amount of non-metallic material in the CFC analytical system is kept to a minimum. Nevertheless because of the corrosive nature of sea water some polymeric material is required to transfer the seawater into the stripping chamber and nylon has been chosen because it is less permeable than other plastics. Nylon will not cause a major contamination problem but will adsorb some CFC with time. It is necessary to condition the nylon components fairly frequently to minimise the effect (see section 4.1 for details of the conditioning procedure).

Even metallic compounds have to be thoroughly cleaned. Often substances used during extrusion coat the surface and these are able to adsorb CFCs. It is important to wash all metal tubing and fittings with hexane (60^{o}-80^{o} fraction) and methanol (reagent grade), rinse well with distilled water and dry with a stream of nitrogen before use.

3.5 Hydrographic bottles

A number of types of hydrographic bottles are on the market, none of which are ideal for the collection of water samples for CFC measurement. There are several sources of contamination:

* The walls of the bottles are made of PVC and are able to adsorb CFCs from their surroundings with time and subsequently desorb them non-linearly. It is, therefore, important to store the bottles in the cleanest possible environment. At sea this is usually on deck or in a laboratory well ventilated with clean air. The same applies on land but it is not so easy to store bottles out of doors. In this case a well ventilated shed or an area where there is a good flow through of clean air would be suitable. Contamination from bottle walls is reduced by using bottles with large volume to wall area ratio. For this reason 10 litre bottles are used by most workers for CFC measurement.

* Rubber springs which pass through the interior of the bottle are often supplied as the basis of the closing mechanism. These are totally unsuitable and must be replaced by metal springs which have been epoxy coated. Scripps Institution of Oceanography will supply springs coated to a very high specification. Springs supplied by hydrographic bottle manufacturers are not ideal and eventually corrode.

* 'O' rings made from silicon rubber are usually fitted to commercially manufactured bottles; these should be avoided at all cost. Viton 'O' rings which do not adsorb CFCs from the atmosphere so readily are available on request. Viton 'O' rings will adsorb CFCs with time and should be conditioned before each cruise (see section 4.2).

3.6 Aerosols

CFCs have been used as propellants for many aerosol products over recent years. This practise is now declining because of concern over the ozone layer and many domestic aerosols like house-hold cleaners, hairsprays and deodorants no longer contain CFCs. However many industrial aerosols do contain CFCs or substances which in turn will absorb CFCs and contaminate. It is important that aerosols are not used in the vicinity of the CFC analytical system, the hyrographic bottles or the syringes in which the samples are collected and stored. It is good practise to keep the use of aerosols on board research vessel to a minimum and to confine their use to areas well away from the CFC equipment. Experience has shown that the CTD rosette can

sometimes develop faults where it is necessary to use such products as WD40. These should be avoided if at all possible. If there is absolutely no alternative remove the hydrographic bottles from the rosette, store well away from the working area and keep the use of all such products to a minimum.

4. PREPARATION FOR SEAGOING AND TRANSPORTATION

4.1 The CFC system

It is obvious that the CFC system should be in good working order before it is sent to sea. A series of carrier gas blanks, standards and zero CFC sea water (see section 4.7) samples should be run to make sure that there is no contamination and that all components are in good working order. Precision of air and standards should be less than 1% and there should be little or no signal from the zero CFC water.

It is sensible to check the cryocool for leakage because the flexible hose is very vulnerable to fracture and the coolant in the refrigeration unit contains CFCs. Enclose the whole system in a plastic bag and leave overnight. Syringe air samples can then be taken from the polythene bag to check if the CFC concentrations are higher than ambient. It is important not to move the cryocool when it is functioning, as this can upset the solenoid valve pressure switch in the system, also the flexible hose is more prone to fracture when cold. Because leakage from cryocools has been shown to be a problem by some CFC workers it is preferable to take at least one spare system to sea. If a cryocool fails and there is a likelihood of coolant leaking move it away from the CFC system as quickly as possible, taking care to restrict coolant loss. Carefully stop excessive leakage and seal the entire unit in polythene. Store well away from the CFC equipment. Do not attempt to fix at sea This could result in a major CFC contamination problem.

For transportation the glass drying tubes, the glass stripping chamber, the Hamilton valve and all the nylon tubing and fittings, are removed from the system. All unions are sealed gas tight with Swagelock blank fittings. The 'O' rings and distributor seals from the drying tube casings and the entire Hamilton valve with all the nylon fittings should be conditioned by heating to 70°C overnight in a vacuum oven purged with nitrogen. They should be allowed to cool in the nitrogen environment and then stored in gas tight containers for transportation to the ship.

All supplies of gases are uncoupled and all unions and inlets sealed gas tight with blank Swagelock fittings.

The CFC analytical system has been designed so that the GC can remain attached to the extraction board during transportation. This allows the gas lines coupling the extraction board to the GC to remain intact, and stops the ingress of contaminating air to the system. Continual

opening and closing of the Swagelock fittings which make up most of the connections in the system is not ideal and should always be kept to a minimum. The whole construction is bolted to a wooden base and enclosed by a wooden box. The cryocool is transported in its own carton making sure that the flexible hose will not be damaged in transit. The computer integrator is mounted in a purpose built wooden box. Ancillary equipment such as vacuum flasks, general laboratory ware, chromatography packing materials, tubing, spare fittings, chart paper, etc are packed in stout boxes.

4.2 Hydrographic bottles

It cannot be over stressed that the quality of CFC measurements is dependent on the quality of the water samples. It is important that the hyrographic bottles are thoroughly cleaned before being transported to sea. New hydrographic bottles are invariably contaminated with CFCs. The bottles should be dismantled, all 'O' rings removed and all parts washed thoroughly with hexane, methanol and distilled water. This will remove all traces of grease and solvents from the surface and most of the CFCs from the bottle walls. The bottles should be left dismantled to dry, preferably in the sun to allow all the cleaning solvents to evaporate. Solar heating will also desorb any remaining CFCs. It is important to ensure that no traces of cleaning solvents remain in the bottles and frequent washing with water and drying may be necessary.

Hydrographic bottles will condition with persistent use at sea provided the bottles are used and stored correctly; the hexane / methanol wash should only be required on new bottles. If there is a fear of contamination it can be reduced by storing the bottles open in the sun. A lockable glass construction would be ideal because this would allow ventilation, also the bottles would be stored away from permanent buildings which are likely to contaminate.

For routine use, the only preparation of the hydrographic bottles that is required is to condition the 'O' rings. This is achieved by heating overnight to a temperature of 70°C in a vacuum oven purged with nitrogen. The rings should be left in the nitrogen environment to cool and then sealed in gas tight containers for transportation to the ship. There are normally five rings in each hydrographic bottle; two fit around the end caps, one in the upper valve and two in the bottle tap. It is sensible to have a number of complete sets of rings for each bottle and keep them conditioned.

It is important to keep the time between conditioning and use as short as possible. Often it is more practical to condition the 'O' rings on board ship and fit them to the bottles as soon as they have cooled. Since a vacuum oven should be taken to sea to cope with any contamination problems which might transpire, conditioning the rings at sea is not a major task. It is not advisable to send the 'O' rings with the equipment, particularly if it is being shipped overseas. Always hand carry the rings to the ship to avoid excess contamination.

The epoxy coated springs should require no more than a routine check for damage of the coating and possible corrosion. Usually they are transported separately and fitted to the bottles when the 'O' rings are inserted. Care should be taken to ensure that the coating on the springs does not become damaged during transportation or fitting. Each spring should be wrapped in paper towel.

AT NO TIME SHOULD THE BOTTLES BE BROUGHT INTO THE MAIN BODY OF THE SHIP. If they are not required but remain on board the vessel they should be stored in their aluminium transit boxes under cover out on deck.

4.3 Vacuum oven

A vacuum oven is an essential piece of equipment for routine CFC measurements. Admittedly it is bulky and heavy to transport but it will prove invaluable when dealing with contamination problems which almost certainly will transpire. It can also be used to routinely condition 'O' rings, syringe tips, the Hamilton valve and it associated fittings. It needs to be transported along with a vacuum pump and a supply of clean dry nitrogen.

4.4 Syringes / syringe tips

The glass syringes should all be given a hexane / methanol wash to remove any grease that has adhered to them. They should be washed thoroughly with water, dried and packed with paper towel. The syringe tips should not be stored on the syringes. They should be conditioned in the vacuum oven in the same way as the 'O' rings, seals and nylon tubing and transported to the ship in gas tight containers. Alternatively they can be conditioned at sea.

4.5 Air line

The airline comprises up to 250 m length of Decabon tubing and a metal bellows pump. The tubing normally does not require any pretreatment before a cruise because the flow rate through it is usually sufficient to prevent contamination. It is well to check that the metal bellows pump is working correctly and that it is not causing a contamination problem. This can be achieved by comparing syringe air samples with those from the airline.

4.6 Carrier gas, standards and chemicals

At least two gas cylinders of 95% argon / 5% methane will be required for average use on a one month cruise. And at least two cylinders of nitrogen will be required for purging the vacuum oven and for preparing CFC-free water. It is always sensible to take a third cylinder of each gas in case of leakage from regulators, etc. Remember there is no gas delivery in the middle of the ocean so always take an excess when possible.

At least two cylinders of calibrated standard gas should be taken to sea. These should not be the primary standard but working standards. Only in exceptional circumstances should the primary standard be taken.

Small quantities of CFC -11 and CFC-12 may also be taken for use in emergency if the chromatography fails and it becomes necessary to check chromatographic identification and separation. But remember that they are going to be a major contamination hazard if the containers become fractured. They should be transported and stored well away from the CFC equipment.

At least 5 litres of both 60^{o}-80^{o} hexane and industrial grade methanol plus a supply of distilled water will be required for cleaning if severe contamination arises. To avoid problems of excessive spillage the quantity should be divided into a number of bottles.

