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A PURGE-AND-TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHIC METHOD FOR THE MEASUREMENT OF HALOCARBONS IN WATER AND AIR.

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Abstract

This report describes an automated, accurate, precise and sensitive capillary column purge-and-trap method capable of quantifying CFC-12, CFC-11, CFC-113, CH_3CCl_3 and CCl_4 during a single chromatographic analysis (17 minute length) in either water or gas phase samples. Incorporated in this analytical system are several unique features. Gas sample loop temperature, water bath temperature and atmospheric pressure are recorded as peaks in the chromatograms permitting straightforward recording of such parameters with any commercially available software package, integrator, or chart recorder. The trap is cooled to a sub-ambient temperature (-15°C) using only compressed air, eliminating the use of cryocoolers, a potential source of CFC-12 contamination. It is estimated that the precision of seawater measurements for the above halocarbons are, respectively, the greater of 3.1 % or 0.01 pmol kg^{-1}, 1.4 % or 0.005 pmol kg^{-1}, 6.4 % or 0.01 pmol kg^{-1}, 1.4 % or 0.01 pmol kg^{-1}, and 1.1 % or 0.005 pmol kg^{-1}. Precision for the same compounds in air are estimated to be 0.9 %, 0.9 %, 2.0 %, 4.8 %, and 2.2 %. Limits of detection in water samples are estimated to be 0.003 pmol kg^{-1} for CFC-12, CFC-11 and CCl_4 and 0.005 pmol kg^{-1} for CFC-113 and CH_3CCl_3.

INTRODUCTION

Purge-and-trap extraction systems for the measurement of chlorofluorocarbons (CFC's) transient tracers in seawater have been described in several previous studies (GAMMON et al., 1982; BULLISTER and WEISS, 1983; BULLISTER, 1984; WALLACE and MOORE, 1985; BULLISTER and WEISS, 1988). All of the instruments described in the previous studies used packed columns and were capable of detecting only CCl_2F_2 (CFC-12) and CCl_3F (CFC-11). More recently the usefulness of CCl_2FCClF_2 (CFC-113) and CCl_4 as transient tracers has been recognized (SMETHIE 1993, 1994; WALLACE and LAZIER, 1988; WALLACE *et al.*, 1994; WISEGARVER and GAMMON, 1988). The main goal was to build a system that was capable of accurately measuring CFC-12 and CFC-11, in addition to CFC-113, CH_3CCl_3, and CCl_4 in a single chromatographic analysis. We also wanted to incorporate the following features in our system: 1) a capillary column (because packed columns do not offer adequate resolution to separate CH_3CCl_3 from CCl_4 or CFC-113 from CH_3I) and a pre-column, with the ability to backflush the pre-column; 2) the ability to analyze water and air samples, and gas-phase standards; 3) the ability to cool the trap below ambient temperature without cryogenic systems; and 4) computer controlled automation and data collection. The system described in this report, with some modifications, is based upon the system briefly described in WALLACE et al. (1994).

METHODS

General Considerations

This analysis system was built with the intention of using it at sea, so we constructed it in a modular fashion in order to facilitate easy breakdown and setup. It is composed of a computer and four modules, namely a molecular sieves module (Fig. 1), a purge and trap module (PAT, Fig. 2), a gas standard selection module (STAN, Fig. 3) and, a gas chromatograph (GC, Fig. 4). The molecular sieves module contains one O_2 trap and two molecular sieves traps that are used to purify the N_2 used as a carrier and purge gas. PAT contains the water and gas sample loops, the water purge chamber, gas flow controllers, 4 electrically actuated valves, and the electronics used to control the valves (total of 7). STAN contains a manually actuated valve and associated tubing used to select a particular gas phase standard or sample. The Varian 3300 GC used for this system is modified to hold the analytical trap and 3 electrically actuated valves.

All of the tubing on this instrument is of stainless steel construction, usually 1/16 inch O.D. x 0.53 mm I.D. Small amounts of 1/8 inch O.D. tubing are used to connect the N_2 carrier gas to the instrument, and to connect the water sample loop and purge chamber to a valve. This instrument also used 0.7 mm O.D. x 0.53 mm I.D. deactivated stainless steel tubing (Frontier Laboratories, Fukushima, Japan) in most areas where halocarbons came in contact with the tubing. Before any 1/16 or 1/8 inch stainless steel tubing is used, it is first rinsed with hexane, acetone and then methanol. After this solvent rinse the tubing is heated to approximately 600°C with a torch, while N_2 is flowing through the tubing. We have found that this solvent rinse and heating procedure are essential in order to clean the tubing of organic contamination (presumably oils). If this procedure is not carried out halocarbons, especially CH_3CCl_3 and CCl_4, can be adsorbed on the tubing.

Eight, two-position, stainless steel Valco valves (Valco Instruments, Inc., Houston TX) are used. In an effort to standardize the valve types and spares required by the system most of the two-position valves (6) are 10-port valves with 1/16 inch fittings (model # C10UW). There is one valve with 10 ports and 1/8 inch fittings (model # 10UW) that is used to load the water sample loop and move the contents of the loop to a purge chamber. In addition, a 4-port valve with 1/16 inch fittings (model # C4UW) and 6-position valve with 1/16 inch fittings are employed (model # CSF6). The former can be replaced with a spare 10-port valve, if necessary.

Carrier Gas Preparation and Flow Control

Ultra high purity N_2 (99.9995%) is used as both the carrier and purge gas. Before supplying PAT, STAN or the GC, this N_2 is passed through an O_2 trap and a trap 12 inch long by 0.5 inch O.D. containing 40/60 mesh molecular sieves 13X (Fig. 1, Molecular sieves module). Two molecular sieve traps are mounted in separate aluminum blocks that can be independently heated to 300°C in order to re-condition the molecular sieves under a stream of flowing N_2. The traps are connected so that one can be used while the other is being re-conditioned (Fig. 1).

After leaving the molecular sieves module the N_2, enters PAT (Fig. 2) and is split into 7 separate streams with a 10-port manifold. One of these streams ("blank" gas flow) is directed to STAN (Fig. 3) and is used to check the analytical blanks of the gas sample loops. This stream is regulated to 50 ml min^{-1} with a flow restrictor (Mott Metallurgical, Farmington, CT). The "makeup" gas stream is controlled with a Porter 4000 pressure regulator (30 psi) and a Porter VCD-1000 flow controller (Porter Instrument CO., Hatfield, PA), and can be used for detector make-up gas if necessary. Two additional streams that are controlled with separate Tylan FC-280A mass flow controllers (Tylan General, San Diego, CA, Fig. 2) supply the analytical column ("column" flow, 8.2 ml min^{-1}) and pre-column ("pre-column" flow, 16.4 ml min^{-1}). A mass flow controller is used on the "column" flow to keep the column flow rate and, thus, detector baseline voltage constant during temperature programming. A mass flow controller is used on the "pre-column" flow so that pressure and, thus, flow rate changes that occur after valve changes are quickly compensated for. The stream ("dry" purge gas) used to transfer the contents of the gas sample loops to the trap is controlled upstream of the loops with a Porter 4000 pressure regulator (25 psi) and downstream of the trap at a rate of ~ 150 ml min^{-1} with a Porter B-125-10A flow controller. The stream ("wet" purge gas) used to transfer the contents of the water sample loop to the purge chamber and purge it, is controlled in the same way and at the same rate as the previous flow. The last stream ("flush" gas) is used to empty the purge chamber after the water has been purged, and to keep the water sample loop flushed with N_2 when not in use. This stream is controlled with a Porter VCD-1000 flow controller (~ 50 ml min^{-1}). As an extra precaution each flow (except the "blank" gas flow to STAN) is passed through a 4 inch by 0.25 inch 60/80 mesh 13X molecular sieves trap downstream of its flow controller. These traps are mounted within an aluminum block which can be heated to re-condition them.

