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INSTRUMENTS AND METHODS

Determination of CCl_3F and CCl_2F_2 in seawater and air

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Abstract—An improved analytical technique has been developed for the rapid and accurate shipboard measurement of two anthropogenically produced chlorofluorocarbons (CFCs), CCl_3F (F-11) and CCl_2F_2 (F-12) in air and seawater. Gas samples (dry air or standard) are injected into a stream of purified gas and then concentrated in a low temperature trap. Seawater samples collected in oceanographic Niskin bottles are transferred into glass syringes for storage until analysis. An aliquot of approximately 30 cm^3 of seawater is introduced into a glass stripping chamber where the dissolved gases are purged with purified gas, and the evolved CFCs are concentrated in the same cold trap. The trap is subsequently isolated and heated, and the CFCs are automatically transferred by a stream of carrier gas into a precolumn and then a chromatographic separating column. The CCl_3F and CCl_2F_2 peaks are detected by an electron capture detector (ECD) and their areas are integrated digitally. CFC amounts are calculated using fitted calibration curves, generated by injection of various multiple aliquots of gas standard containing known concentrations of CFCs. Preliminary concentration values for these compounds are printed at the completion of each analysis. Total analysis time for air and water samples is <10 min, allowing detailed vertical profiles of the concentrations of these compounds in the water column and concentrations in the overlying atmosphere to be determined within a few hours of the completion of a hydrographic station. Typical relative standard deviations for analyses of CCl_3F and CCl_2F_2 in near-surface seawater containing equilibrium levels of these compounds are approximately 1%. Limits of detection for both compounds in 30 cm^3 seawater samples are about 0.005×10^{-12} mol kg^{-1}.

INTRODUCTION

THE concentrations of CCl_3F (F-11) and CCl_2F_2 (F-12) in the atmosphere have increased rapidly since commercial production of these compounds began in the 1930s. Pioneering measurements of the concentrations of F-11 in air were made by LOVELOCK (1971) using electron capture gas chromatography. Since the mid-1970s, a number of studies have been undertaken to measure the temporal and spatial increases of CFCs in the atmosphere. Atmospheric chlorofluorocarbons (CFCs) cross the air–sea interface and dissolve in surface seawater. At equilibrium, the concentration of dissolved F-11 or F-12 in surface seawater is a function of the temperature and salinity of the water (WARNER and WEISS, 1985) and of the concentration of the gas in the overlying atmosphere. Using potential temperature and salinity data, and models of the increases of atmospheric CFCs, the equilibrium CFC concentrations in the surface mixed layer of the ocean can be reconstructed as a function of time and position. As these dissolved compounds are

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carried from the surface into the interior of the ocean, the resulting distributions can be used to trace ocean mixing and circulation pathways, and estimate the rates of these processes. Recent studies of the vertical and horizontal distributions of dissolved F-11 and F-12 in the ocean have demonstrated clearly the usefulness of these anthropogenic compounds at time-dependent tracers.

The methods discussed in the following sections incorporate a number of modifications to earlier techniques used by GAMMON *et al.* (1981) for measuring dissolved CFCs in seawater. These modifications have led to significant improvement in the accuracy and precision with which CFC distributions in the ocean and atmosphere can be determined.

METHODS

Water sampling

Seawater to be analysed for dissolved CFCs is normally collected in 5 or 10 l Niskin oceanographic sampling bottles. After return of the cast to the deck of the ship, aliquots of seawater are transferred from the Niskin bottles into sample containers for various subsequent analyses. Water samples for CFC and other dissolved gas analyses are normally collected first, since the concentrations of dissolved gases can change rapidly once the Niskin bottle drain and vent valves are opened, and air enters the headspace of the bottle. Water samples for CFC analysis are especially vulnerable to contamination during this transfer process, since shipboard air can contain CFCs at concentrations orders of magnitude greater than those of clean marine air. To minimize contamination, transfer of water samples outdoors in clean air is preferred when weather conditions permit.

Seawater for CFC analysis is transferred into 100 cm^3 precision ground-glass syringes by inserting the tip of the syringe valve (Pharmaseal model K-71) directly into the Niskin drain valve. With the syringe and Niskin valves open, the hydrostatic pressure of the water in the Niskin bottle is sufficient to force the syringe plunger outward, and allow seawater to fill the syringe rapidly. Since the water entering the syringe is under positive pressure during filling, there is no tendency for air bubbles to be sucked into the sample, and seawater samples are transferred with minimum contact with air. Each syringe is flushed several times by partially filling with seawater, detaching from the Niskin bottle, and expelling the water and any air bubbles contained in the syringe. After final filling, the syringe valve is closed, and a rubber band is stretched over the syringe barrel to maintain positive pressure on the water sample. Typically, about 300 cm^3 of seawater are required for the flushing and filling process. The water-filled syringes are then immersed until processing in a bath of flowing surface seawater to isolate the samples from contact with laboratory air. Total time for rinsing and filling each syringe is about 2 min.

An epoxy-coated stainless steel spring is substituted for the length of highly permeable elastic tubing normally used inside standard Niskin bottles to close and hold the end-caps. Niskin bottles contain several small O-rings in the drain and vent valves, and large Buna-N O-rings at each end of the bottle. After the Niskin bottle end-caps are closed, the large O-rings remain partially exposed to the seawater sample. The concentrations of F-11 and F-12 in seawater held in closed Niskin bottles have been observed to increase over time. Under normal conditions, the rates of increase of F-11 and F-12 in 10 l bottles are typically $<0.005 \times 10^{-12}$ mol kg^{-1} seawater h^{-1}, but significantly higher rates have been observed. These increases are in part due to the release of CFCs from the O-rings in the bottles. Several precautions are taken to lessen the extent of contamination from this source. The O-rings are heated to 60°C in a purged vacuum oven for several days to

degas the Buna-N material, and stored in a gas-tight container until installation on the bottles at sea. To reduce the amount of CFCs diffusing into the walls and O-rings of the Niskin bottles between stations, efforts are made to store the bottles outdoors or in an area where the air is not heavily contaminated with CFCs.