About 250 g of fine mesh magnesium perchlorate will be required for the drying tubes. This amount will be sufficient for a 4 - 6 week cruise. Magnesium perchlorate is used as the drying agent because it has the best water retention properties of chemical dryers. However, it can be contaminated with CFCs because of its strong affinity for water and will absorb water vapour containing dissolved CFCs from the atmosphere if the storage container is not properly sealed. It is advisable to heat the perchlorate to $70^{o}C$ in the nitrogen environment vacuum oven overnight and store it in a number of small containers for use at sea rather than one large one.

At least 5 litres of propan-2-ol will be required for the -30°C cold bath. Again this should be divided into a number of smaller bottles.

Chemicals and gas cylinders are a safety hazard and must be packed according to the UN hazard regulations. The solvents are normally transported in glass bottles packed into safe-break containers. As a double protection these are then packed into a large heavy duty plastic storage bin. Gas cylinders must be firmly closed, regulators removed and the protective end-caps replaced over the valve for transportation. They should be laid flat and well secured in transit.

There are stringent regulations regarding the shipment of gases and chemicals overseas. It is therefore preferable to buy gases and chemicals locally if the quality can be assured. Obviously calibrated gas standards will have to be shipped, but since these are usually compressed air, they can be air-freighted. It is always preferable to air-freight overseas as this reduces the risk of contamination during long sea voyages.

4.7 Zero-CFC water

IOSDL has built a specially designed, transportable stripping system for purging CFCs from clean seawater using nitrogen gas. It comprises a large glass stripping vessel mounted on a magnetic stirring unit. The entire system is enclosed in a wooden box. The system should always be taken to sea so that CFC-free water is available to check for contamination. Since it is used routinely in the laboratory it should not require any pretreatment prior to transportation. Suffice it to say that the system is fragile and every care should be made to ensure it is not damaged in transit.

5. SETTING UP THE CFC EQUIPMENT

5.1 The CFC system

A photograph of the CFC equipment in is working position is shown in Figure 2. The components are from left to right, the integrator with its integral chart recorder, the CFC extraction system, and two vacuum flasks with the cryocool behind. A computer for data processing is linked to the integrator and is usually positioned to the left hand side. The equipment occupies a bench area of 3 m length by 0.85 m depth and requires a minimum height of 1.0 m. Normally the extraction system is left bolted to the base of its transit box and this is securely fixed to the bench or bulk head. Likewise the integrator is left in its wooden box for use at sea because it stops water from dripping onto the electronics and also protects the chart paper from sun light. The integrator box is constructed with a small lift up flap to allow the power leads and junction cables to pass through to the rear of the equipment. The door at the front lifts off and can be stored until the end of the cruise.

The integrator is attached to the GC via the integrator socket at the rear. It can also be attached via the chart recorder socket. 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. In the absence of a chart recorder it is best to put the integrator in the correct socket. This is because the integrator socket takes the signal prior to the instrument attenuator so that attenuation can be set entirely from the integrator, whereas the take-off point for the recorder socket is after the signal is attenuated. When using the recorder socket for the integrator the instrument attenuation must be set to 1 and the attenuation adjusted as required at the integrator. If the instrument attenuation is not set to 1, the signal will be attenuated twice and errors can result when comparing data.

Once the hardware is securely bolted down, three glass drying tubes are filled with magnesium perchlorate and fitted in the system.

5.2 Carrier gas and standards

Gas cylinders are a hazard at sea. They must be securely fixed to the ships bulk head and deck. Usually the argon / methane carrier gas and nitrogen for the vacuum oven is stored outside the laboratory and the gases piped to the equipment. In contrast, calibrated gas standards are

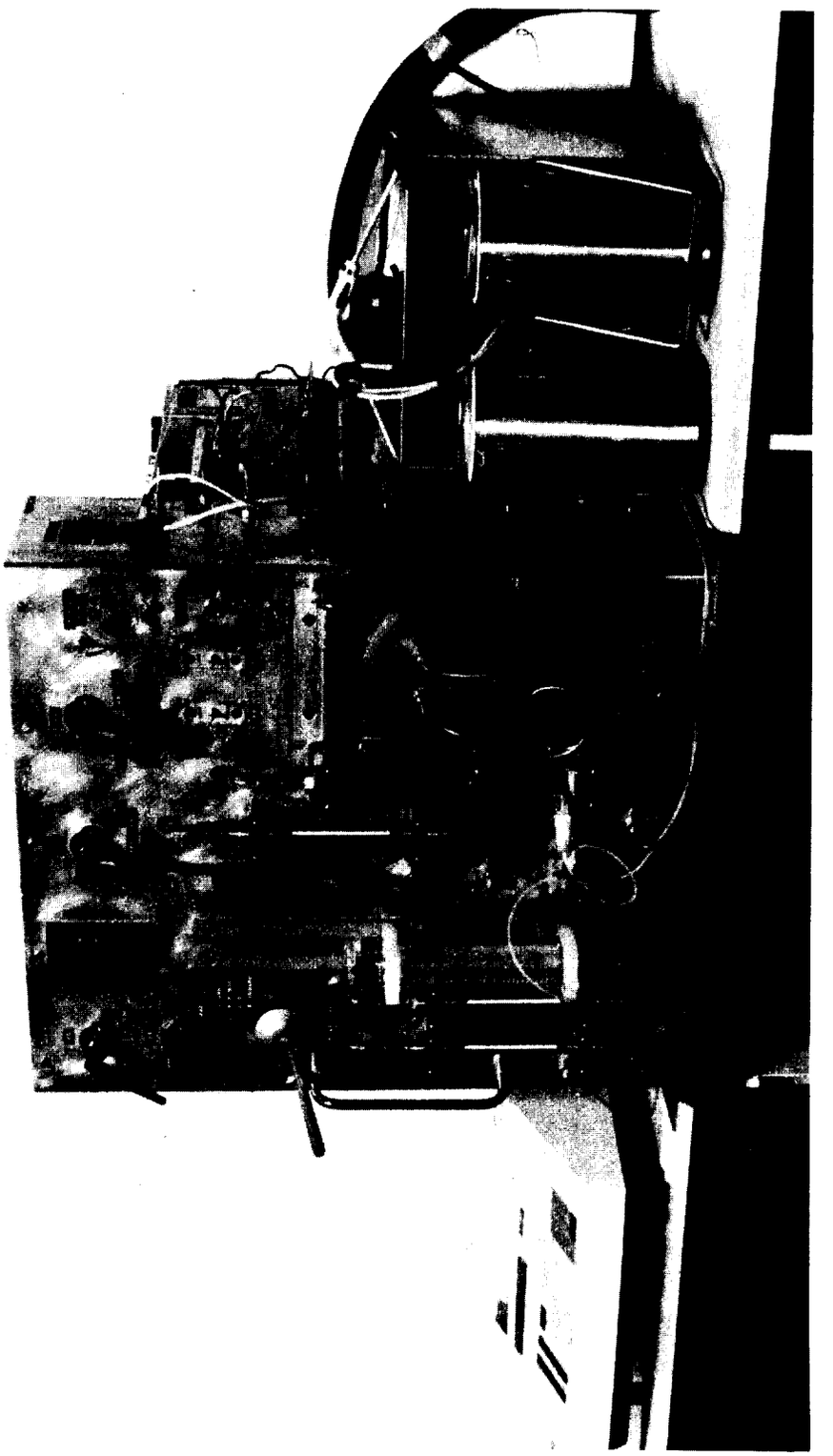


Figure 2 The CFC Analytical System in its working position

securely fixed in the laboratory because they need to be kept at room temperature. Also they are usually in aluminium cylinders and these will severely corrode if exposed to sea salt. Both the carrier gas and standard cylinders are fitted with special regulators that have metal diaphragms and no teflon parts. The use of PTFE tape for seating the regulators should be kept to a minimum. Experience has shown that small quantities do not pose a problem. Both supplies are connected to the appropriate inlets of the extraction board (see Figure 3) using 1/8 inch stainless steel tubing. If possible the tubing should be one single length. The carrier gas pressure is reduced to 70 psi at the regulator and the standard to about 20 psi. The carrier gas flow through the system is adjusted using the pressure regulator in the GC to a rate of approximately 30 cc per minute as measured at the ECD vent. The stripping gas flow is adjusted using a Porter Instruments pressure regulator mounted on the extraction board. The stripping flow is normally about 50 cc per minute as measured at the purge housing vent on the front of the extraction board. Gas flow rates through the system are critical for good quality measurements. They have to be balanced to prevent surging when the valves are switched and finely tuned to achieve optimum stripping and chromatographic separation. This will be dealt with in Section 9. Suffice it to say here, the reader should be totally familiar with the gas flow criteria and should bear it in mind when setting up the equipment.