Water Sample Purge-and-Trap

Water samples that are collected in 100 ml ground glass syringes (Popper and Sons, Inc., New Hyde Park, NY) are loaded into a 31.04 ml stainless steel sample loop attached to valve #1 (Fig. 2, PAT diagram). The sample loop is calibrated on the valve using the weight difference between the empty loop and the loop filled with distilled water to a precision and accuracy of ± 0.05 % following the procedure in Wilke *et al.* (1993). After the loop is rinsed and loaded with a water sample, valve #1 is switched from the "load" to the "purge" position (Fig. 2), and a stream of N_2 ("wet" purge gas), which has been saturated with water by passing the N_2 through a purge chamber filled with distilled H_2O (humidifier, Fig. 2), transfers the sample into a glass purge chamber equipped with a coarse glass frit. The "wet" purge gas stream is saturated with H_2O to prevent salt crystals from forming in valve #1 (salt crystals scratch the valve and rotor and cause the valve to leak). Valve #7 switches to the "wet" position (Fig. 2) simultaneously with valve #1 switching to the "purge" position, directing the "wet" purge flow from a flow-restricted vent to the trap. The sample is purged for 3.6 min with N_2 flowing at a rate of 150 ml min^{-1}. A glass tube (3 inch by 0.25 inch) packed with anhydrous magnesium perchlorate, located immediately downstream of the purge chamber (Fig. 2) dries the "wet" purge gas stream before it enters the trap. The extraction efficiency at 25°C is > 99 % for all compounds except for CH_3CCl_3 (~95 %).

Halocarbons are trapped (pre-concentrated) within a 1/8 inch x 18 cm stainless steel tube packed with 80/100 mesh Porapak N (Alltech Associates, Inc., Deerfield IL). This trap is mounted on the side of the GC (Fig. 4, GC diagram), close to the column inlet, and is held at -15°C during trapping. The trap is cooled with a Vortex Tube (Model # 106-8-H, Vortec Corp., Cincinnati, OH), which uses only compressed air (minimum inlet pressure 80 psi, minimum flow rate 8 CFM) to cool. Cool air is produced because the Vortex tube produces two distinct vortices traveling at different speeds which causes a simple heat exchange to take place. The cold air from the Vortex tube is directed into a length of 3/8 inch glass tubing. The Porapak N trap is mounted inside this glass tubing and is thus cooled. Under these conditions Porapak N traps all five halocarbons of interest without any breakthrough (Fig. 5, breakthrough test chromatograms) but did not trap N_2O. N_2O, which is a perennial interference problem for CFC-12 analyses, is partially retained on many other trapping materials that are commonly held at lower temperatures, necessitating additional separation strategies. It has been shown that Porapak N can even be used to trap the halocarbons when held at ambient temperatures (~20°C, WALLACE et al., 1994). However, cooling the trapping material to -15°C causes the halocarbon peaks to be sharper, allows the use of a greater purge gas flow rate (150 versus 60 ml min^{-1}) and, consequently, a larger water sample size (31 versus 20 ml), than that described in the WALLACE et al. (1994) study. Cooling the trap significantly improves the analysis of CFC-12.

After the water sample has been purged valve #1 is changed to the "load" position, valve #7 is changed to the "dry" position and a separate flow of N_2 ("flush" gas) is used to push the water out of the purge chamber to a drain (Fig. 2). This N_2 flow is also used to continually flush the water sample loop when it is not in use. The purpose of valve #7 is to select which purge gas supply ("wet" purge gas or "dry" purge gas, see below) is directed towards the trap (Fig. 2). The purge gas flow which is not directed to the trap is vented through a 10 ml min^{-1} flow restrictor

(Mott Metallurgical, Farmington, CT). After the water sample has been purged the "dry" purge gas flow is allowed to sweep the trap and the tubing leading to it for 0.4 min in order to remove any traces of N_2O. Purge blanks are determined by flushing the sample loop with the "flush" gas and then trapping the "flush" gas under the same conditions as a water sample.

Gas Phase Standards and Air Samples

A 6-position Valco valve is used to select the gas to be analyzed (Fig. 3, STAN). There is a manual choice between 3 different standards, blank N_2, syringe air or pump air. After the gas to be analyzed has been selected, its flow to the gas sample loops is regulated by a computer controlled pneumatic actuated valve (Fig. 3). Air samples can be delivered either from a syringe or continuously from an Air Cadet pump (Model # 7530-40, Cole-Palmer Instrument Co., Chicago, IL). The air pump is left on at all times, passing air through two magnesium perchlorate drying traps (10 inch by 1 inch and 5 inch by 3/8 inch), and vents through an open port on the 6-position valve.

The gas to be analyzed is used to flush and load sample loops located on valves #4 and #5 (Fig. 2). Valve #4 has 2 and 10 ml sample loops attached to it, while valve #5 has 1 and 5 ml sample loops attached to it. The exact volume of each loop (volume of loop + injected volume of valve ports) is determined, with a precision and accuracy of ± 0.05 %, by the procedure described in WILKE *et al.*, 1993. The plumbing of valves #4 and #5 is arranged so that when one sample loop on a valve is being loaded with a gas sample the other is being purged by the "dry" purge gas (Fig. 2). The arrangement of valves #4 and #5 allows the contents of either one or two separate loops (one from each valve) to be transferred to the trap simultaneously. This results in the following available sample sizes: 1, 2, 3, 5, 7, 10, 11, and 15 ml. Larger samples can be injected by loading and purging loops sequentially to achieve the desired volume. Smaller samples can be injected by replacing the 1 ml sample loop with a smaller sample loop. After the sample loop(s) have been loaded for 1.8 min, the standard flow is stopped for 0.2 min so that the loop(s) come to atmospheric pressure. The appropriate valve(s) are switched and the contents of the loop(s) are transferred to the -15°C Porapak N trap over a period of 2.0 min with a N_2 flow of 150 ml min^{-1}.

Porapak N Trap Desorbtion and Sample Injection

It takes 4 minutes to either purge a water sample, or load and purge the gas sample loops and then trap the halocarbons from either type of sample. After 4 min the Porapak N trap is isolated (valve #3 to trap out position, Fig. 3) and heated to 120°C in order to desorb the halocarbons. The trap is heated by passing a low-voltage, high amperage DC current directly through the trap. The cables of a 12-volt, high amperage battery charger are clamped directly to the ends of the trap. The battery charger is plugged into a Variac, resulting in ~25 amps at ~3 VDC being passed through the trap. The trap is electrically isolated from the GC by using a 10 cm long length of 0.7 mm O.D. x 0.53 mm I.D. deactivated fused silica tubing on one end of the trap. The trap temperature is monitored and maintained at 120°C using a thermocouple attached to the trap, together with an Omega CN370 temperature controller which controls a solid-state relay and turns the battery charger on and off. At 4.5 min, after the trap has reached 120°C, valve #3 is switched to the "trap in" position, valve #2 is changed to the "foreflush" position and valve #6 is changed to the "desorb" position (Fig. 3). These changes supply column flow to the trap, in the opposite direction of the purge N_2 flow, causing the trapped components to be backflushed onto the pre-column.

Chromatography

A Varian 3300 GC (Varian Associates Inc., Walnut Creek, Ca.) equipped with a Varian 02-001972-00 electron capture detector (ECD) is used. The analytical column is a 70 m x 0.53 mm I.D. fused silica DB-624 (0.3 mm film thickness) capillary column (Alltech Associates, Inc., Deerfield IL). Approximately a 10 m length of this column is used as a separate pre-column. The column oven temperature is held at 40°C for 9 min (i.e. for 4.5 min after the contents of trap are injected). The oven temperature is raised to 60°C at 5°C min^{-1}, then raised to 120°C at 20°C min^{-1} and held for one minute. This results in a total sample analysis time of 17 min (see Fig. 6 and 7 for examples of chromatograms). The ECD is held at 350°C.

Valves #2, #3, and #6 are mounted inside the oven of the GC and are equipped with high temperature rotors (Valco Instruments, Inc. part # SSAC10UWT, maximum temperature 340°C). To prevent halocarbons from absorbing to the walls of the tubing, all of the tubing between these valves and the Porapak N trap is 0.7 mm O.D. by 0.53 mm I.D. deactivated stainless steel. Valve #6 acts to control the direction of gas flow through the Porapak N trap. The purpose of valve #3 is to isolate the trap. When valve #2 is in the foreflush position (at 4.5 min), sample purge gas and pre-column flows are vented, and the column flow is directed through the heated (120°C) trap (valve #2 in trap in position, valve #6 in desorb position), the pre-column and then the main column (Fig. 3). Valves #2, #3, and #6 were left in this arrangement from 4.5 to 7.5 min, allowing all five halocarbons to elute from the pre-column onto the main column. At 7.5 minutes valve #2 is turned to the backflush position and valves #3 and #6 are left in their previous positions. In this arrangement, the column flow is routed only through the main column. The pre-column flow is directed through the pre-column in the opposite direction to the column flow, backflushing later eluting compounds from the pre-column, and the "dry" purge gas flow is directed to the Porapak N trap (Fig. 3). Valves #3 and #6 are reset to their starting positions (trap out and adsorb) and the Porapak N trap is cooled at the end of the analysis (16.9 min). At 17.0 min the GC column oven starts cooling. In order to decrease the time needed to cool the oven, the cold air outlet of the Vortex tube is directed through a piece of insulated tubing to the oven vent. It takes ~ 2 minutes to cool the column oven to 60°C. At this point the next sample can be started, and during the 4 min needed to purge-and-trap the sample, the column oven reaches a stable temperature of 40°C. Approximately 75 samples (any combination of water samples, air samples, blanks, and/or standards) can be analyzed in a 24 hr period.