The extent of CFC contamination in seawater samples may also be affected by the presence of silicones, greases and other materials on the O-rings and surfaces of the sampling bottles and in the analytical system. In cases of high or persistent levels of F-11 and F-12 contamination from sampling bottles or syringes, the surfaces can be rinsed with appropriate solvents.

When available, 10 l Niskin bottles are preferred to smaller bottles for water column sampling programs that include CFC studies. Measured F-11 and F-12 blank levels (0.005×10^{-12} mol kg^{-1}) for water samples collected in clean 10 l Niskin bottles are usually lower than those for 1.7 or 5 l Niskin bottles, due to more favorable O-ring surface area/water volume ratios in the larger bottles. Larger (e.g. 30 l) Niskin bottles are available, but are unwieldy for general use in hydrographic sampling programs. We have made comparisons between CFC samples collected in 10 l Niskin bottles and samples collected using other types of containers. Pairs of deep water samples have been collected at the same depth and time using piggyback *in situ* syringe samplers (CLINE *et al.*, 1982) mounted on 10 l Niskin bottles. We have also made comparisons between CFC samples collected in 10 l Niskin bottles, and those collected at the same depth using 270 l Gerard barrels. From a limited number of such comparisons, the CFC blank levels in 10 l Niskin bottles are similar or lower than those in samples obtained using the other samplers. Future modifications in sampler design and construction materials may reduce CFC contamination resulting from O-rings or other sources, and allow the use of smaller bottles for the collection of high quality seawater samples for the analysis of dissolved CFCs.

Air sampling

For air sampling during oceanographic expeditions, air intake lines, consisting of lengths of 3/8 in. o.d. Dekabon tubing (Samuel Moore Co.), are installed from the bow and stern of the ship into the laboratory. Dekabon tubing is of a composite construction, using an aluminum diffusion barrier coated on the inside with Mylar plastic and covered with a polyethylene sheath. The inlet ends of the tubing are mounted as high above the deck as possible, and shielded to avoid direct entry of rainwater or sea spray. Wind speed and direction are monitored to determine the pathway of air flow over the ship, and a selector valve inside the laboratory allows either inlet to be chosen as a source of uncontaminated marine air.

An Air Cadet Model 7530–40 pump is used to draw air at the rate of approximately 9 l min^{-1} continuously through the inlet line into the laboratory. An in-line back pressure regulator is used to maintain the pressure downstream of the pump at about 0.7 atm above ambient. A stream of air (approximately 70 cm^3 min^{-1}) is split from the main stream and directed into sample loops for CFC analyses. The remainder of the stream passing through the pump and back pressure regulator is vented to the room. This high flow rate of air through the system serves to keep both the Dekabon tubing and diaphragm of the pump thoroughly flushed, and avoids the need for ultra-clean materials in the air intake system. Clean marine air samples also can be collected in ground glass syringes and carried into the laboratory for CFC analysis. Grab samples of laboratory air

also can be introduced into the sample loops using syringes, and are routinely used to monitor the levels of F-11 and F-12 contamination inside the ship.

Extraction system

A schematic of the extraction and analysis system is shown in Fig. 1. Pressure from a gas cylinder containing 95% Ar/5% CH_4 is first reduced to approximately 3 atm above room pressure using a high purity two-stage pressure regulator. Downstream of this regulator, the gas supply is split into two pathways: the transfer gas stream, and the gas chromatograph (CG) carrier gas stream. Fine adjustment of the flow rate of the GC gas stream [approximately 30 cm^3 min^{-1} as measured at the electron capture detector (ECD) vent] is made using a metal bellows pressure regulator on the gas chromatograph. The flow rate of the transfer gas (approximately 50 cm^3 min^{-1} as measured at the purge housing vent) is adjusted by a Porter Model 8286 metal diaphragm pressure regulator.

To remove any traces of F-11 and F-12 present in the Ar/CH_4 supply, each stream is passed through a 1.5 m length of 1/4 in. o.d. stainless steel (ss) tubing packed with 60/80