5.3 Air line and GC exhaust vent

The air line and GC exhaust vent is usually installed whilst the vessel is at the dockside. Air samples are taken directly from the bows of the ship using a length of Decabon tubing and a metal bellows pump. The inlet should be positioned as far forward and as high as possible above the deck and the tubing fed back into the laboratory. It is preferable to have the line as a single length. The size of the metal bellows pump determines the flow rate. The IOSDL system flushes several litres per minute of air into the laboratory. The line should be set up so that the air flow is split after the pump. Using 1/8 inch stainless steel tubing approximately 100 cc per minute of air is passed into the extraction system through the air line connection on the left hand side of extraction board. This flow rate is adjusted using the Nupro needle valve immediately above the air line inlet. The remaining air flow is vented around the metal bellows pump to prevent laboratory air, which could contaminate, entering the pump. To check that contamination is not occurring air samples from the air line should be frequently compared with syringe air samples collected from

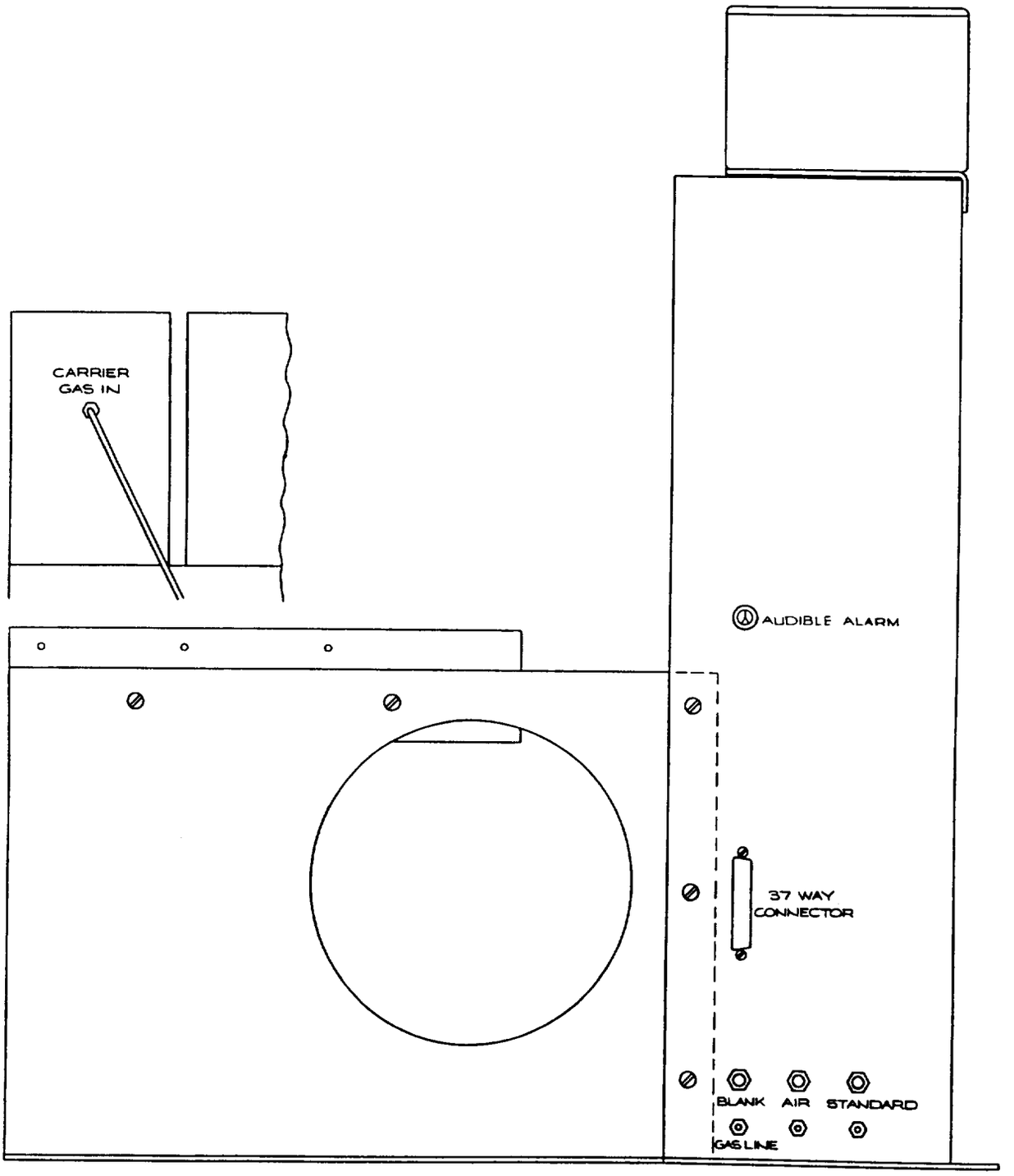


Figure 3 The Left hand side of the extraction board showing the gas inlets

the bows of the ship. It is very important to make such a comparison as soon as the air line is installed as, although not impossible, it can be difficult to relocate the air line once the ship is at sea. No appreciable difference should be noticed. (On land the air line is usually positioned high up on the outside of the building where it will sample a source of prevailing clean air).

A copper tube must be fitted 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) to allow the exhaust gases to vent. This usually means up a mast or ship's stay. (On land the exhaust usually vents into a fume hood or onto the roof).

5.4 Conditioning molecular sieves and bake-out

Molecular sieves have been incorporated in the CFC analytical system to remove traces of CFC-11, CFC-12 and other potentially interfering gases such as dinitrogen oxide in the carrier gas. Under normal usage the traps last about 1 week after which they become saturated and the contaminating gases begin to break through: it is apparent because the analytical signal becomes noisy and/or interfering peaks appear in the chromatography. The sieves must then be regenerated. This is done by switching the selector switch positioned on the right hand side of the extraction board to the heating tape position. The Eurotherm controller is set to 250^{o}C and the system left for between 8-12 hours. During this period the gas flow through the system is left as normal. The compounds retained on the sieves are quickly eluted from the traps and vent through the extraction board. The terminology used for this procedure is bake-out. Its function is twofold; the sieves are regenerated and the hot gas removes any traces of contamination which may have entered the system during transit.

To ensure that the system is entirely clean at the beginning of a cruise, it is important to carry out the bake-out procedure before commencing analyses. It is recommended that this be done as soon as the equipment is set up and bolted down. It should also be done at frequent intervals during a cruise. However, it must be remembered that bake-out will cause changes to the chromatography. For maximum accuracy and precision a new calibration curve must be constructed before further use. This will take time and it is advisable to allow between 18 and 20 hours to carry out the bake-out procedure correctly. For routine working at sea it is advisable to plan bake-outs for times of minimum workload. If there is a major contamination problem then downtime will obviously result.

5.5 The gas chromatograph

The GC should be switched on as soon as possible after the initial bake-out has been completed because it will take some time for the baseline to stabilise. There is little point switching it on during bake-out. The procedure is as follows;

* Set the carrier gas to 3.0 kg cm^{-1} at the GC pressure regulator. This should approximate to 30 cc min^{-1} as measured at the ECD vent. If in doubt check and make sure the exhaust vent is subsequently sealed gas tight.
* Set the detection temperature to 300°C. Open the GC oven lid.
* Make sure the temperature programme switch is in the off position and the column temperature below ambient.
* Switch on the power.
* Set current to 1.0 or 2.0 nA. The latter will give better sensitivity and should be used where possible even though the baseline noise level may be higher.
* Wait until the detection temperature is reached. Set the oven temperature to 70°C and close the oven lid.
* Once the oven has reached temperature start plotting the chromatographic signal and wait for the baseline to stabilise. This may take over 24 hours.

The reader is referred to the GC handbook for general use, maintenance and trouble shooting. It is important that no highly electro-negative compounds such as oxygen enter the GC as these will swamp the ECD. If the ECD appears to become contaminated increase the detection temperature to 350°C and leave overnight. DO NOT EXCEED THIS TEMPERATURE. IT IS THE MAXIMUM RECOMMENDED BY THE MANUFACTURER.

REMEMBER THAT THE ECD IS A ^{63}Ni SOURCE AND THAT GENERAL LABORATORY RADIOACTIVE LICENCES DO NOT PERMIT SEALED SOURCES TO BE OPENED. If there is any doubt about the integrity of the detector switch the instrument off, isolate it from the extraction board and seal all entrances and exits gas tight. Replace the GC with the spare and return the defective one to the manufacturer.

5.6 Hydrographic bottles

If the 'O' rings have not been conditioned before going to sea or if the conditioning procedure occurred sometime back and there has been a risk of contamination on route, then the 'O' rings should again be heated in the vacuum oven before being fitted into the hydrographic bottles. At no time should the bottles be brought into the main body of the ship. 'O' rings and springs must be fitted in a well ventilated clean air environment. UNDER NO CIRCUMSTANCES should silicon grease be used on the 'O' rings to improve sealing capability. If there is leakage change the 'O' ring or if all else fails replace the bottle. Care must also be taken when handling the bottles to ensure that no grease is transferred from one's hands. Make sure that the epoxy-coating on the springs is not damaged. Even the slightest chip will corrode and this will effect oxygen determinations.

5.7 Zero-CFC water supply

The CFC-free water system should be securely bolted to the bulkhead or bench at the dockside and a supply of nitrogen attached to the gas inlet fitting at the front of the unit. The glass stripping vessel should not be filled with seawater at the dockside unless a clean supply can be guaranteed. However a supply of CFC free water will be required to check for contamination prior to the first hydrographic station so it is important to set up the system as soon as clean seawater is available. The water should be purged with nitrogen for about 12 hours before use.

5.8 Syringes

Once the CFC system is up and running the syringes should be unpacked, checked for damage and clean syringe tips fitted. If there has been any chance of contamination during transit, the tips should be reconditioned in the vacuum oven before use. The syringes should be washed 3-4 times with clean seawater and left filled with the syringe barrels under positive pressure (usually with an elastic band) in a bath of clean running seawater. After a few hours air bubbles will appear in the syringe as the glass becomes wetted. The syringes should be emptied and carefully refilled to evacuate the air. This procedure should be repeated until no air bubbles appear in the syringe. The syringes should be stored full of seawater under a stream of clean running seawater for the entire cruise.

6. SAMPLE COLLECTION AND STORAGE

It cannot be stressed too strongly the need for carrying out all sampling in a very well ventilated environment. The precision of the technique relies heavily on the collection of good quality contamination free samples. At no point should air be allowed to enter a sample. Clean air is high in CFCs but ship air can be orders of magnitude higher.

THE CONTAMINATION FROM THE ATMOSPHERE IS ORDERS OF MAGNITUDE HIGHER FOR CFCS THAN ANY OTHER ROUTINELY MEASURED TRACER.

SAMPLES FOR CFC ANALYSIS MUST BE COLLECTED AS SOON AS THE ROSETTE IS INBOARD.

THEY SHOULD ALWAYS BE THE FIRST SAMPLES DRAWN FROM THE HYDROGRAPHIC BOTTLES.

ALWAYS DRAW THE DEEPEST SAMPLES FIRST.