The ability to add makeup gas (N_2) to the detector is provided for. It has been found that makeup gas is not needed during the analysis. The makeup gas is currently only used so that the ECD can be kept hot on occasions when the column has to be removed for maintenance of the valves inside the oven.

Computer Automation and Data Collection

The Baseline software package (Waters Inc., Milford, Massachusetts) is used for system automation and data collection. Valves #1 through #7 (via electric valve actuators), trap heating and cooling, and gas sample flow (on or off) are directly controlled by Baseline. All events can also be controlled and over-ridden manually by switches on the control panel. The operator has to manually inject a water sample, or choose a gas sample, and then push the start button; the rest of the analysis is controlled by the software. The system can also be run in "auto-start" mode. At the end of a run the GC oven cools down to 40°C, and a ready signal from the GC prompted the system to begin running and collecting data. This allows calibration runs to be made automatically without the operator being present. This system can also be attached to an underway equilibrator and run in "auto-start" mode for continuous underway analyses.

Another feature of the system is its ability to record water bath temperature, gas-sample temperature and atmospheric pressure as peaks on the chromatogram. We chose to record the temperatures and pressure in this way because the Baseline A/D board would only accept one input signal (ECD signal). This approach would also be of value for systems which utilize integrators or chart recorders to record chromatograms. The gas-sample temperature and atmospheric pressure are used to calculate the mass of gas sample in the gas samples loops, while the water bath temperature is used to determine the density of water in the water sample loop. Temperature and pressure peaks are recorded on the chromatograms via the use of four Potter & Brumfield CNT series time delay relays (Potter & Brumfield Inc., Princeton, IN). One relay is set to mode C (interval on) with a time of 4 min. When a run is started, this relay turns on and switchs the signal Baseline records from the ECD to the relay signal for a period of 4 min. After 4 min the relay switchs off and Baseline again records the ECD signal. The other three relays are set to mode A (delay on operate) with time intervals of 1, 2, or 3 min. In mode A these 3 relays do not turn on until the elapsed time had passed. Two of the mode A relays are connected to LM35 semiconductor temperature sensors, while the other mode A relay is connected to a ICS piezo-resistive pressure sensor. All three sensors are wired to a separate 22 µF capacitor and a 33 K resistor, so that when the corresponding relay is off, the capacitor is charged. After the time set on the mode A relays elapses, the relay turns on and the capacitor discharges through the resistor and produces a peak with a width of 0.75 seconds (see Fig. 8 for a wiring diagram of the connections between relays and sensors). The height of each of the three peaks produced is related to either a temperature or atmospheric pressure, depending on which type of sensor is connected to the relay.

The temperature sensors were calibrated against a NIST traceable, Hg thermometer, and were found to have a linear response between 20 and 32°C ($R^2 \geq 0.99996$), and are stable to better than 0.05°C over 6 months. The pressure sensor was calibrated against a Paroscience barometer and the output is linear to 0.01% between 12.5 and 15.6 psia.

RESULTS AND DISCUSSION

Calibration Curves

Typical calibration curves, generated at sea during a research cruise, can be found in Figure 9. Detector response (peak area) versus the number of picomoles injected for each halocarbon is plotted. Third order polynomials give the best fit to the data for all five halocarbons. At sea, full calibration curves are generally run approximately every 2 days, depending on the stability of the ECD (see below) and the availability of free time due to work stoppages (i.e. storms, equipment maintenance, etc.) The R^2 for each curve was generally ≥ 0.999 and residuals were ≤ 4 %.

Electron Capture Detector Response Drift with Time.

Because the ECD response can potentially change with time between full calibration curves, a 5 mL (mid-range) injection of the standard is made after every 7 to 8 water and/or air samples. The detector response (peak area), corrected for sample loop temperature and atmospheric pressure, is plotted against time for each halocarbon. Second order polynomials are fitted to the data for each halocarbon (Fig. 9). The ECD response drift for each halocarbon is generally ≤ 1 % over 24 hours. The appropriate ECD response drift versus time equation is then used to normalize the peak area of the halocarbons in samples to the peak area of the 5 mL injection in the calibration curve.

Precision and Limit of Detection

The precision of seawater samples analyses are the greater of 3.1 % or 0.01 pmol kg^{-1} for CFC-12, 1.4 % or 0.005 pmol kg^{-1} for CFC-11, 6.4 % or 0.01 pmol kg^{-1} for CFC-113, 1.4 % or 0.01 pmol kg^{-1} for CH_3CCl_3, and 1.1 % or 0.005 pmol kg^{-1} for CCl_4. These precision estimates are based on the pooled standard deviation of 15 duplicate samples collected in the Greenland and Norwegian Seas from the surface to the bottom during November 1994. The precisions for the same compounds in air samples are, respectively, 0.9 %, 0.9 %, 2.0 %, 4.8 %, and 2.2 %. These precision estimates are based on one standard deviation of 240 air samples collected during a cruise in the Greenland and Norwegian Seas in November 1995. Hence, these estimates of precision include any "real" variance

Limits of detection in seawater samples, based on the system blanks, baseline noise level and the precision estimates given above, are 0.003 pmol kg^{-1} for CFC-12, CFC-11 and CCl_4 and 0.005 pmol kg^{-1} for CFC-113 and CH_3CCl_3.

CFC-113

There is a potential problem with this analysis system for CFC-113. There is at least one unknown compound (not CH_3I) that co-elutes with CFC-113. This co-eluting compound(s) seems to be most concentrated in tropical ocean surface waters. Apparent CFC-113 concentration in surface water of the tropical Atlantic Ocean is ~ 150 % saturated, while CFC-12 and CFC-11 are ~ 100 % saturated (HAPPELL *et al.*, 1996). This problem has been previously reported by

WALLACE *et al.* (1994). Research in alternative separation methods continues, however there are a wide range of ECD sensitive compounds in the upper ocean. The relatively low concentration of CFC-113 (compared to the other anthropogenic halocarbons) makes it particularly susceptible to significant interference problems which may not be noticed for the other compounds

CONCLUSIONS

This report describes an accurate, precise and sensitive purge-and-trap method for the determination of CFC-12, CFC-11, CFC-113, CH_3CCl_3 and CCl_4 in seawater and air. Several unique features have been incorporated in this system. Gas sample loop temperature, water bath temperature and atmospheric pressure are recorded as peaks in the chromatograms permitting straightforward recording of such parameters with any commercially available software package, integrator, or chart recorder. The trap is cooled to a sub-ambient temperature (-15°C) using only compressed air, eliminating the use of cryocoolers; a potential source of CFC-12 contamination. Unlike many other halocarbon analysis systems our system is highly automated. After the operator manually chooses a gas sample or loads the water sample loop, the rest of the analysis is controlled by a computer. Calibration and air sample analyses can be accomplished automatically, without the operator being present. This free time allows the operator to collect samples or work on data while continuing to analyze samples previously collected.

This analysis system could also be easily adapted to measure many other volatile compounds in seawater. In its current configuration, compounds such as CH_3Cl, CH_3Br, CH_3I and $CHCl_3$ could be measured without any additional analysis time. Other later eluting, volatile, ECD sensitive compounds could be measured by simply allowing more time before backflushing the pre-column. Other non-ECD sensitive compounds could be measured by using different detectors, such as a mass spectrometer, flame photometric, or flame ionization, etc.