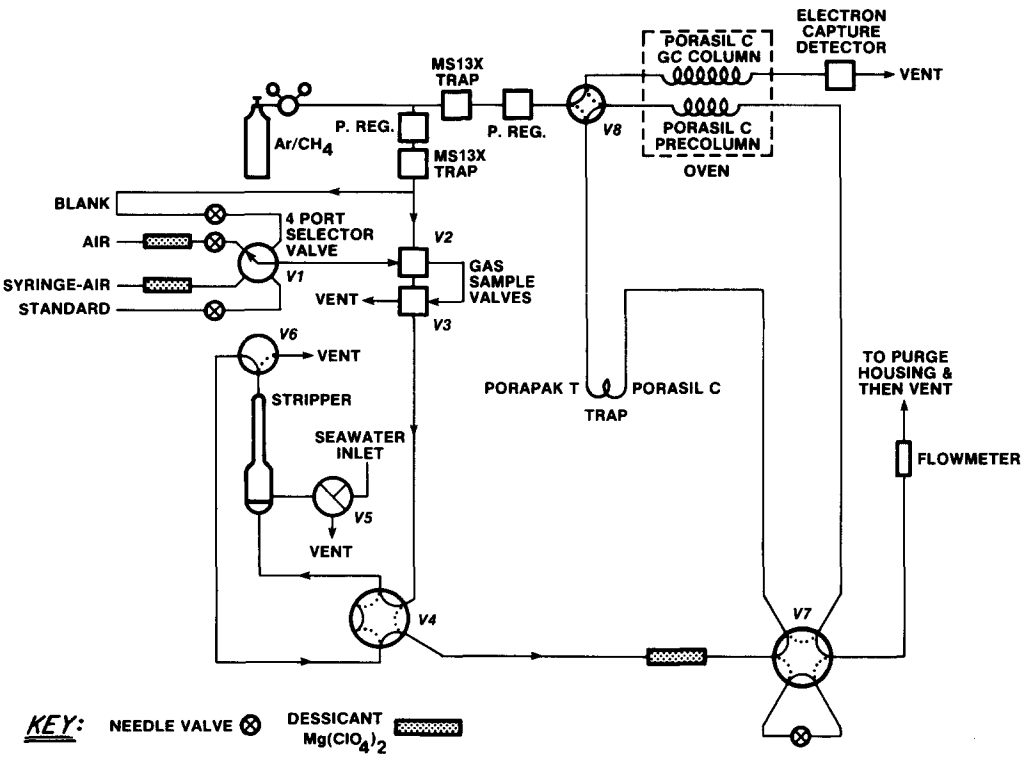


Fig. 1. Schematic of the CFC analytical system. The solid lines within the circles, representing valves V4 and V6–V8, show the flow pathways used for stripping dissolved gases from a seawater sample and collecting CFCs in the trap (held at −30°C). During this stripping process, the GC gas stream flows via valve V8 directly into the GC column and through the ECD. The dotted lines within valves V4, V7 and V8 show the flow pattern used for backflushing the contents of the heated trap into the Porasil C precolumn. After the F-12 and F-11 pass through the precolumn and enter the GC column, valves V7 and V8 are returned to the positions indicated by the solid lines. Slowly eluting compounds retained in the precolumn are backflushed to the vent, while F-12 and F-11 continue through the GC column and into the ECD.

mesh molecular sieve 13X adsorbent (MS13X). These coiled MS13X traps are wrapped with electrical heating tapes and are activated initially by baking at 300°C for 12 h, using an adjustable transformer to control voltage to the heating tapes. A flow of several hundred cm^3 min^{-1} of gas is used to flush the MS13X traps during this period, and the effluent from the traps is vented directly to the room. After conditioning, the traps are cooled to room temperature and connected to the flow system. At normal flow rates, these MS13X traps are effective in removing all measurable traces of F-11 and F-12 from the gas streams. Under normal usage, these MS13X traps prevent F-11 and F-12 in the supply gas from entering the system for a period of 1–2 weeks. The gradual elution of F-12 from the MS13X traps is usually observed first, and is detected as a small baseline shift during the analysis of system blanks. For re-conditioning, the MS13X traps are heated to 200°C for 4 h without disconnecting from the flow system. Compounds retained on the traps are eluted rapidly, and are vented through the extraction board. After cooling for 1–2 h, the re-conditioned MS13X traps again produce GC and transfer streams containing no detectable levels of F-11 or F-12.

Detector response for both F-12 and F-11 can change abruptly following re-conditioning of the MS13X traps. Response normally stabilizes within about 4–6 h after cooling of the traps. Following re-conditioning of the MS13X, a complete calibration curve is normally run before continuing with the processing of air or water samples.

Valves and components

Valve V5, a three-way inlet valve, is used for introducing seawater samples into the glass stripping chamber (Fig. 1). Valve V1 is a Carle selector valve, used for introducing gas samples into the system. Nupro needle valves are used to regulate the flow rate of sample gas supplied to this valve. Valves V2–V4 and valves V6–V8 are manufactured by Valco Instruments. A gas sample loop, consisting of a length of coiled 1/8 in. o.d. ss tubing, is connected to each gas sampling valve (V2 and V3). To improve temperature stability, these gas sample loops are placed around an aluminum cylinder and are insulated by layers of glass wool and aluminum foil. A thermometer bulb is mounted near the center of the aluminum cylinder to monitor the temperature of the sample loops. Valves V4 and V6 are used to direct the flow of transfer gas through the stripping chamber. Valves V7 and V8 are equipped with electric actuators, and are used to route the flow of gases through the cold trap, precolumn and GC column.

The rotors of the Valco valves, which come in contact with the gas streams, are constructed of a graphite filled fluorocarbon polymer blend. Although permeable to CFCs, this material is chosen for its sealing properties, durability and chemical inertness. To prevent F-11, F-12 and other gases in laboratory air from slowly diffusing through the valve rotors and entering the gas streams, the bodies and rotors of the Valco valves are enclosed in purge housings. The purge housings are connected in series and are continuously flushed with the stream of CFC-free gas eluting from the transfer gas vent.

The valve bodies of V4 and V6–V8 are constructed of Hastelloy C, an alloy which is much more corrosion resistant to seawater than is stainless steel in the low oxygen environment typically present in the extraction system. The tubing connecting valves V4 and V6 to the stripping chamber, and connecting V4 to the drying column is constructed of 1/8 in. o.d. titanium. Due to their similar half-cell potentials with respect to electrolysis in seawater, titanium and Hastelloy C can be used in contact with each other in this part of the system.

The lower part of the borosilicate glass stripping chamber is fitted with a coarse sintered-glass frit. The upper part consists of a section of glass burette, and the upper and lower ends of the stripping chamber are constructed of lengths of 1/4 in. o.d. glass tubing. The drying columns are made of 3/8 in. o.d. glass tubing, and contain $Mg(ClO_4)_2$ dessicant, held in place with wads of glass wool. Connections to the glass stripping chamber and drying columns are made using Swagelok fittings with Teflon ferrules. One-eighth in. o.d. nylon tubing is used to connect the seawater inlet to V5, and to connect V5 to the stripping chamber. The CFC permeability of this tubing has been measured and found to be insignificant in this application. The remaining tubing and fittings used in the parts of the system that contact only dry gases are constructed of 1/16 in. o.d. ss.