Seawater samples are collected directly from the hydrographic bottle by inserting the syringe tip into the bottle tap. The filling procedure is as follows:

* open the tap at the bottom of the bottle, check that the bottle is not leaking and then open the air valve at the top. If water comes out of the bottom tap before the air valve is open then it is likely that air may have already entered the bottle and the sample contaminated. If contamination is suspected, flag the sample.
* Allow water to flush through the tap and over the syringe tip for a couple of seconds then insert the syringe tip into the tap.
* Let the syringe fill by gravity do not pull back the barrel just rotate it so as to keep it moving freely. Try not to let any air enter the syringe. Fill the syringe about half full.
* Holding the syringe vertical with the tip uppermost depress the barrel and force out any air bubbles that may have formed.
* With almost a continuous action finish emptying the syringe and put the tip back into the bottle tap. MAKE SURE YOU DON'T PUT WATER BACK INTO THE HYDROGRAPHIC BOTTLE. Refill the syringe making sure that no bubbles enter.
* Fill and empty the syringe at least three times further. Two fillings should be above the 100 cc graduation mark.

* On the final filling close the syringe tip tap before removing the syringe from the bottle and then close the hydrographic bottle tap. In this way air in not sucked back into the bottle. Do not reclose the air valve at the top (see section 8.2 for reasoning).

* If at any stage air enters the syringe it must be flushed again at least three times before the sample is taken.

Once samples have been collected, the syringe barrels should be subjected to positive pressure, usually with an elastic band arrangement, to stop ingress of air or water into the syringe. The syringes should then be totally immersed in a bath of clean surface seawater which is continuously being replenished. This is usually achieved by placing a rack arrangement, which acts as a holder for the syringes, in one of the ships sinks. This is fitted with a drain which syphons off the water when it reaches a certain height and prevents overflowing. The supply of clean seawater is fed in through the bottom.

Ideally it would be preferable to have the hydrographic rosette outside on deck throughout the cruise and all samples taken out doors. However this is not always practicable. In poor weather conditions rain and spray can easily contaminate salinity and other samples. Particles from the ship's funnel can be blown down and cause problems. For this reason it is more sensible to have the area on deck covered with a three-sided temporary-type structure probably made of wood, the sides of which are constructed to let the wind blow freely through. Alternatively the rosette can be moved into a specially designed water bottle laboratory which has large doors that can be left open continuously at sea. It is imperative that the laboratory has a free flow of continuously replenished clean air.

7. ANALYTICAL METHODS

7.1. Setting up the analytical programme software

A simple Shimadzu BASIC programme has been written to drive the electronic valves and to operate the audible alarm. Coupled to this, there is a programme which calls up the subroutines supplied by Shimadzu for logging and integrating the chromatographic signal. (Details of the integration parameters will be discussed in section 9). The program is stored on a ROM in the integrator and is called up by depressing 'run'. It is conceivable that the programme could be lost due to sudden failure of the power supply or the back up batteries in transit. Normally the back up batteries last about one month; they are recharged under normal use. A copy of the program is given in Appendix 1. It is a tedious task to type it in but should not take too long. Remember to check that it is functioning correctly and the timing controlling the electronic valve switching is correct before continuing with the analyses.

Program timing is an essential part of the analytical technique. It is important that sufficient time is allowed for the trap to heat and cool and for optimum stripping and trapping efficiency. Also the time allowed for the CFCs to elute from the trap and pass into the GC column must be adjusted to allow all the CFCs to pass through, but at the same time be sufficiently short to stop unwanted compounds entering the GC column and causing unnecessary signals on the chromatogram.

7.2 Start up procedure

At the start of each working day or beginning of a station the following procedure is required.

* Switch the power selector switch to the Hot Rod position. Ensure that the Eurotherm is at the 100^{o}C setting. Switch the power 'on' (switch on the front of the extraction board) and heat the water bath.

* Ensure that valve V6 is in the 'load' position and place the heating bath under the trap. The bath does not need to be up to temperature at this point. It can reach temperature while heating the trap. Make sure that the trap is heated at full temperature for at least ten minutes. This will drive off any contaminants which may have entered since last used. If this is the first run for some time then it is preferable to heat the trap for about 30 minutes.

DO NOT LET THE WATER BATH RUN DRY. This will not only damage the Hot Rod and the vacuum flask but could result in irreparable damage to the trap itself. Porasil C does not like being heated above 120°C.

* Check the level of the propan-2-ol in the cold bath. The trap has been designed so that the packing material is in the lower part. However, as much of the trap as possible should be immersed in the liquid. Check that the temperature is an even -30°C. Often temperature layering will occur in the cold bath so it should be periodically stirred during working.

* Check the magnesium perchlorate in the drying tubes. If is looks at all damp, particularly at the bottom where the gas flow enters then it must be replaced. Damp perchlorate will adsorb CFC-11 from the samples.

* Open the standard gas cylinder and flush the regulator and the intake line three times. Set the regulator pressure to 20 psi.

7.3 System blanks and standards

When gaseous samples are being analysed valve V4, the stripper valve, is switched to 'bypass' and the stripping column is isolated out of the system. The procedure for analysing system blanks and standards is virtually identical and is as follows:

* select either 'position 1' (for blank) or 'position 5' (for standards) on the selection valve and let the gas flush through the system for two minutes. Valves V2 and V3 must be in the 'load' position at this stage.

* Manually switch V6 to 'inject'. Place the cold bath under the trap. Depress 'run' on the integrator to start the 30 second alarm.

* During the 30 seconds wait time take temperature readings for either one or both sample loops as displayed on the digital readouts at the top of the extraction board. Take the pressure reading from the barometer fixed to the side of the integrator box. Make a note of the readings.

* After 30 seconds the audible alarm will be heard.

* Switch the selection valve to 'position 2' or 'position 6' (ie the 'off' positions). Wait approximately 8 seconds to allow the gas pressure in the valves to come to equilibrium.

* **For a system blank, or a routine standard to check for sensitivity changes and drift**, only one large loop of sample is injected. Simultaneously switch V2 (the large sample loop) to the 'inject' position and V6 to 'load'. Press '7' on the integrator; this will activate the audible alarm after a four minute delay, ie at the end of the trapping time.

* **For multiple standard injections** switch either V2 (large loop) or V3 (small loop) or both to the 'inject' position and V6 to load and depress 7 on the integrator to activate the four minute alarm. *With the aid of a stop watch wait 30 seconds. Switch V1 to 'position 5' and V2 or V3 or both back to 'load'. Wait another 30 seconds. Switch V1 to 'position 6' (ie 'off') and the sample valve(s) to 'inject'. Repeat from * as required to inject up to four samples. The audible alarm will bleep after 4 minutes. Do not exceed the normal trapping time. This is because, with time, CFC-11 breaks through the Porasil C packing material and is trapped on the Porapak T and unless trapping time is consistent for all standards and samples comparison is not like for like.

* At the end of the trapping time V6 will be changed automatically to the inject position by the software. Switch sample valve(s) back to the 'load' position immediately.

* Place heating bath under trap and press 'start' on the integrator. The chromatographic run will begin and the chromatogram printed by the integrator.

* After 40 seconds V7 will automatically switch to the 'inject' position and gas flow will be reversed through the trap.

* After 65 seconds the more quickly eluting compounds including the CFCs will have passed from the trap, through the precolumn and into the GC column.

* V6 and V7 will automatically return to the load position.

* After 300 seconds the chromatogram will terminate. The integration parameter codes, the retention times and the peak heights for the run will be printed out by the integrator.

* Processing of the next sample can begin once V6 and V7 return to the load position. However remember that calibrated standard is precious so do not overflush the gas injection system; two minutes is quite sufficient.

7.4 Constructing calibration curves

Two sample loops of differing 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. The volume of the larger sampling loop has been chosen so that the amount of F-12 injected in one aliquot of standard (whose F-12 concentration is close to that of modern air) is in the same range as that for a 30 cc surface seawater sample.

Calibration curves should cover the range for both gases and seawater samples from zero (ie system blank) to above the highest measured amount. There is no need to extend the calibration curve beyond this range. Replicate calibrations should be run for one large loop of standard and for those multiples which correspond to surface water CFC concentration. The minimum calibration curve is usually one small loop and up to 4 multiple injections of the large loop. It is impossible to inject more than four large loops in the four minutes trapping time. Often four large loops are impossible, This is because the passage time through the system is slow and the compounds from the final injection which are not normally retained by the trap, do not have time to pass through and are swept into the GC column ahead of the CFCs and mask the early part of the chromatogram.

It can take some time to carry out the analyses for a calibration curve but where possible a curve should be constructed each day. An ideal curve would consist of the following;

* one small loop
* one small loop plus one large loop combined
* two small loops plus two large loops combined
* two small loops
* three small loops
* four small loops
* one large loop
* two large loops
* three large loops
* four large loops

Replicates of one small loop, one large loop and two large loops should be carried out.

A minimum calibration curve curve would consist of:

* one small loop
* two small loops
* one large loop
* two large loops
* three large loops

It is preferable not to run all the small or all the large samples consecutively, but to intersperse the order for example, 2 large followed by 3 small, 1 large, 4 small, etc.

IT IS IMPERATIVE TO CONSTRUCT A NEW CALIBRATION CURVE AFTER A SYSTEM BAKE-OUT.

7.5 Seawater samples

Sea water samples should be left under water until immediately before they are required. Each syringe is positioned on the extraction board in turn. Deep water samples should always be analysed first since these usually have the lowest values and are more susceptible to contamination.

* Attach the short flexible Nylon tube from the 3 way Hamilton valve to the Pharmaseal syringe tip. The other ports of the valve are connected to waste and to the nylon Swagelock reducing adaptor (1/4 -1/8 inch) which fits onto the side arm of the glass stripping column. See Figure 4 to show the orientation of the valve; the waste outlet should always be the one which points upwards to allow air bubbles, trapped in the nylon tube when changing the syringe, to escape.