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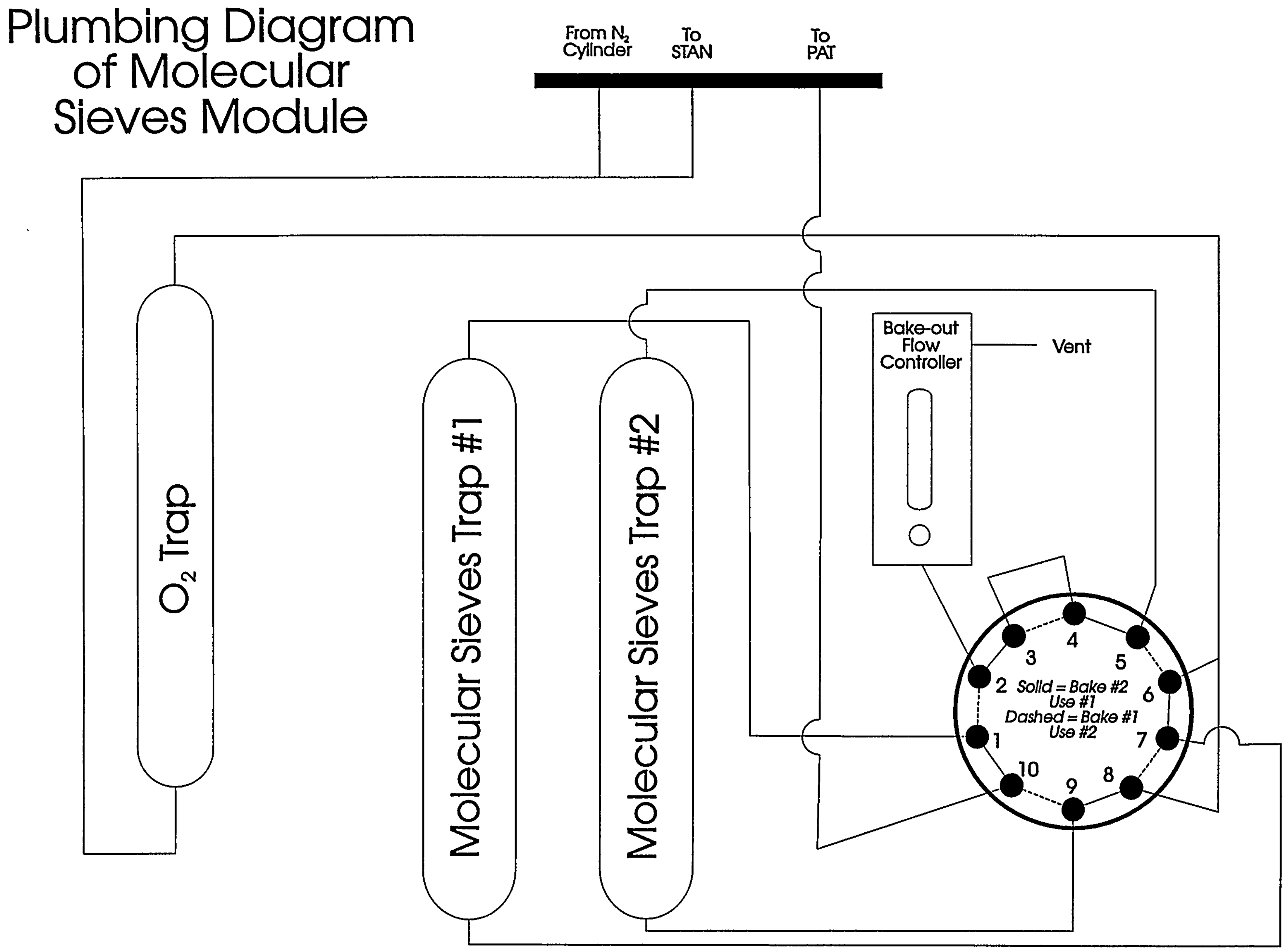


Figure 1) Plumbing diagram of molecular sieves module. STAN = standards module. PAT = purge and trap. The molecular sieves traps are mounted in separate aluminum blocks and can be heated independent of each other.

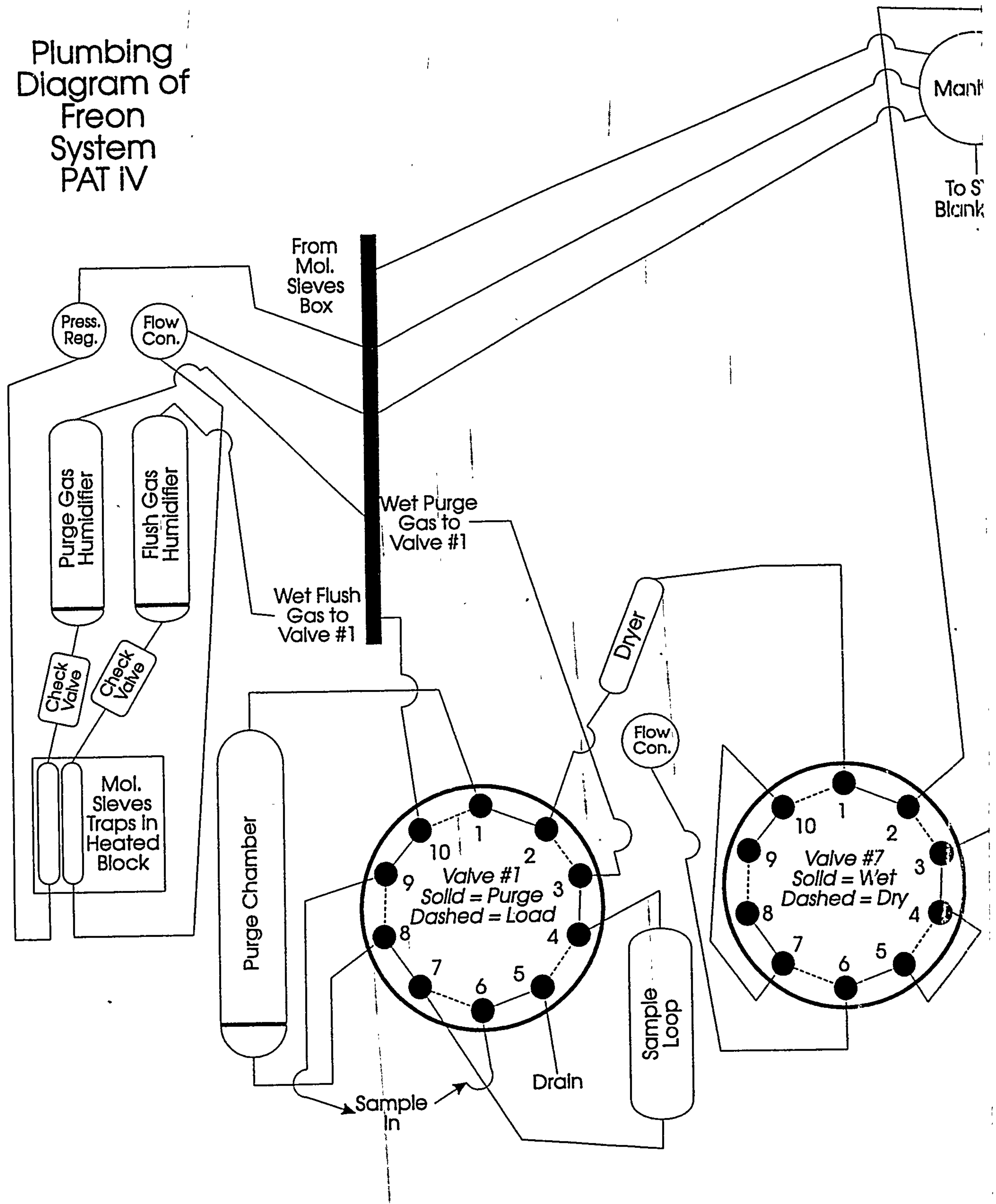
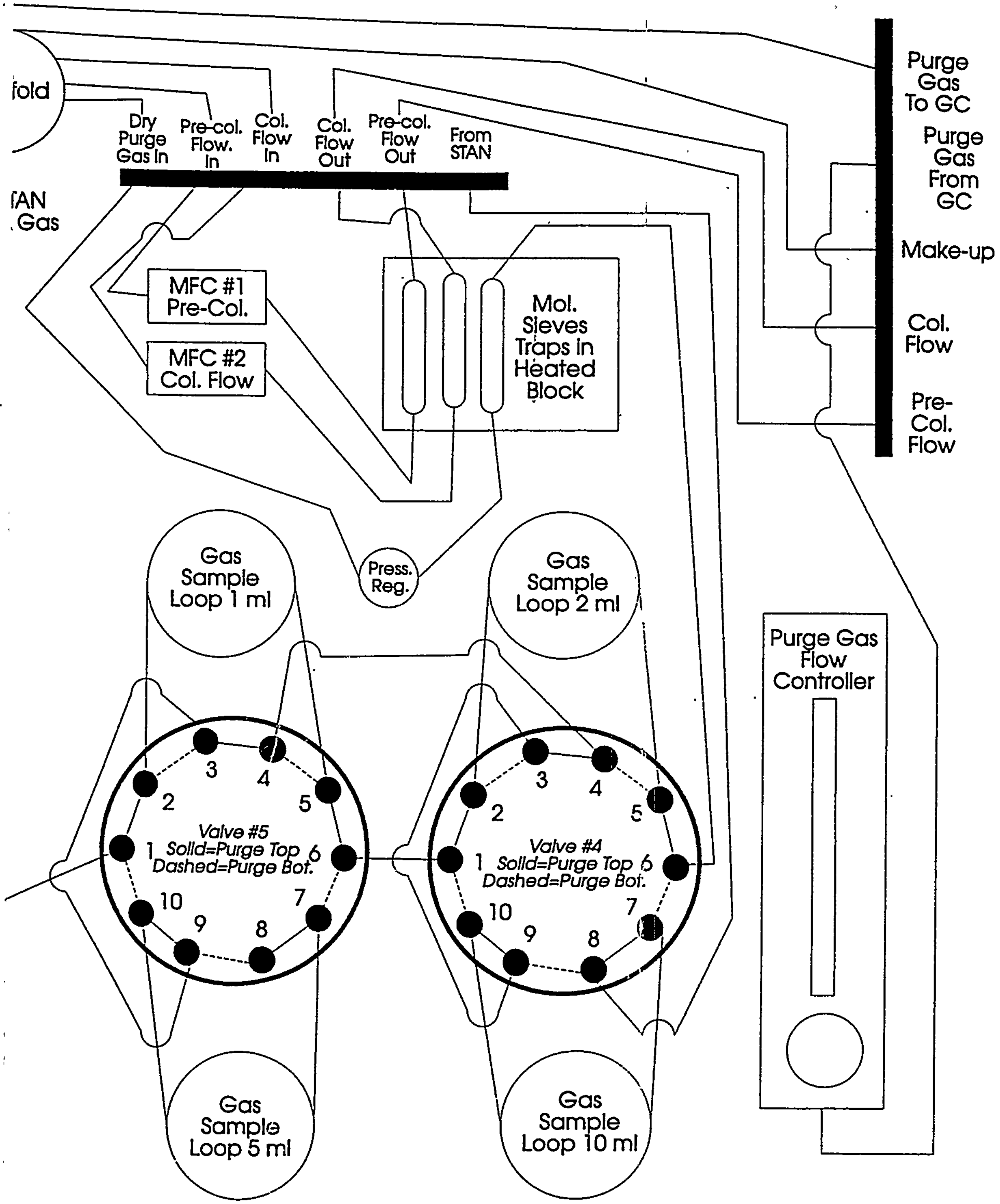