EXTRACTION OF CFCs

Water samples

For water sample processing, the valve on a seawater-filled syringe is connected via a Luer–Lok fitting to the nylon seawater inlet tube on V5. Approximately 20 cm^3 of seawater is flushed through this valve to the vent. V5 is then positioned to allow water to enter the stripping chamber. Gas displaced during the water filling process passes to the vent through V6 and a 60 cm length of 1/8 in. tubing. The volume of water transferred to the stripping chamber is determined in two ways. The travel of the syringe barrel during filling is measured by a precision caliper, and is multiplied by the cross-sectional area of the individual syringe. In the second method, the volume of water is determined from a series of calibrated buret lines on the upper wall of the stripping chamber. In either case, the volume of water in the sidearm connecting V5 with the stripping chamber is not stripped of CFCs. This volume (approximately 0.2 cm^3) is determined geometrically, and is subtracted from the injected volume. Typically, the volume of seawater stripped is approximately 30 cm^3. Estimated accuracy for the determination of the volume of seawater transferred is approximately 0.2%. After filling the stripping chamber, valves V5 and then V6 are closed immediately. In the bypass position for valve V4 (see dotted lines, Fig. 1), the internal porting blocks seawater held in the stripping chamber from draining downward through the frit.

In order to extract the CFCs from a seawater sample, the transfer gas stream is directed into the stripping chamber via V4. The transfer gas enters the bottom of the stripper, bubbles through the glass frit and water sample, and flows out of the stripping chamber through V4. The gas stream then passes through the dessicant column and into the trap, where the CFCs are collected (Fig. 1). Prior to the initiation of the transfer process, the trap is pre-cooled for 30 s by immersion in a stainless steel Dewar containing isopropanol at –30°C. The temperature in the bath is maintained by the cooling probe of a Neslab Cryocool refrigeration unit with temperature controller.

Stripping time is 4 min, at a flow rate of about 30 $cm^3\ min^{-1}$ at the pressure inside the stripping chamber. Dissolved CFCs in the seawater sample are removed via the transfer gas stream by a first order stripping process. An estimate of the efficiency of the stripping process can be obtained by re-stripping a water sample for an additional 4 min. At a temperature of 25°C, no measurable amounts of F-11 and F-12 remain in surface seawater samples after the first 4 min of stripping. At 0°C, essentially all dissolved F-12, and approximately 99.7% of dissolved F-11 are removed in 4 min. An estimate of the "stripper blank" resulting from the stripping and trapping procedure can be obtained by

passing transfer gas through the empty stripping chamber for 4 min. Such stripper blanks are normally below the detection limits of the analytical system.

TRAPPING AND INJECTION

The trap used to hold F-11 and F-12 consists of a length of 1/8 in. o.d. ss tubing packed with 5 cm of glass beads, followed by 5 cm of Porasil C (80/100 mesh), 5 cm of Porapak T (80/100 mesh), and 5 cm of glass beads. These materials are held in position by small wads of glass wool. The transfer gas stream (with sample) enters the trap at the Porasil C side (Fig. 1). The F-11 in the transfer gas stream is held quantitatively in this section of the trap at –30°C. During the 4 min trapping period, the F-12 carried into the trap by the transfer gas stream slowly migrates through the Porasil C, but is held quantitatively on the Porapak T section. Although both F-11 and F-12 can be retained at –30°C on a trap containing only Porapak T, the use of a two-component trap with Porasil C to trap the F-11 results in sharper F-11 chromatographic peaks.

During trapping of the CFCs, the transfer gas and most of the O_2 and N_2O from the sample pass through the cold trap. Lower transfer gas flow rates and colder temperatures tend to retain more N_2O in the trap, which can interfere with the F-12 peaks in the resulting chromatograms.

After passing through the trap, the transfer gas stream enters the precolumn (15 cm of 80/100 mesh Porasil C packed in a 1/8 in. ss tube and held in the GC oven at 70°C). Slowly eluting higher molecular weight compounds remaining in the precolumn from injection of previous samples are backflushed and carried off the precolumn by this gas stream during the trapping process. The transfer gas then passes through a flowmeter and through the series of Valco purge housings before venting to the atmosphere.

Gas samples

Four types of gas sample can be flushed through the sample loops via valve V1: the "standard" inlet is connected to a cylinder of compressed calibration standard gas, the "syringe air" inlet is used to inject grab samples of air collected with syringes, the "air" inlet is connected to the supply of outside air provided by the pumping system, and the "blank gas" inlet is connected to a source of CFC-free Ar/CH_4 gas (see Fig. 1). Needle valves are used to set the flushing rates of these inlets to approximately 75 cm^3 min^{-1}. Dessicant columns are placed in the air and syringe air inlets, allowing concentration measurements to be made and reported directly in the units of mole fraction of CFC in dry air. This avoids the need to make corrections due to variations in the water vapor content of air samples. Both the standard and blank gases are prepared from dry gases, so no dessicants are required in these inlets.

The pressure of the standard cylinder is reduced to approximately 1 atm above ambient using a two-stage Lif-O-Gen regulator with a stainless steel diaphragm. These regulators have very small internal volumes, and do not measurably alter the CFC content of the standard flowing through them. The blank gas supplied to valve V1 is split from the purified stream of transfer gas and can be introduced into the sample loops and injected in a similar fashion to other gas samples, thus providing an estimate of the F-11 and F-12 "system blank" accumulated during the processing of a gas sample. Such system blanks are run frequently during processing of water and air samples, and are normally below the detection limit of the analytical system.