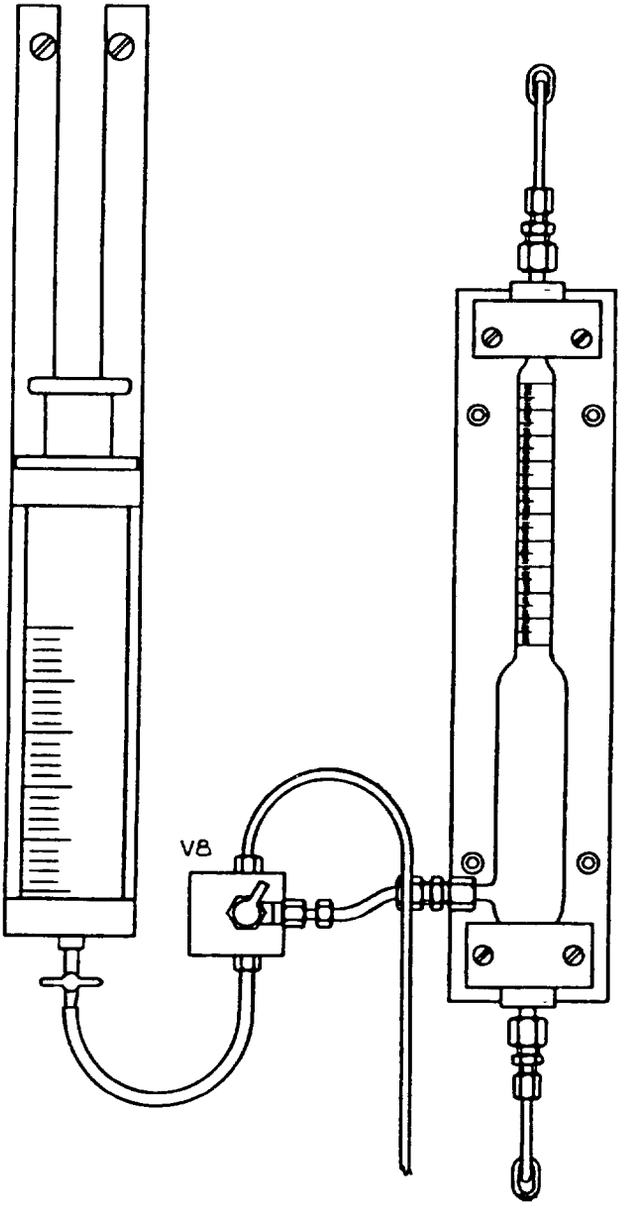


Figure 4 A schematic of the Hamilton Valve showing the orientation of the ports and the connections

* The following should be carried out in one continuous action. Open the Pharmaseal tap and place pressure on the syringe barrel. Open the Hamilton valve so that a small volume of water passes through the valve to waste. Ensure all gas bubbles are flushed out. Still keeping pressure on the syringe barrel open V5, the stripper vent# and as simultaneously as possible change the position of the Hamilton valve to allow water to fill the stripping column. Fill the column to about the 14 cc mark (this is about 35 cc of water). Close V5, close the Hamilton valve and close the Pharmaseal valve. Take an accurate reading from the calibration marks of the quantity of water in the column. The water sample is now ready for stripping.

* Switch V6 to the 'inject' position and place the cold bath under the trap. Depress 'run' on the integrator.

* After 30 seconds the audible alarm will bleep.

* Simultaneously switch V4 to the 'inline' position and V6 to 'load'. Depress '7' on the integrator. Purge gas enters the bottom of the stripping column and passes through a course frit into the water sample. The coarse frit breaks up the gas stream to give an even flow of bubbles and consequently even purging. It is important to watch that water does not leak from the column when purging; this can happen if the Hamilton valve has not been closed correctly.

* After 4 minutes the audible alarm will bleep to indicate the end of the trapping time and V6 will automatically change to the 'inject' position.

* Switch V4 to 'offline'. Bubbling in the stripping chamber will then cease.

* Change the cold bath for the hot bath and depress 'start' on the integrator. The chromatographic run will then proceed as described for blanks and standards.

* Once V6 and V7 have returned to the load position the stripping column can be emptied.

Valve V5 has been incorporated in the CFC analytical equipment in order to vent gas displaced during the filling process. To stop the ingress of air during the venting procedure a length of stainless steel tubing is run from V5 to the lower front of the extraction board. Care should be taken during the filling and emptying procedure to prevent air backflushing into the system.

* Switch V4 to the 'online' position and orientate the Hamilton valve so that the water in the stripping column flushes to waste. Gas will bubble through the column and drive the water out. Continue purging until all the sample is expelled. Close V4 and the Hamilton valve. Processing of the next sea water sample can then begin.

It is important to empty the stripping column as described. Purge gas is bubbled through the column during the draining process to keep it free of CFC contaminated air. It is better during routine working not to leave the column empty. Only drain it when ready for the next sample and do not leave a sample standing in the column for more than a couple of minutes before analysing.

7.6 Sample handling blanks and restrips

Sample handling blanks should be based on deep samples which are expected to have zero CFC levels. In some areas such as the North Atlantic the CFC signal has penetrated to the bottom and such waters are unavailable. In this instance CFC stripped seawater should be used. The procedure for analysis is the same as that described for the seawater samples.

Restrips of a sample are required to check the efficiency of stripping. These are carried out in the same way as the water sample described above. The only difference is that the sample is not emptied from the stripping column between each run.

7.7 Air samples

Air samples are run in much the same way as blanks and standards.

* Turn the metal bellows pump on and leave it running for about 30 minutes before starting any analysis. It is preferable to have the selection valve at position 3 at this stage so that the air sample can flush right through the system.

* Make sure that the magnesium perchlorate drying agent is dry. Often the air can be very wet and after the 30 minutes flushing time the dessicant will need changing. If humidity is so high to make it impossible to dry the gas satisfactorily it is possible to insert a Nafion dryer in the flow line between the metal bellows pump and the air inlet on the side of the extraction board. These work very well and do not pose either a positive or negative contamination threat.

* With the selection valve switched to position 3 commence the procedure described above for one large loop of standard.

* Remember to accurately record the temperature and pressure of the sample loop prior to the injection stage.

* Check with the ship's officers for relative wind, ships position and heading and note accordingly.

It is important to bracket air samples with standards and blanks see section 8.3.

8 ROUTINE WORKING PROCEDURES AT SEA

8.1 Contamination

The contamination problems associated with CFC measurements have been strongly emphasised throughout this document. It is important to keep a watch for any potential problems at all times. Syringe air samples from the laboratory and from the area around the hydrographic bottles/rosette should be measured at frequent intervals. If values above ambient transpire then the source should be investigated and eliminated. It has been suggested that a large air pump be available on the ship to pump clean air into the working environment and so flush out any contamination should it arise.

8.2 Order and method of drawing water samples for routine hydrographic measurements

Obviously this depends on the number of water samples collected from depth (assume 24) and on what samples are to be drawn. CFC samples should always be drawn first. A rough rule of thumb guide is as follows:

* Two scientists should collect CFC samples one commencing with the deepest sample and the other at hydrographic bottle 12. It is normal for 6 syringes to be filled before they are transferred to the water bath for storage. The CFC workers should be responsible for opening the taps on the hydrographic bottles because leaking taps indicate if contamination has occurred. After the CFC samples have been collected the air valve at the top of the bottle should NOT be closed. In this way it is easy to recognise if a sample has been missed. Once other workers have drawn samples from a bottle it precludes a good quality CFC sample from being taken.

* Samples for Helium/Tritium should be drawn in a similar order by two operators. These samples are not analysed on board ship. **It is important that luminous watches are not in the working laboratory or in the vicinity of the hydrographic bottles as these contain small quantities of tritium and can severely contaminate the samples rendering the data useless.**

* Two scientists should closely follow behind the Helium/Tritium workers collecting oxygen samples following the same sequence. These should be fixed immediately they are drawn. It is no use collecting a number of samples and taking them into the laboratory to

add the reagents. The oxygen concentration in the samples can quickly change once they are exposed to the atmosphere.

* Samples for oxygen isotope ratios should be drawn next. Again following the same sequence.

* Finally samples are collected for nutrients and salts.

It can take over 2 hours to draw the full suite of samples from a 24 bottle station. If the above procedure is followed it can be carried out smoothly and without errors because personnel should follow on one after another.

8.3 Air samples

Routine air samples should be run for CFCs twice a day and these should be bracketed with standards and blanks. Normal practice is to run:

* a system blank

* one large loop of standard

* another large loop of standard

* a large loop of air

* a second large air sample

* a third large air sample

* a large loop of standard

* a further large loop of standard

* another blank.

Provided the blanks are low and the air and standards are within 1% there is no need to measure further samples. Syringe samples should also be measured if appropriate. A running log of air concentration, versus position and time, should be kept and plotted as appropriate.

8.4 Sample handling blanks

The nylon tubing and the Swagelock adaptor are the only non-metallic connections in the system and during normal usage the CFC permeability of the nylon can cause a contamination

problem. This usually appears as a non zero sample handling blank. Sometimes it can be cleared by continuous back and forth flushing from the syringe to the stripping column. If not it is important to bake the Hamilton valve and its associated tubing in the vacuum oven. At the very least the Hamilton valve, etc should be conditioned at the beginning of a cruise before any analytical work is undertaken.

Routine sample handling blanks should be made each day. If CFC-free seawater occurs at depth, then it is possible to check sample handling blanks during the normal seawater measurement run. If not then such water must be prepared at sea as described in sections 4.7 and 5.7.

If a sample handling blank does occur then every effort should be made to eliminate it by conditioning all the components or by replacing them with clean conditioned components. If this fails then make a note of the sample handling blank value. If it is consistent it is possible to subtract the value from all subsequent samples. This is not ideal but will suffice if absolutely necessary. If the value is not constant then this practice is not appropriate. It is better to have a day of downtime to clear the problem rather than press on regardless.