Figure 2) Plumbing diagram of purge-and-trap (PAT). Valve #1 - 2 position, 10 port, 1/8 inch fittings, Nitronic-60 valve bodies. Dryer = magnesium perchlorate drying trap. MFC = mass fl



fittings, Hastelloy C valve body. Valves #4, #5, #7 - 2 position, 10 port, 1/16 inch
ow controller. Col. = column. Press. Reg. = pressure regulator. Con. = controller.

Plumbing Diagram of STAN

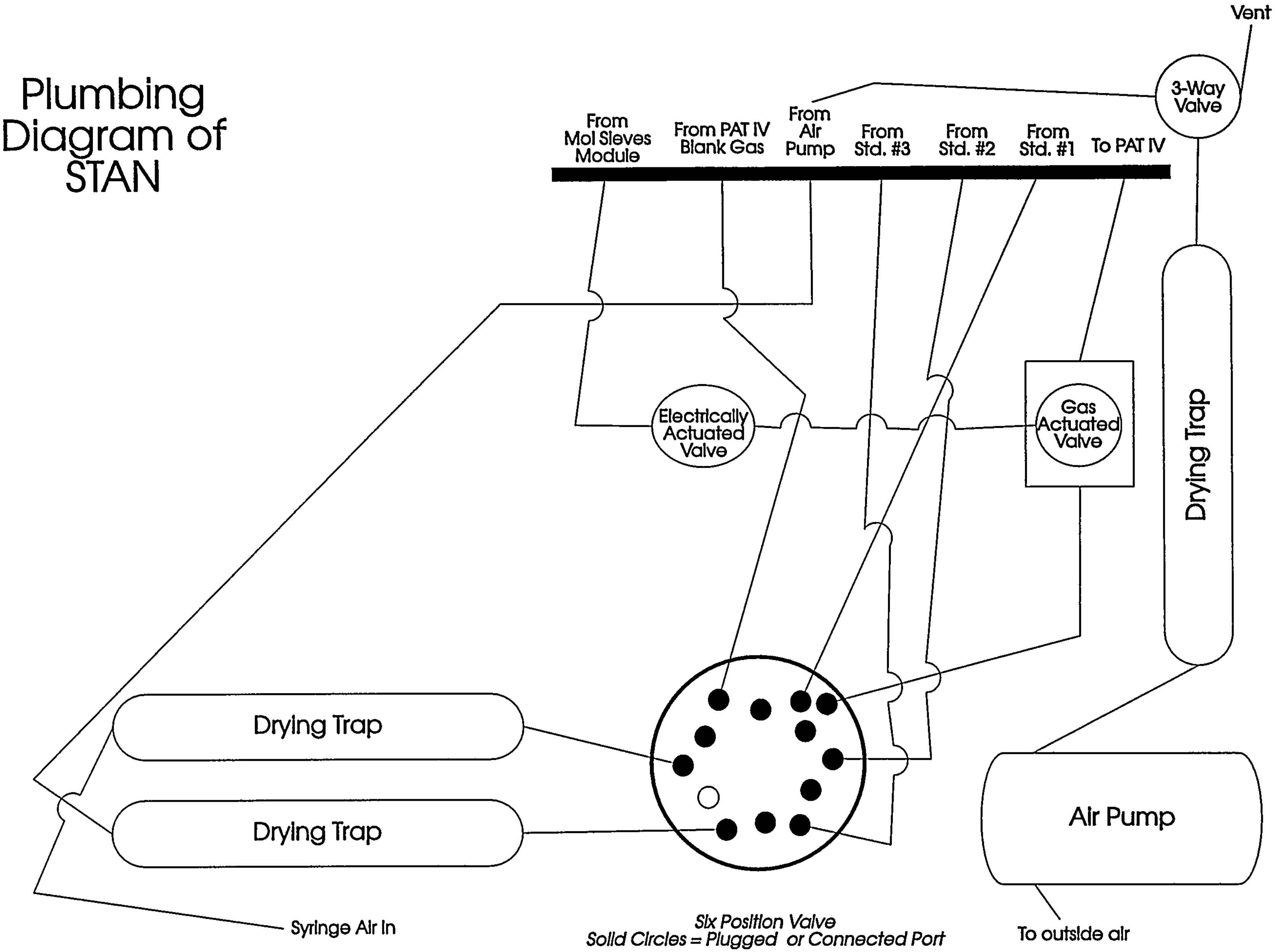


Figure 3) Plumbing diagram of standards module (STAN). Mol. = molecular. Std. = standard. Drying traps are packed with magnesium perchlorate.