During flushing, the selected sample stream passes from V1 through the two sample loops in series, and then through an isolation coil (a 3 m length of 1/8 in. o.d. ss tubing) before venting to the atmosphere. After flushing for 2 min, the flow is halted by V1, and the gas in the loops is allowed to equilibrate to room temperature and atmospheric pressure for 10 s before injection. The isolation coil restricts the entry by diffusion of CFCs from lab air into the sample loops during this period. At the time of injection, the atmospheric pressure is measured to an accuracy of 0.1 mbar using a precision aneroid barometer, and the temperature at the center of the sample loop aluminum cylinder is measured to an accuracy of 0.01°C. V2 and/or V3 are then switched into the inject position, and the gas sample is carried out of the sample loop by the transfer stream. Once past V4, the gas sample then follows the same pathway through the system to the cold trap as do gases extracted from the stripping chamber during a water sample analysis. For multiple aliquots of a gas sample volume, V2 and V3 can be returned to the filling position, the loops flushed with additional sample, injected, and collected together on the cold trap.

Chromatography

After 4 min of trapping, the transfer gas flow is diverted from the trap via V7, the trap is isolated and the cold bath removed, and then the trap is rapidly heated to 100°C by immersion in a Dewar flask of boiling water. A needle valve at V7 maintains a constant flow of transfer gas during the switching and prevents surges when the transfer gas is shunted directly to the flowmeter and purge housings. After 30 s of heating, the chromatographic run begins as V8 is switched and the GC gas stream is directed into the trap. Plotting and integrating of the signal generated by the ECD begins at this point. Both V7 and V8, which control the injection and backflushing of a sample, are equipped with Valco electric actuators, and the timing of these sequences is controlled automatically by a Spectra Physics SP4100 digital chromatographic integrator (SP4100).

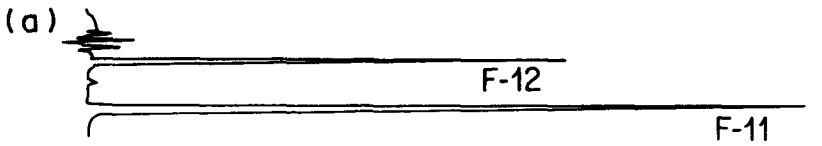
The GC gas stream enters the trap on the Porapak T side (Fig. 1), thus backflushing the trap contents out through the Porasil C and into the precolumn. The separation of F-11 and F-12 from more slowly eluting compounds occurs on the precolumn during the initial 40 s of the run. After the F-11 and F-12 pass through the precolumn and onto the main GC column, V7 and V8 are returned to their original positions.

Separation of F-11 from F-12 occurs on the GC column (3 m of 80/100 mesh Porasil C packed in a coil of 1/8 in. o.d. ss tubing) held at 70°C in the oven of the Shimadzu Mini-2 gas chromatograph. The standard temperature control circuit of this instrument has been modified to improve oven temperature stability, and aluminum blocks are mounted in the detector zone to increase the thermal mass and improve the temperature stability in this region.

The gas chromatograph is equipped with a ^{63}Ni ECD held at 250°C, and utilizes a constant-current, variable-frequency amplifier. As electron capturing compounds pass through the detector, current flow is maintained at a constant level by varying the pulse frequency across the cell. The frequency signal from the ECD is converted to a D.C. output, and sent to the SP4100 for plotting and integration of peak areas.

The time required for a chromatographic run (300 s) is determined by the need to adequately separate F-12 from N_2O during the early part of the run, and by the need to allow any late peaks to elute before beginning the next run. During each analysis, information on sample identification, temperature, pressure and volume are entered

manually via a keyboard into the SP4100. At the completion of each run, a BASIC program in the SP4100 is used to identify the F-11 and F-12 peaks, based on retention time. Retention times for these components do not normally drift more than 1–2 s per week. The sample data and chromatographic peak data are printed, and are also encoded in FSK (frequency shift keying) and stored on an audio cassette tape. The cassette tapes can be replayed later in the laboratory and the data transferred to a computer for further processing. During the chromatographic analyses, preparations for the next sample can begin, so that processing and analysis of a series of samples is overlapping.

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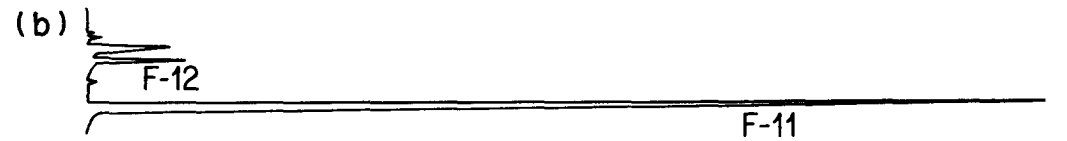


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F11/F12 RATIO 2.280
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Fig. 2. (a) Chromatogram of a shipboard analysis of 3.135 cm^3 sample of marine air, at a pressure of 1005.7 mbar and a temperature of 21.4°C, collected on 10 March 1987 in the northwestern Weddell Sea (58°20'S, 52°13'W). Chromatographic run begins at the top of the figure. The backflush of the precolumn at 40 s into the run is followed by three unidentified small peaks. The retention times for F-12 and F-11 are 126 and 240 s, respectively. The small peak at 175 s may be $C_2Cl_2F_4$ (F-114). At completion of each run, F-11 and F-12 peak areas are interpreted using fitted calibration curves, and preliminary values for F-12 and F-11 concentrations in mole fraction × 10^{12} (ppt) are printed as the final line of the report. (b) Chromatogram resulting from the shipboard analysis of a 26.3 cm^3 sample of near-surface seawater, collected on 9 March 1987 in the northwestern Weddell Sea. The chart attenuation is a factor of eight greater than that of the chromatogram shown in (a). The large peak preceeding F-12 is N_2O, which is partially retained in the cold-trap. Preliminary values for concentrations (in pmol/l^{-1}) and the dissolved F-11/F-12 ratio are calculated and printed in the final two lines of the report.