9. RESULTS AND QUALITY CONTROL

9. 1 Integration parameters.

A number of integration methods are stored in the equipment's ROM. The instrument handbook gives comprehensive details of the various parameters and the required settings. Integration method and final presentation of the chromatogram is often a personal preference and so no hard and fast rules for integration will be given here. Suffice is to refer the reader to the instrument handbook and to remind them that adjustment of the integration parameters may be necessary to optimize peak integration.

It is important that the slope and the doubling time (T.DBL) settings are correct.

Slope can be determined using the S.TEST facility and this will automatically set the sensitivity to a value which is appropriate for the noise level of the baseline. If broad peaks are not being detected then reduce the S.TEST value by half and enter the slope value manually. If small unimportant peaks are being integrated unnecessarily then increase the S.TEST value; but make sure it is not so large as to lose the main peaks. The S.TEST function should be carried out fairly frequently to allow for baseline changes. Always note the value of the slope before you carry out the S.TEST in case you are not happy with the new value; the old one can always be re-entered manually.

The T.DBL parameter determines the time when sensitivity (slope) and peak width (width) are doubled. This is important since, for isothermal analysis, the early eluting peaks will be sharp and the peak detection sensitivity need not be high; however the width of the peaks will become broader over time and the peak sensitivity will need to be increased. With T.DBL set to 0, peak detection sensitivity is automatically increased. The automatic setting is not adequate where a broad peak follows a sharp peak after a long lapse time. This can sometimes be the case with CFC analysis so it may be necessary to determine a non -zero T.DBL setting by trial and error.

Up to 50 chromatograms can be temporarily memorised by the CR3A and reprocessed as necessary. If the integrator is switched off or a new SAVE instruction is given, the old chromatograms will be lost so take care.

9.2 Surging

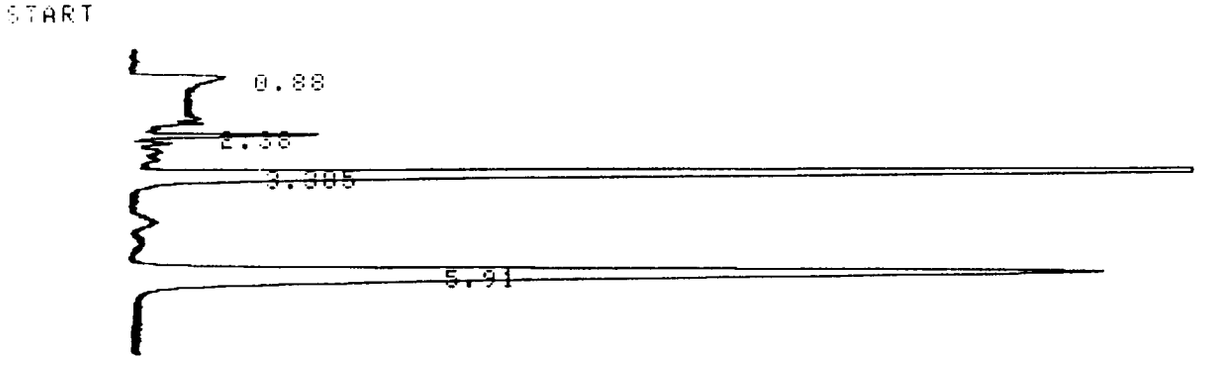
When V6 and V7 are switched to the inject position the carrier gas diverts through the trap and the precolumn before entering the chromatograhic column, and the stripping flow vents to waste (see Figure 1). If there is a pressure drop during this changeover, the flow rate through the chromatographic column will change and a surge will appear on the chromatogram. During normal usage a small surge such as that shown in Figure 5 will not cause a major problem. However, if the surge is large, as shown in Figure 6, then it is possible that the chromatogram will not have reached the baseline before the chromatographic peaks emerge and this can result in integration problems. For this reason it is good practice to spend considerable effort adjusting the relative flow rates to keep surging either in a positive or negative direction to a minimum. Sometimes a restrictor, made from a small length of 1/16 inch diameter stainless steel tubing and placed in the flow line between valve V7 and the GC has proved helpful.

9.3 Stripping / Trapping efficiency

It is important that the stripping flow rate and the trapping time are set for optimum stripping efficiency. If the flow rate is low then a long trapping time will be required. This is not advisable because, with time, the CFC-11 begins to break through the Porasil C and is retained on the Porapak T in the trap. Conversely if the stripping flow rate is high the gases will not be adequately retained on the trap. In addition, the shorter the trapping time the higher the risk of leaving some of the CFC, particularly CFC-11, behind in the water sample. The relationship between stripping flow rate and trapping time is empirical. The optimum should be determined by repeated measurement of one or more large loops of standard to determine trapping time and by restrips of high CFC water to achieve optimum stripping flow rate. 100% stripping efficiency is very difficult to achieve, particularly for high CFC surface samples. A consistent 95% level or above will suffice provided the efficiency is known; the final results can then be adjusted accordingly.

9.4 Chromatographic separation

The essence of good chromatography is the degree of separation of the peaks. There are a number of compounds in seawater samples which elute close to the CFCs. In particular dinitrogen oxide can cause substantial interferences with the CFC-12 signal. Seawater,



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 2581

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.88	2182			3.335	
2	2.38	1492			2.2809	
3	3.385	29524			45.1217	
4	5.91	32233			49.2624	
	TOTAL	65431			100	

Figure 5 A chromatogram with a small surge peak at the beginning of the run.

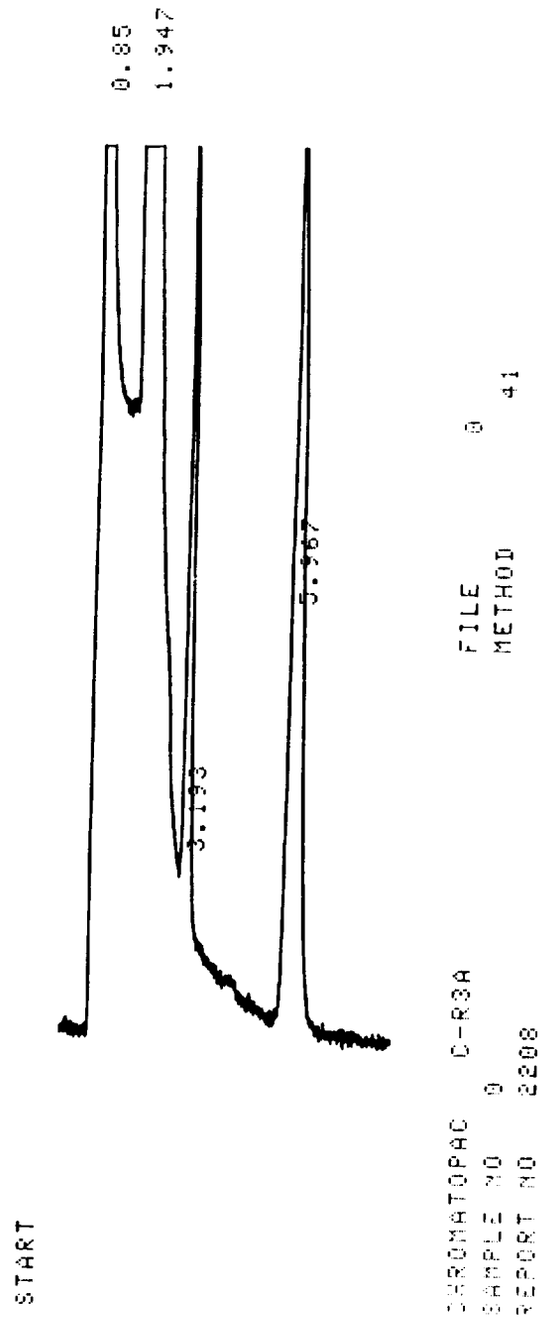


Figure 6 A chromatogram with a large surge peak at the beginning of the run.

particularly surface water, can be high in dinitrogen oxide. This is often compounded by the fact that the carrier gas can also have traces of dinitrogen oxide and if this starts to break through the molecular sieves it can reinforce the signal from the seawater. It is therefore essential to carry out the bake-out procedure frequently.

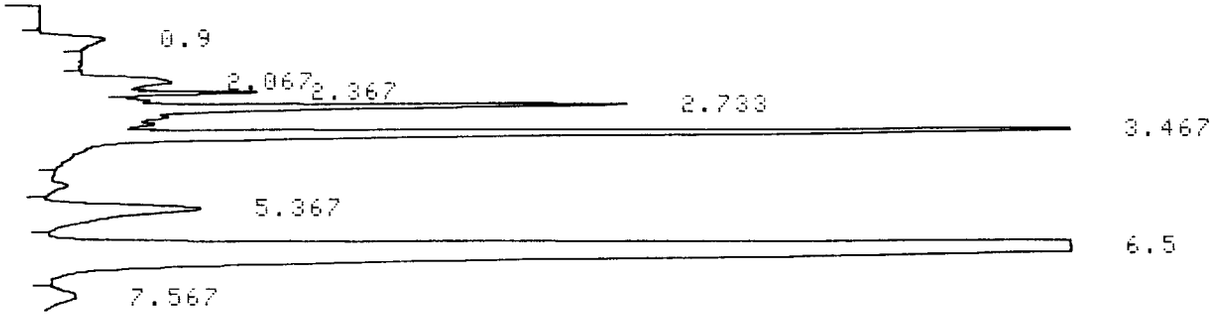
Figure 7 illustrates how the signal from dinitrogen oxide (peak at 2.733 minutes) can be a problem with the CFC-12 signal (peak at 3.467 minutes). Under the normal trapping temperature of -30°C the majority of the dinitrogen oxide should not be retained on the packing material in the trap but should pass through to waste along with the oxygen and nitrogen. If dinitrogen oxide is being retained excessively then check the trapping temperature. Often thermal gradients form in the cold trap making the lower sections much colder than the surface. For this reason it is important to agitate the cold trap from time to time. If the problem persists try increasing the temperature slightly. Alternatively increase the stripping flow rate, but take care to maintain the balance between minimal surging and good stripping efficiency.