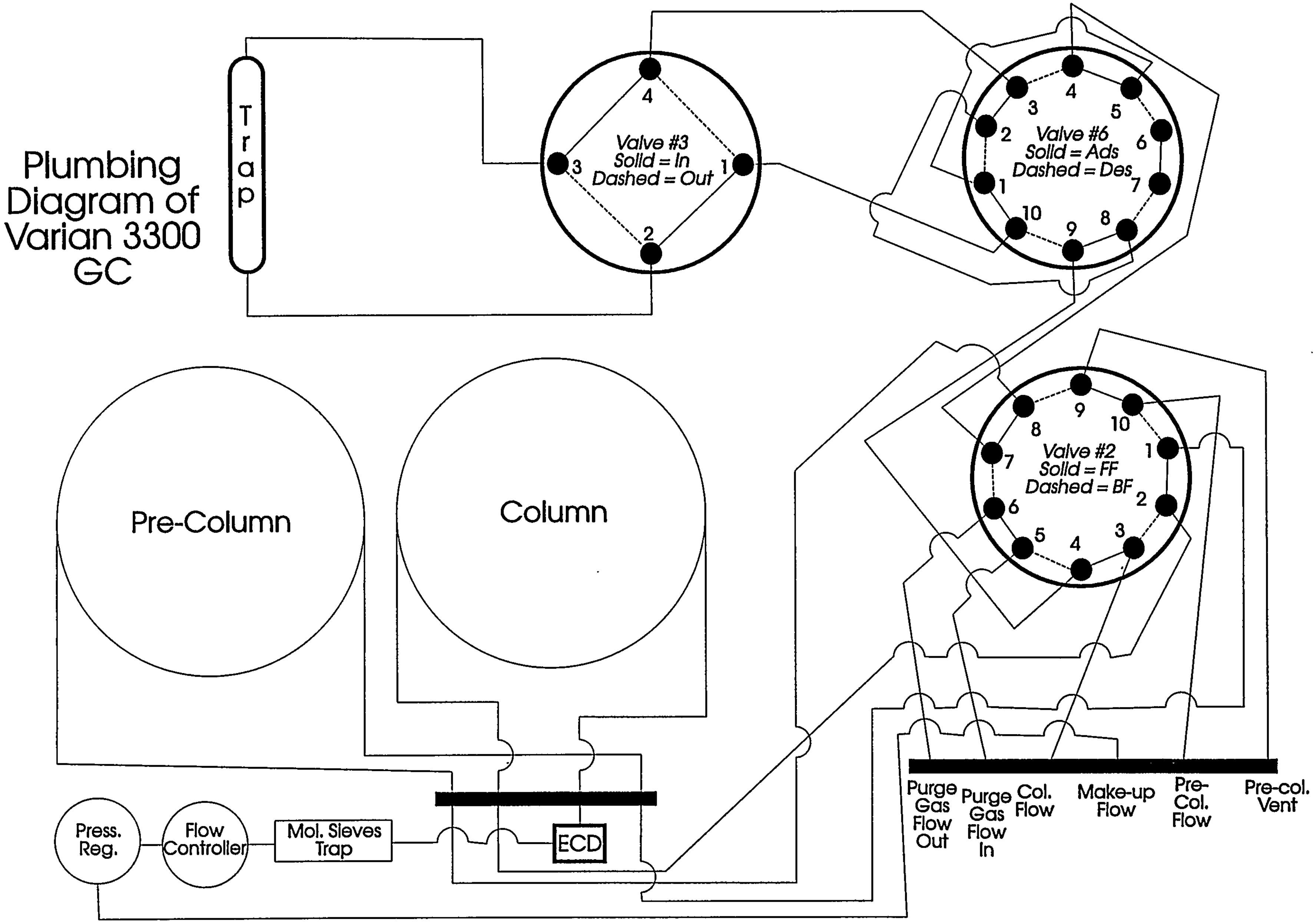


Figure 4) Plumbing diagram of Varian 3300 GC. Valve #3 - 2 position, 4 port, 1/16 inch fittings, Nitronic-60 valve body. Valves #2 and #6 - 2 position, 10 port, 1/16 inch fittings, Nitronic-60 valve bodies. Ads. = adsorb. Des. = desorb. FF = foreflush. BF = backflush. Col. = column. Mol. = molecular. Trap = Porapak N trap. ECD = electron capture detector.

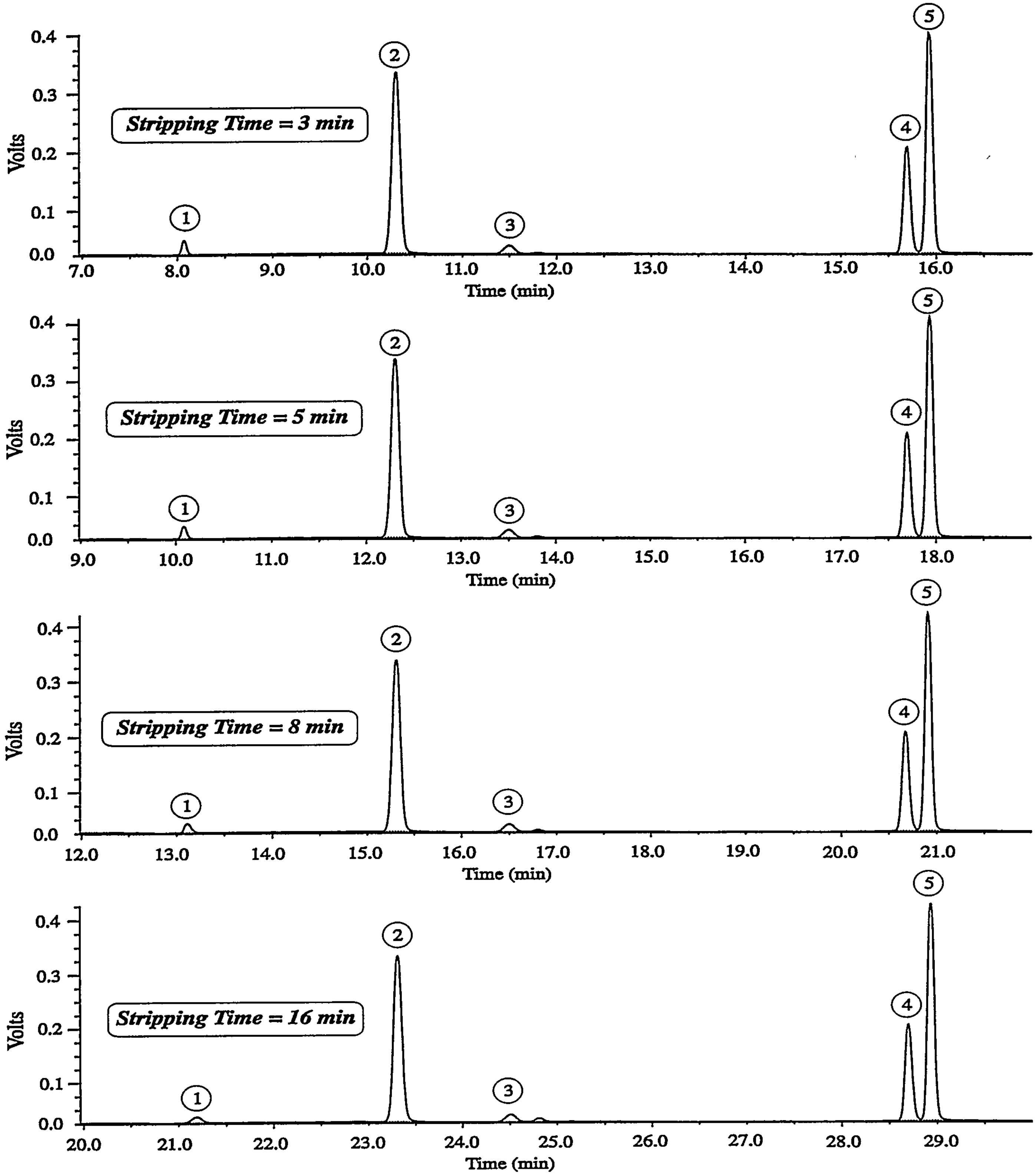


Figure 5) Breakthrough test chromatograms. Peak labels in circles: 1 = CFC-12, 2 = CFC-11, 3 = CFC-113, 4 = CH_3CCl_3, and 5 = CCl_4. Only the portion of the chromatograms with the halocarbon peaks of interest is shown. The standard used was 5.02 mL of S31. Stripping time refers to the time used to transfer the contents of the gas sample loop to the trap at a flow rate of 150 mL min^{-1}. The 3 min stripping time is normally used. None of the peak areas decreased with increased stripping time. The most volatile compound's (CFC-12) peak shape did change however. With increasing stripping time the peak became wider and shorter, probably because it spread out on the trap. CFC-12 peak heights and areas with increasing stripping time are as follows: 26666, 77176; 21553, 77907; 16515, 77993; 11125, 77968.