A chromatogram generated from a sample of dry marine air is shown in Fig. 2a. The mole fractions reported for F-11 and F-12 are 219.3 parts per 10^{12} (ppt) and 394.5 ppt, respectively. The precolumn and trap backflush occurs at 40 s into the run, and is followed by a series of small peaks. The F-12 and F-11 peaks are eluted at 126 and 240 s after injection, respectively. Figure 2b shows a chromatogram generated from the analysis of a near-surface seawater sample collected at a nearby location. The large peak preceeding the F-12 peak is generated by a trace amount of N_2O, which is not completely purged through the cold trap during the processing of water samples. The preliminary concentrations of F-11 and F-12 reported for this sample are 5.32 pmol l^{-1} (1 pmol = 10^{-12} mol) and 2.33 pmol l^{-1}. The volume of seawater analysed is approximately 8.5 times greater than the volume of the air sample analysis shown in Fig. 2a. The F-11/F-12 ratio in the surface water sample is about 3.3 times greater than that in the overlying air, reflecting the higher solubility of F-11 in seawater (WARNER and WEISS, 1985).

CALIBRATION

Standards

CFC gas standards, with F-11 and F-12 concentrations near those of modern air, are prepared in a two-step "bootstrap" process described in detail in BULLISTER (1984) and WEISS and BULLISTER (1988). Precisely measured aliquots of pure F-11, F-12 and N_2O in approximately their atmospheric ratios are mixed together in a static gas dilution system. A small aliquot of this mixture is then transferred to an Airco Spectra-Seal high-pressure aluminum cylinder which is subsequently filled with synthetic air (prepared from ultrapure O_2 and N_2) that is free of F-11, F-12 and N_2O. From the initial ratios of the gases in the added aliquot and from accurate measurements of the resulting N_2O concentration (WEISS, 1981), the F-11 and F-12 concentrations in the air mixture can be calculated accurately. The SIO calibration scale is based on this method, and has an estimated accuracy of 1.3% for F-11 and 0.5% for F-12. A comparison of air measurements reported on the SIO scale to those based on the ALE scale (RASMUSSEN and LOVELOCK, 1983) is given by WEISS *et al.* (1985) and by WEISS and BULLISTER (1988).

Airco Spectra-Seal aluminum cylinder, filled with clean and dry marine air collected at La Jolla, are used as working standards. These cylinders are calibrated against the SIO primary standards, and are routinely used for shipboard CFC calibration.

Calibration curves

Calibration curves used for determining CFC concentrations in air and water samples are generated by multiple injections of known volumes of standard gas. In creating calibration curves, the number of aliquots of CFC standard injected is chosen to span the range of CFC levels encountered in air and water analyses. The volumes of the two sample loops are determined gravimetrically by filling with distilled water, and are known to an accuracy of approximately 0.05%. The volumes of the two gas sample loops used are approximately 3 and 0.5 cm^3. The volume of the larger sample loop is 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 the amount of F-12 present in 30 cm^3 surface seawater samples.

During periods of intensive air or seawater processing, complete calibration curves are normally generated at daily intervals. Analyses of a large loop of standard gas are

performed at approximately hourly intervals to monitor short-term changes in detector sensitivity (peak area mol^{-1}) for each CFC. Drift in detector sensitivity in usually <1–2% over a 24 h period, but can be significantly greater for several hours following the conditioning of the MS13X traps.

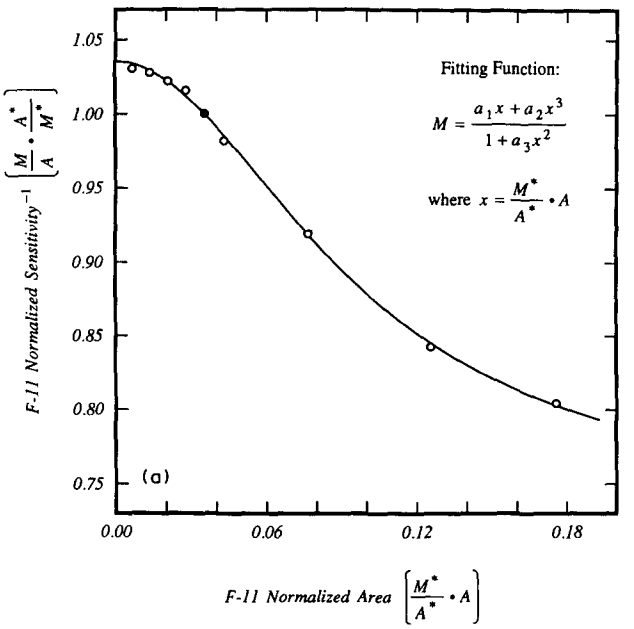
Aboard ship, after each system blank or stripper blank analysis, the F-11 and F-12 peak areas are stored in the SP4100 as the current blank values. After each standard or air analysis, the measured F-11 and F-12 peak areas are corrected by subtracting the current system blank values. After each water analysis, the F-11 and F-12 are corrected by subtracting the current stripper blank values.

To compensate for slow drift in detector sensitivity between calibration curves, a re-normalization factor is calculated for F-11 and F-12 after each new analysis of a large loop of standard gas. This factor is obtained by comparing the blank-corrected sensitivity for the most recent run of the large loop of standard to that for a loop of standard analysed at the time that the runs used in the calibration curves were made. This method of correcting for changes in detector response assumes that the changes in absolute detector sensitivity are more significant over these time scales than are changes in the non-linearities of the response curves.