If the amount of dinitrogen oxide passing into the GC column cannot be reduced, then it is important to achieve separation by lowering the GC oven temperature. This will alter the flow rate so adjustments to the timing of valve switching and to the carrier gas flow rate will be necessary to compensate.

Unfortunately, there are no fixed temperatures or flow rates for the CFC system. Both must be fine tuned to achieve optimum results.

9.5 Calibration Curves

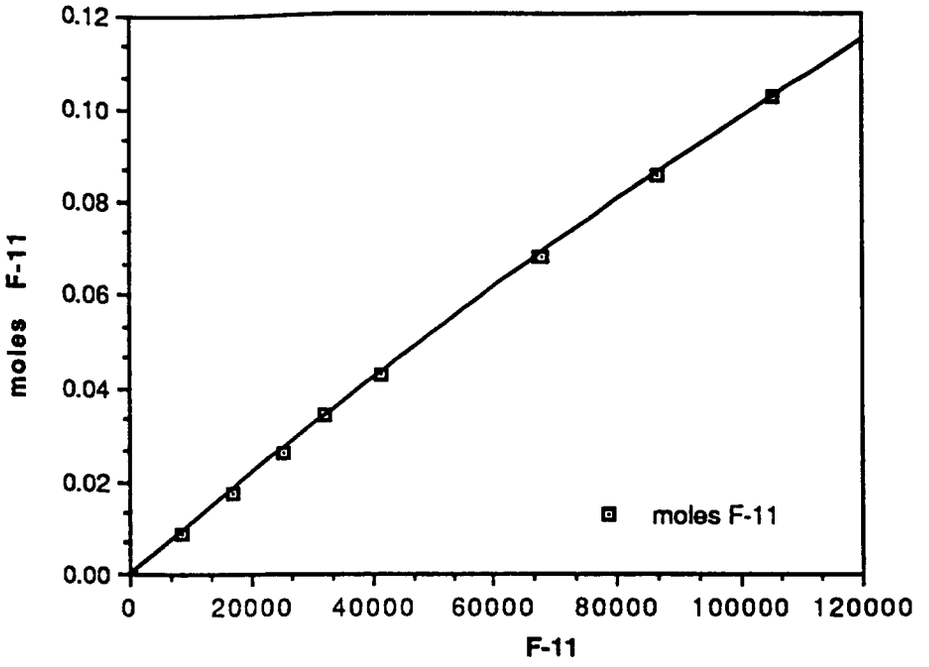
Routine calibration curves should be constructed both in terms of moles of CFC (for seawater samples) and parts per trillion (for air and gas samples). Examples of calibration curves are shown in Figures 8 and 9 for CFC-11 and CFC-12 respectively. A simple polynomial curve is fitted to the data and used for a first pass calculation of concentrations in the seawater and gas samples. More elaborate calibration curves may be constructed to compensate for sensitivity and drift changes but these will be the subject of a further IOS Report on CFC data management (see section 10).



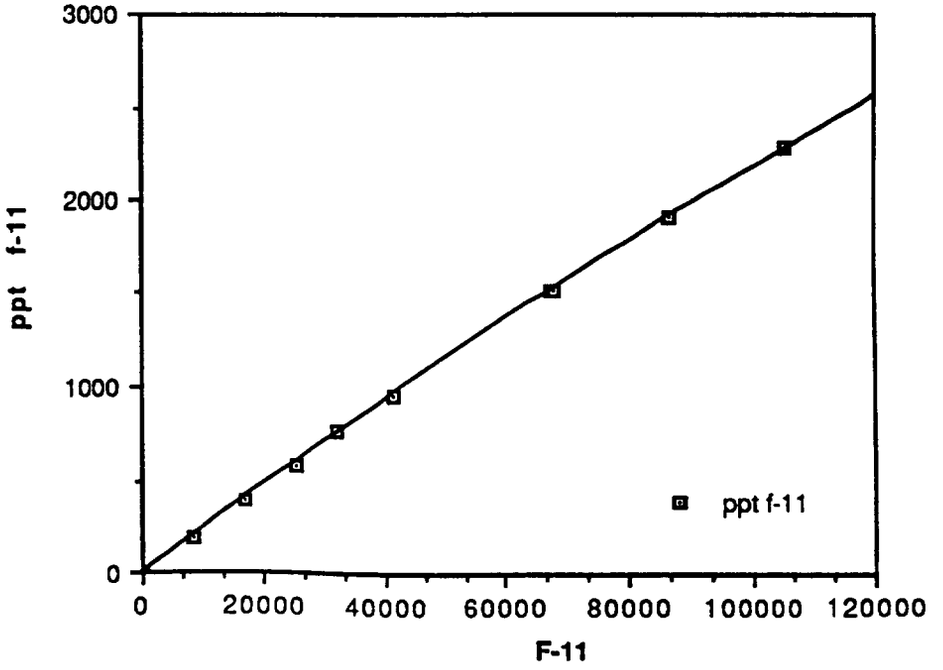
CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 21
REPORT NO 2819

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.9	1451			1.0242	
2	2.067	3319			2.3427	
3	2.367	2550	V		1.7999	
4	2.733	14746	V		10.4076	
5	3.467	22134	V		15.6219	
6	5.367	6502			4.589	
7	6.5	89500	V		63.1683	
8	7.567	1483	V		1.0465	
	TOTAL	141684			100	

Figure 7 A chromatogram showing the interfering effect of a dinitrogen oxide peak