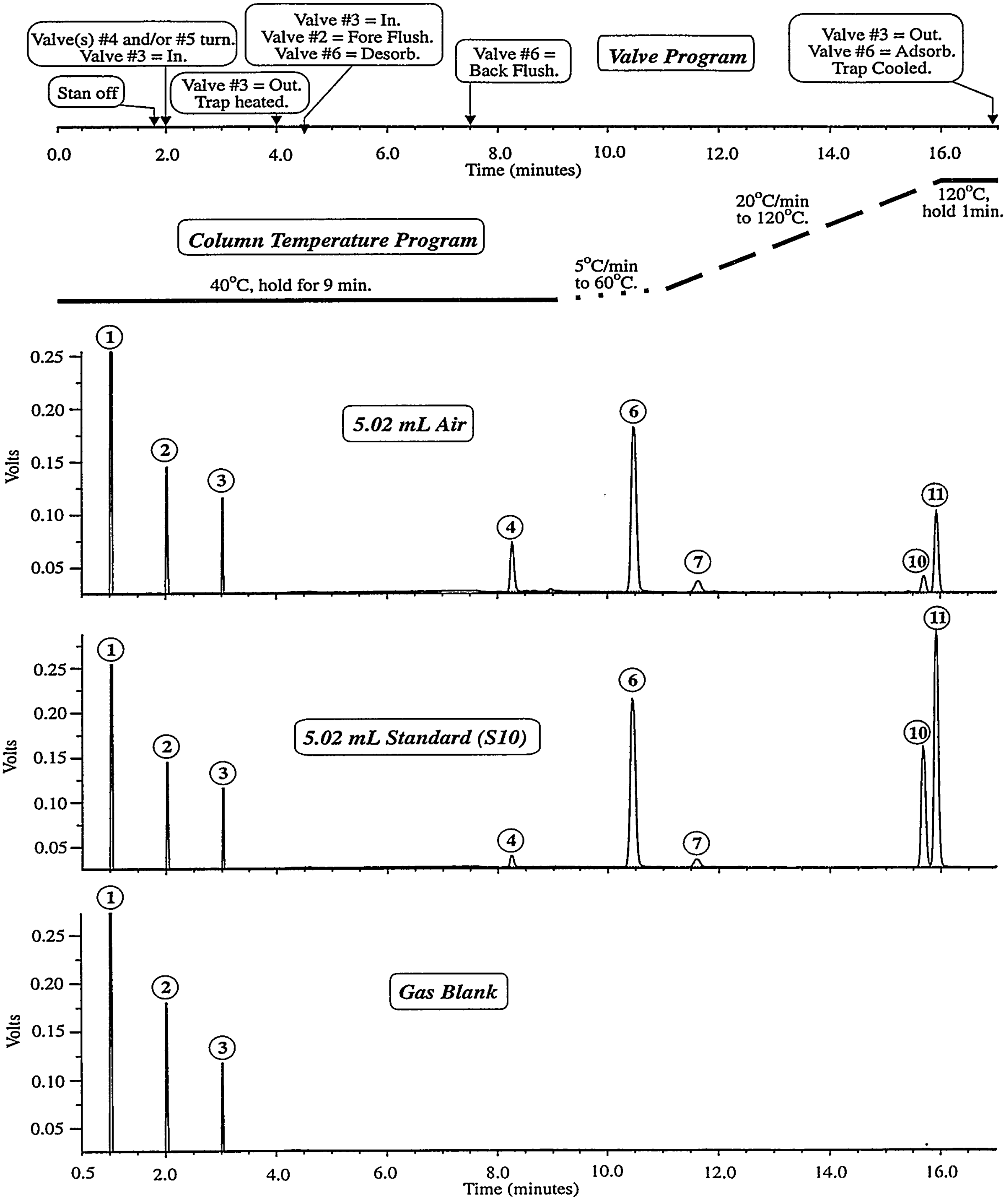


Figure 6) Chromatograms of gas blank, standard S10, and air. Peak labels in circles: 1 = gas sample loop temperature, 2 = water bath temperature, 3 = atmospheric pressure, 4 = CFC-12, 5 = CH_3Cl, 6 = CFC-11, 7 = CFC-113, 8 = CH_3I, 9 = $CHCl_3$, 10 = CH_3CCl_3, and 11 = CCl_4. Also shown for reference are the column temperature program and the valve program. The initial position (time = 0) of the valves were as follows: #1 = load, #2 = backflush, #3 = out, #6 = adsorb, #7 = dry, STAN on, and Porapak N trap cooling. The position of valves #4 and #5 was dependent on which loop(s) were being loaded (see Fig. 2).

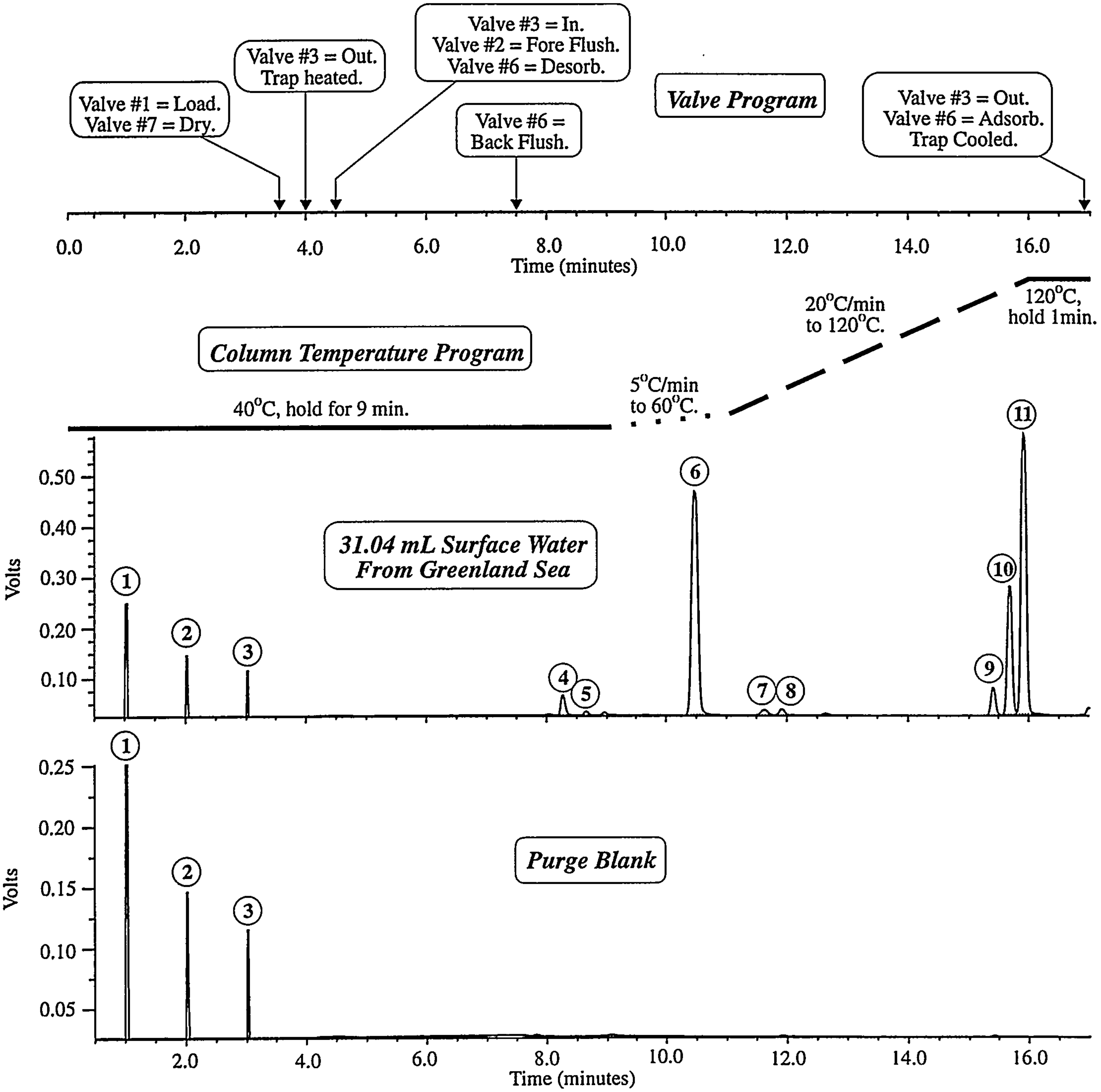


Figure 7) Chromatograms of purge blank and surface water from the Greenland Sea. Peak labels in circles: 1 = gas sample loop temperature, 2 = water bath temperature, 3 = atmospheric pressure, 4 = CFC-12, 5 = CH_3Cl, 6 = CFC-11, 7 = CFC-113, 8 = CH_3I, 9 = $CHCl_3$, 10 = CH_3CCl_3, and 11 = CCl_4. Also shown for reference are the column temperature program and the valve program. The initial position (time = 0) of the valves were as follows: #1 = purge, #2 = backflush, #3 = out, #4 and #5 = purge bottom, #6 = adsorb, #7 = wet, STAN off, and Porapak N trap cooling.