Using polynomial expressions that relate F-11 and F-12 sensitivities to numbers of moles injected, the corrected peak areas are converted into moles. These polynomial expressions are obtained onboard ship by least squares fitting to the calibration data. Preliminary CFC concentrations (either mole fraction for gas samples, or mol l^{-1} for water samples) are then calculated by dividing the numbers of moles of F-11 and F-12 by the sample volume analysed. The results of these calculations are printed within a few seconds of the completion of each run as part of the shipboard run report. Although preliminary, since bracketing standards and blanks are not available at the time of these calculations and the curve fits to the calibration data are not final, these values are usually within a few percent of the final calculated concentrations. At sea, these preliminary results can be used to plot profiles and sections of CFC distributions within a few hours of the completion of each station. This allows interesting features of CFC distribution in the water column to be identified and subsequent sampling strategy for CFC and other tracers to be modified accordingly.

Following the expedition, the data cassettes are returned to the laboratory for final computer processing. System blank peak areas, interpolated linearly as a function of run number, are subtracted from the peak areas of all air or standard gas samples. For each measurement of one large loop of standard, the number of moles of each CFC injected is calculated from the temperature, pressure, volume and standard concentration data, and is then divided by the blank-corrected peak area to obtain a reciprocal sensitivity in moles per unit area. The peaks of all standard, air, water and stripper blank analyses are multiplied by this reciprocal sensitivity, linearly interpolated as a function of run number, to obtain normalized responses which are corrected for time-dependent sensitivity changes.

The resulting normalized calibration curves for each CFC are then fitted by least squares to empirical fitting functions, which are ratios of two-term or three-term polynomials selected to best represent the shapes of the response curves. Examples for F-11 and F-12, showing opposite signs of the nonlinearity corrections for these two CFCs, are plotted in Fig. 3a and b. The fits are constrained to pass exactly through the origin (zero blank-corrected response for zero CFC), and through the points for one large standard loop analysis against which the curves are normalized.



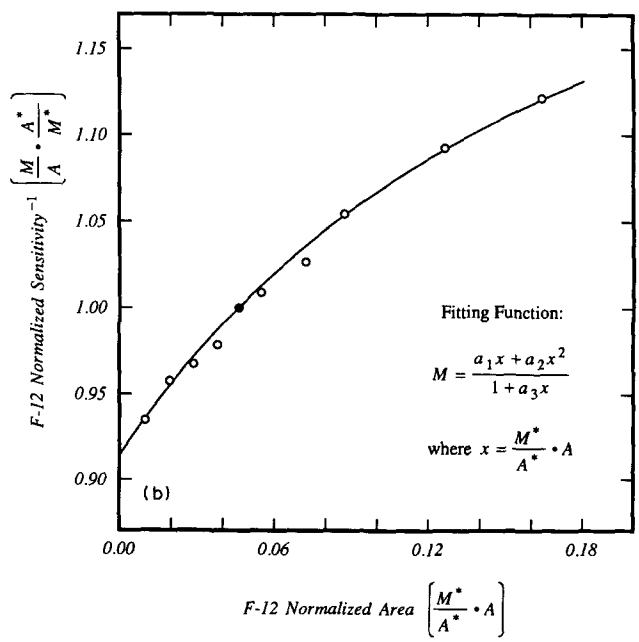


Fig. 3. Normalized calibration curves for F-11 (a) and F-12 (b) together with the empirical fitting functions used for each curve. The points for one large loop of standard, through which the fits are constrained to pass (see text) are shown as filled circles. The open circles represent the normalized detector responses for other amounts of standard gas. M is the number of picomoles of CFC in the injected standard, and A is the corresponding peak area in integrator counts, where the starred quantities are for one large loop of standard gas. The a's in the fitting functions are the fitted constants.

For air samples, the number of moles of each CFC in the sample are calculated from the blank-corrected normalized peak areas using the calibration curve, and concentrations are reported as mole fractions in dry air. Water samples require an additional correction for the stripper blank. This blank is calculated in moles using the calibration curve, and is then interpolated between stripper blank analyses as a linear function of run number. The number of moles of each CFC in the water sample is calculated from the calibration curve, and the stripper blank is then subtracted. If the stripper efficiency is not 100%, as is sometimes the case for F-11 when the stripping temperature is cold (see above discussion), then the measured number of moles is corrected accordingly. Water sample CFC concentrations in pmol kg^{-1} are calculated using the volume, salinity and injection temperature of the sample.

There is an important approximation in this calculation procedure. The number of moles of CFC injected with one large loop of standard varies slightly with temperature and barometric pressure. The slope of the calibration curve in the region of one large loop of standard is required to correct for this variation, so we fit the calibration curves with two iterations, applying the correction on the second pass.

RESULTS

The concentrations of F-11 and F-12 in air and water samples are reported relative to the SIO calibration scale. Using the techniques described in this paper, relative standard deviations for replicate analyses of gas standards containing F-11 and F-12 concentrations in the range of modern tropospheric air (about 220 ppt for F-11 and 400 ppt for F-12) are 0.3 and 0.7%, respectively. Analyses of marine air samples at 10 min intervals along cruise tracks in uncontaminated open ocean areas typically show similar precisions.