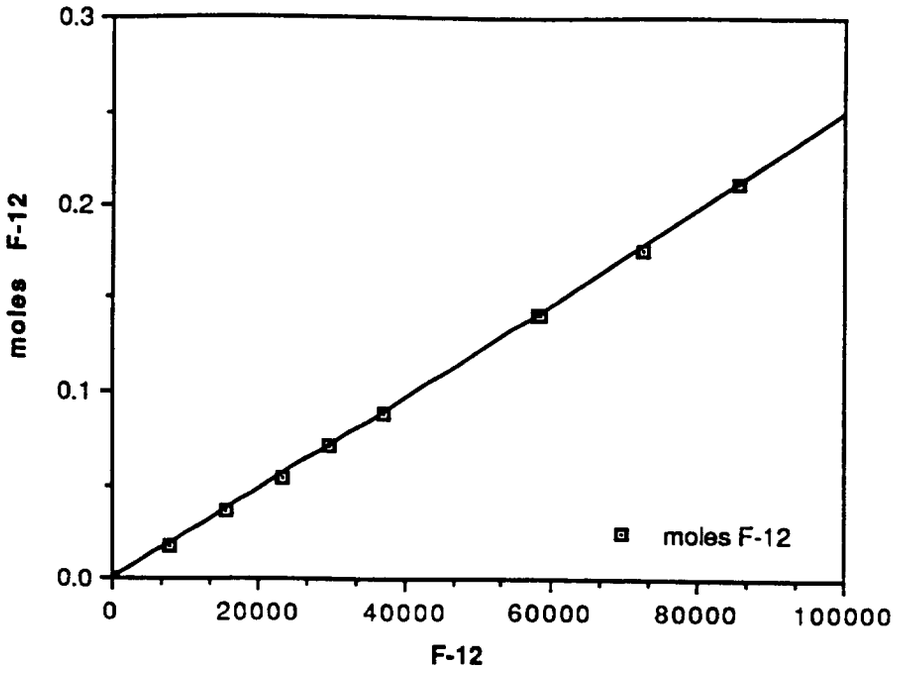


y = - 6.7464e-6 + 1.0921e-6x - 1.1935e-12x^2 R^2 = 1.000

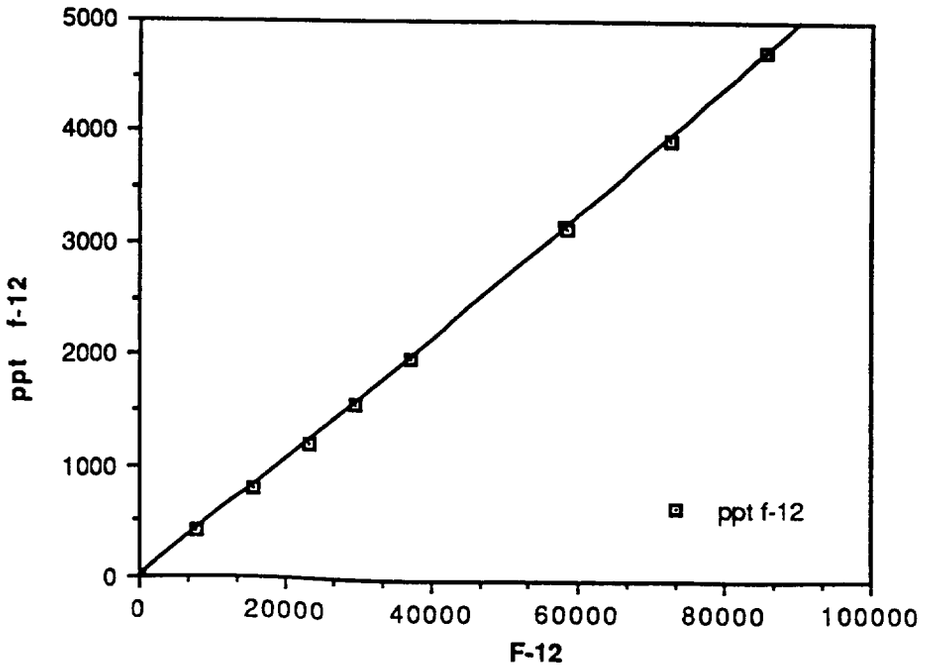


y = - 0.15119 + 2.4476e-2x - 2.6749e-8x^2 R^2 = 1.000

Figure 8 Examples of calibration curves for CFC-11



y = - 7.2178e-6 + 2.3261e-6x + 1.5888e-12x^2 R^2 = 1.000



y = - 0.16175 + 5.2133e-2x + 3.5609e-8x^2 R^2 = 1.000

Figure 9 Examples of calibration curves for CFC-12

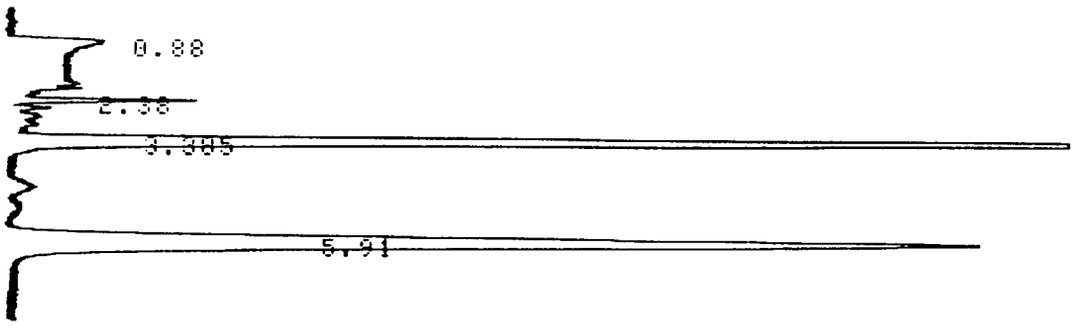
9.6 Final Results

Examples of the expected chromatograms for standard gas, air, blank and high and low CFC seawater samples are given respectively in Figures 10-14. The retention times for the CFC peaks are a function of flow rate and the tightness of packing of the GC column and precolumn. As is often the nature of gas chromatographic techniques, the retention times vary slightly from sample to sample. In the examples shown the retention times for CFC-12 and CFC-11 are of the order of 3.3 - 3.5 and 5.9 - 6.6 minutes respectively.

At the end of the chromatographic run a report which includes details of the integration method, the retention times and peak areas is printed out. A first pass calculation of the concentration of the CFCs in an air or seawater sample can be made by substituting the peak area value in the best fit polynomial equation for the corresponding calibration curve.

For seawater samples the concentration should be given in terms of moles per litre or preferably moles per kilogram if the salinity and hence density of the sample is known. The volume of water stripped is determined from a series of calibrated lines on the stripping column. However a small volume of water is retained in the side arm connecting the column to the Hamilton valve which is not stripped of dissolved gases during the analytical procedure. This volume is constant for a particular stripping column and has to be calculated geometrically. It is subtracted each time from the volume of water determined from the calibration marks.

START

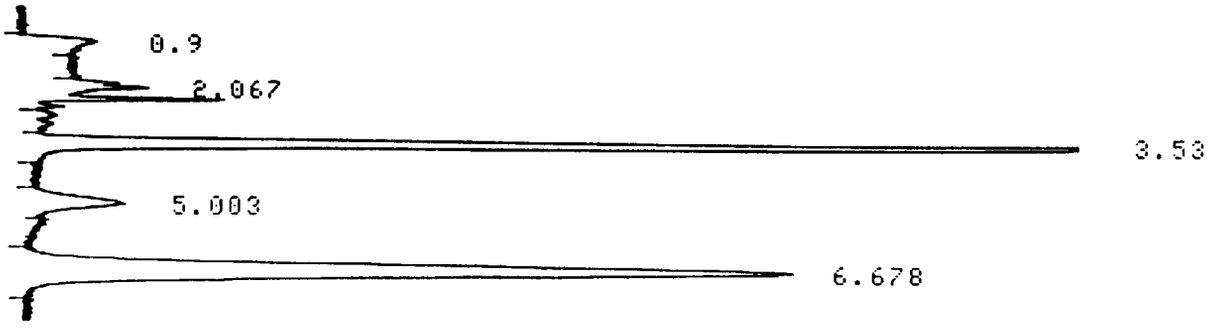


CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 2581

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.88	2182			3.335	
2	2.38	1492			2.2809	
3	3.385	29524			45.1217	
4	5.91	32233			49.2624	
	TOTAL	65431			100	

Figure 10 A chromatogram of a large standard gas sample

START



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 21
REPORT NO 2722

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.9	1625			2.5458	
2	2.067	3643			5.7082	
3	3.53	24782			38.8291	
4	5.003	2931			4.5917	
5	6.678	30842			48.3253	
	TOTAL	63822			100	

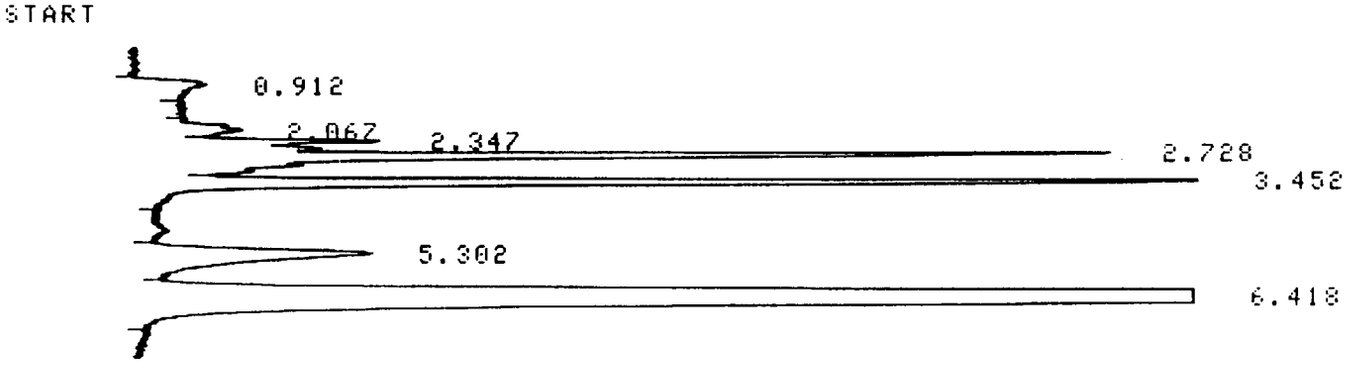
Figure 11 A chromatogram of a large air sample

START

CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 2578

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.847	2400			100	
	TOTAL	2400			100	

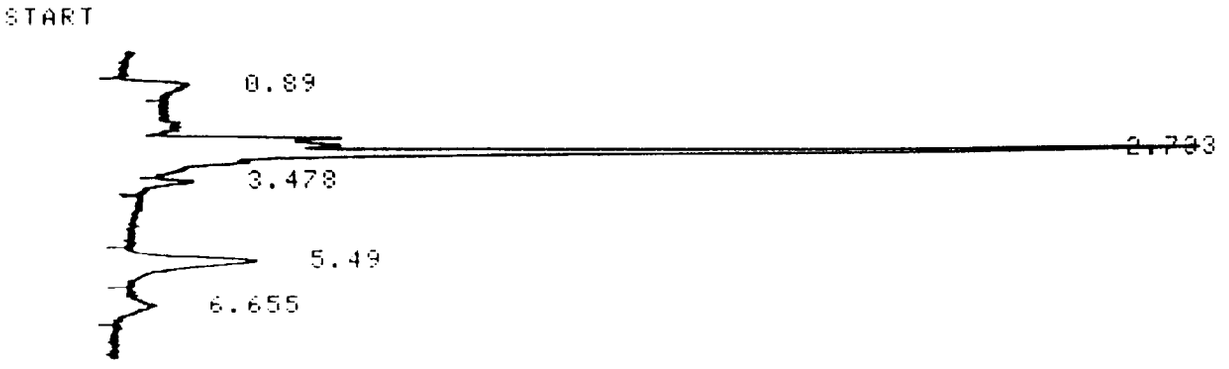
Figure 12 A chromatogram of a system blank



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 21
REPORT NO 2787

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.912	1798			1.1752	
2	2.067	1732			1.1318	
3	2.347	3165	V		2.0687	
4	2.728	21693	V		14.1772	
5	3.452	21290	V		13.9139	
6	5.302	8597			5.6187	
7	6.418	94736	V		61.9145	
		---			---	
	TOTAL	153011			100	

Figure 13 A chromatogram of a seawater sample with a high CFC concentration



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 21
REPORT NO 2753

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.89	1726			4.9113	
2	2.733	26207	S		74.5875	
3	3.478	542	T		1.5412	
4	5.49	5047			14.3648	
5	6.655	1615	V		4.5952	
	TOTAL	35136			100	

Figure 14 A chromatogram of a seawater sample with a low CFC concentration

10 CONCLUSIONS

It was stated earlier that the purpose of this document is to give a detailed account of how to analyse seawater and air samples for CFC content using the IOSDL CFC system. Many of the procedures have been derived empirically by the author and other CFC workers. The dos and don'ts are based on experience. It is likely that the IOS equipment will be continually upgraded and procedures refined accordingly, but it is unlikely that the basic principles of the analysis will change drastically.

The document, purposefully, does not have a section relating to data management. A first pass calculation of the CFC concentration in a sample can be made by comparison with simple calibration curves. This will subsequently have to be adjusted for sample handling blanks, drift, changes in sensitivity, density and any contamination errors before the data is in a final publishable state. Often more complex calibration curves need to be constructed. Such data clean up is usually done on land after the cruise using specially developed programs. A further IOS Report covering data management and interpretation is in preparation. Suffice it to say that unless there are severe problems during the analytical work the final results should not vary substantially from the first pass calculation. The latter can often be very usefully employed at sea for tracking water masses. Ventilation, transport and mixing rates should always be calculated from the final data set.

REFERENCES

SMYTHE-WRIGHT, D. 1990. Chemical Tracer Studies at IOSDL - I. The design and constriction of analytical equipment for the measurement of chlorofluorocarbons in seawater and air. Institute of Oceanographic Sciences Deacon Laboratory Report 274, 78 pp

APPENDIX 1

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
```