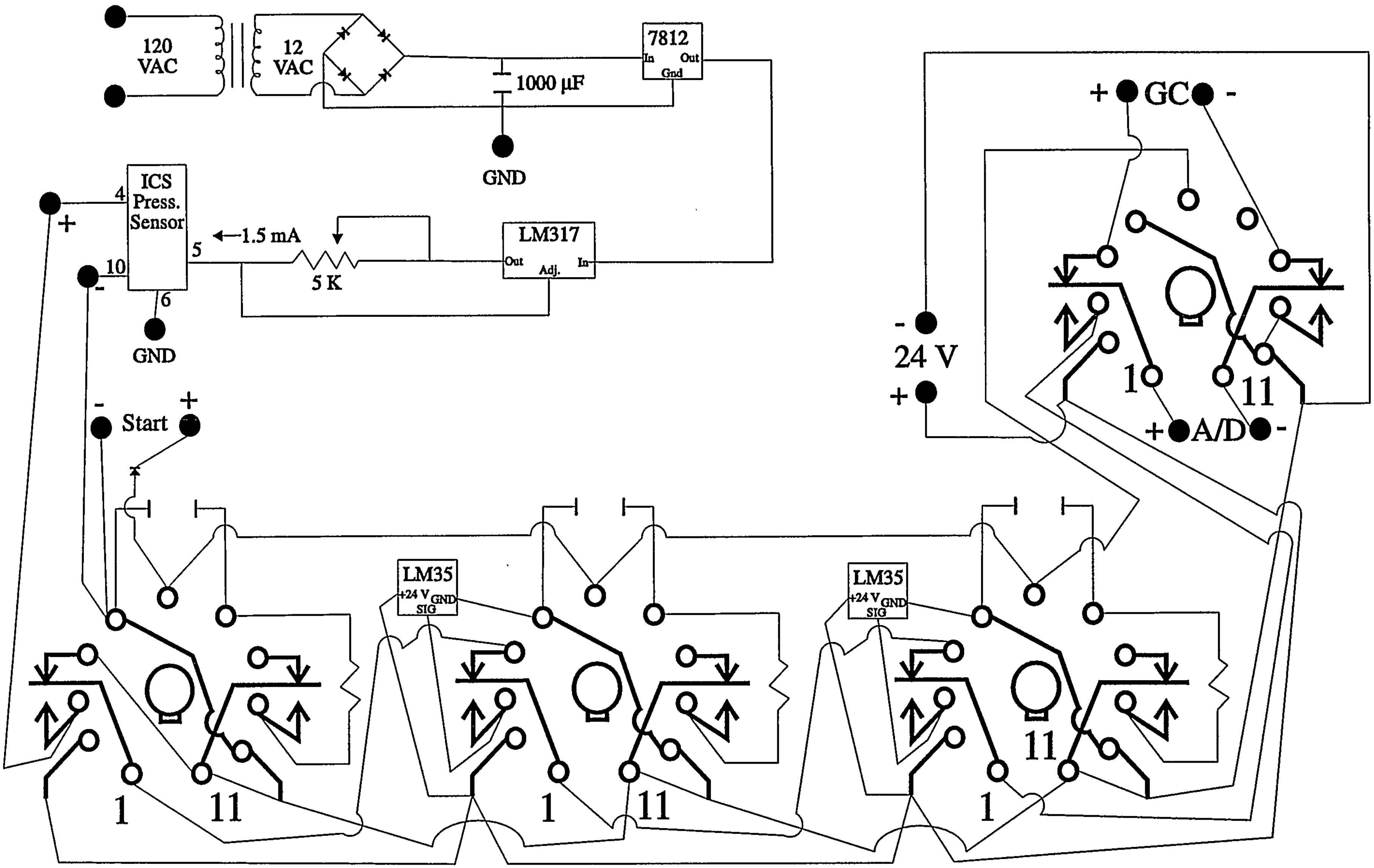


Figure 8) Wiring diagram of connections between Potter & Brumfield CNT series time delay relays and temperature and pressure sensors. Thick lines represent plug-in bases for the relays and internal connections. Thin lines are external connections. Unlabeled capacitors are 22 µF. Unlabeled resitors are 33 K. GC = gas chromatograph. A/D = analog to digital conversion board. Gnd = ground. Sig = signal. Press. = pressure.

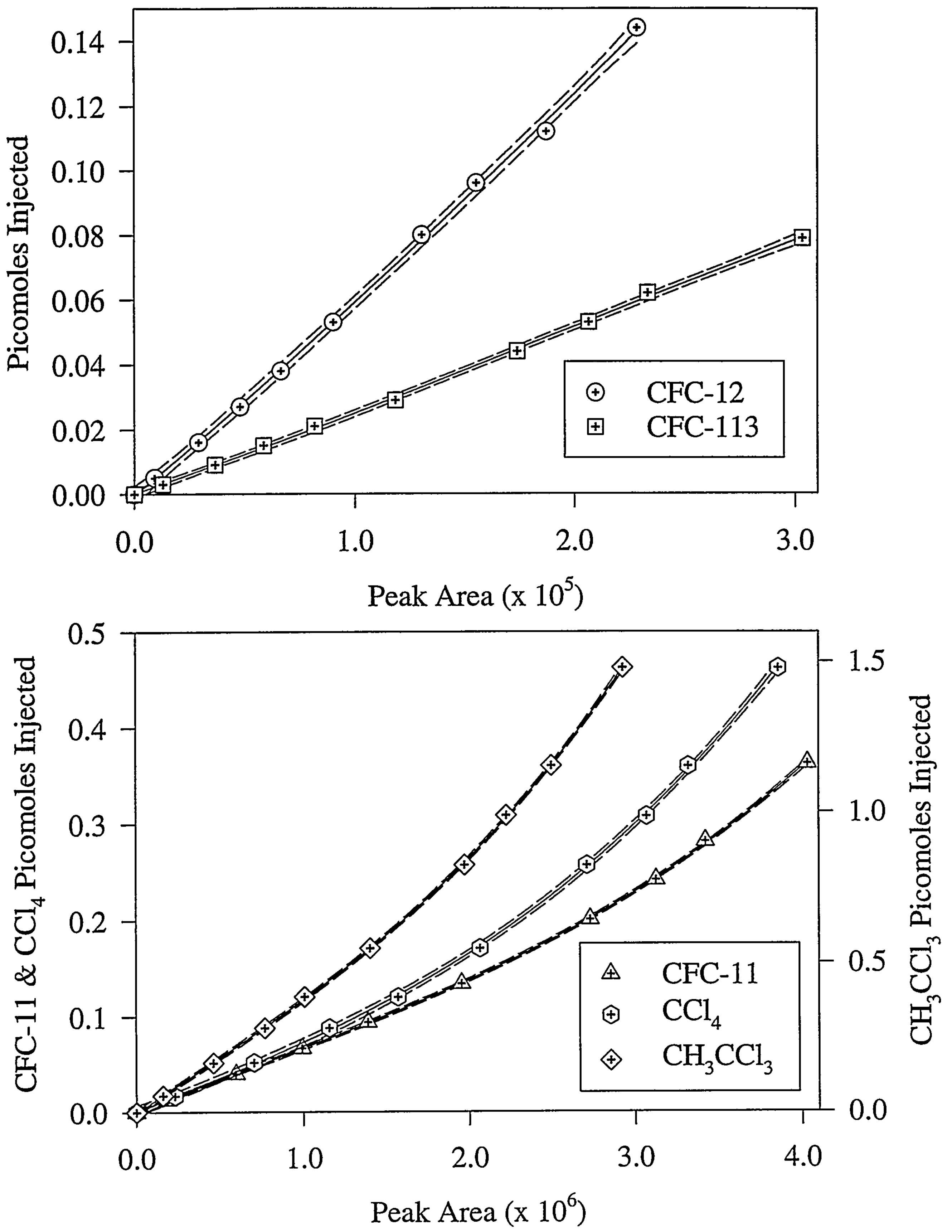


Figure 9) A typical set of calibration curves generated while at sea. The standard used was S10 (Happell and Wallace, 1996) and it contained CFC-12 (136.1 ± 3.1 pmol mol^{-1}), CFC-11 (331.9 ± 5.6 pmol mol^{-1}), CFC-113 (74.1 ± 2.0 pmol mol^{-1}), CH_3CCl_3 (1263.2 ± 33.1 pmol mol^{-1}), and CCl_4 (434.0 ± 14.5 pmol mol^{-1}) in N_2. The solid line through each set of points is the 3rd order polynomial fit to the data. The dashed lines around each solid line are the 95 % confidence intervals. The R^2 for the calibration equations for CFC-12, CFC-11, CFC-113, CH_3CCl_3 and CCl_4 are, respectively, 0.9992, 0.9999, 0.9994, 0.9999, and 0.9997.