Concentrations of dissolved CFMs in the ocean cover a wide range. Since the solubilities of F-11 and F-12 in seawater are strongly dependent on temperature, highest concentrations are typically found at high latitudes in cold near-surface water. A profile of dissolved F-11 and F-12 as a function of depth in the northwestern Weddell Sea is shown in Fig. 4. At this station surface temperatures were about −0.9°C and measured concentrations were about 5.5 pmol kg^{-1} for F-11 and about 2.3 pmol kg^{-1} for F-12. Below the surface, CFC concentrations decrease rapidly. Replicate analyses of pairs of near-surface samples collected in 10 l Niskin bottle casts during this expedition yielded mean relative standard deviations of about 1% for both F-11 and F-12. The precision of analysis for lower concentration samples, as determined from analysis of replicate samples, is approximately 1–2%, or ±0.01 pmol kg^{-1} seawater, whichever is greater. Examples of additional water column profiles and sections of dissolved CFC data obtained using these analytical techniques are presented by Weiss *et al.* (1985).

Estimates of the F-11 and F-12 blanks due to the combined sampling and analysis procedures can be made using seawater samples collected in areas of the deep ocean where the concentrations of these compounds are almost certainly zero. Based on tritium and radiocarbon studies, deep water samples collected in the eastern North Pacific should be completely free of anthropogenic CFCs. Deep water samples collected in this region on several recent expeditions showed consistently low values of 0.005–0.010 pmol kg^{-1} for both F-11 and F-12. Such samples give an indication of the maximum CFC blank for low concentration seawater samples, as well as an indication of the variability in blank levels for the 10 l Niskin bottles used in sampling.

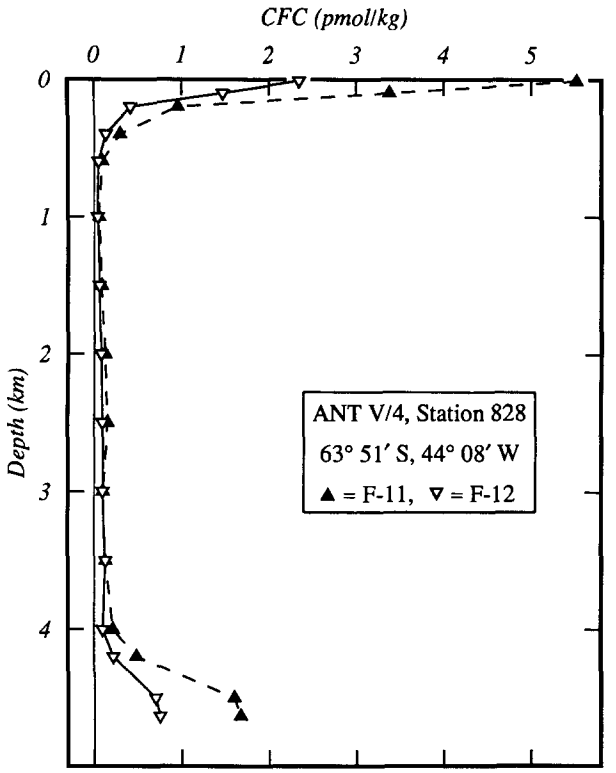


Fig. 4. Profiles of F-11 and F-12 concentration vs depth at a station in the northwestern Weddell Sea, sampled on 9 March 1987. Dissolved F-11 and F-12 concentrations in surface water are near equilibrium with concentrations in the overlying atmosphere. Elevated concentrations of F-11 and F-12 are present in samples collected below a depth of 4000 m at this station. Atmospherically derived CFCs are carried into the abyssal waters of this region in a deep boundary current of cold, dense, newly formed Weddell Sea Bottom Water.

A comparison of maximum modern equilibrium levels of these compounds (approximately 5.5 pmol kg^{-1} for F-11 and 2.3 pmol kg^{-1} for F-12) found in cold surface water to minimum detectable levels (0.005 pmol kg^{-1} for both F-11 and F-12) yields a dynamic range for seawater samples of up to 1000:1 for F-11 and up to 400:1 for F-12. Further improvements in the analytical procedures, especially for low concentration samples, may allow this range to be expanded and useful measurements to be extended to deeper and more isolated regions of the ocean.

The techniques for CFC analyses described in this paper have been used successfully on several oceanographic expeditions to process more than 15,000 seawater samples. At present a set of 24 water samples from a hydrocast, together with blank and standard runs, can be processed in less than 8 h. Since CFC analyses require small sample volumes, and can be performed relatively rapidly aboard ship, F-11 and F-12 tracer data can be obtained with spatial resolutions similar to those of more traditional hydrographic parameters such as dissolved O_2 or nutrients. The development and further automation of CFC analytical techniques may allow the measurements of these tracers to become more routinely incorporated into large-scale hydrographic studies.

The most serious obstacle to the more routine use of F-11 and F-12 as tracers of ocean circulation and mixing is the problem of sample contamination. CFCs are often released in kilogram quantities aboard ship, as leaks from refrigeration or air conditioning systems, or from a number of other sources. On several oceanographic expeditions, CFC samples from some hydrocasts have been found to be severely contaminated. A number of less severe sample contamination episodes have also been observed. During one expedition, a small but persistent blank developed in the analytical system. In some cases, a contamination problem can be related to a specific shipboard event, such as the recharging of a refrigeration system or the use of aerosol propellants containing CFCs. In other cases, the specific cause of a contamination episode aboard ship has not been identified. Improvements in the ability to routinely and accurately measure CFCs in low level samples, and to study the subtle variations of the F-11/F-12 ratio in various regions of the ocean, will depend upon the ability to significantly reduce these contamination problems.

We are continuing our efforts to improve this technique for measuring CFCs in seawater. We believe that these methods can easily be modified to include measurements of other dissolved CFCs, including CCl_2FCClF_2 (F-113) following the recent pioneering work by WISEGARVER and GAMMON (1988). Higher levels of automation will eliminate most of the manual procedures now required during each analysis. Materials are being examined which may allow quantitative trapping of CFCs at higher temperatures. Our shore-based data processing routines are being adapted to allow final processing on board ship using portable small computers.

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