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Instruments and Methods

The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater

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ABSTRACT

Methods are described for the rapid (11 min) automated shipboard analysis of dissolved sulfur hexafluoride (SF_6) in small volume (~200 cm^3) seawater samples. Estimated precision for the SF_6 measurements is ~2% or 0.02 fmol kg^{-1} (whichever is greater). The method also allows for the simultaneous measurement of chlorofluorocarbon-11 (CFC11) and chlorofluorocarbon-12 (CFC12) on the same water sample, with significantly improved sensitivity over previous analytical methods.

1. Introduction

A number of chemical compounds have been widely used as tracers of ocean circulation and mixing processes. These include substances (such as nutrients, dissolved oxygen) which have a natural background level and whose distributions in the ocean are in quasi-steady state. The background levels of a number of other substances (e.g., radiocarbon, tritium, ^{13}C) have been significantly altered by recent anthropogenic activities, and the propagation of these changes into the ocean can provide additional information on the rates of a variety of ocean processes.

Production and release of CCl_3F (chlorofluorocarbon-11 or 'CFC11') and CCl_2F_2 (chlorofluorocarbon-12 or 'CFC12') into the atmosphere began in the 1930s and increased rapidly during the following five decades. The concentrations of these anthropogenic compounds in the atmosphere (Fig. 1a) can be reconstructed as functions of location and time (Walker et al., 2000). Atmospheric CFCs dissolve in surface seawater and the equilibrium concentrations can be calculated as a function of seawater temperature and salinity (Warner and Weiss, 1985). Sensitive analytical methods are available for the rapid shipboard analysis of CFC11 and CFC12 in seawater (e.g., Bullister and Weiss, 1988) and these compounds have been measured on a large number of oceanographic expeditions during the past two decades. The entry of these compounds into the surface layer of the ocean and their subsequent transfer into the ocean interior makes them extremely useful as transient tracers to estimate rates and pathways of ocean circulation and mixing processes (e.g., Weiss et al., 1985), to estimate the rates and variability of water mass formation (e.g., Orsi et al., 1999; Smethie and Fine, 2001; Rhein et al., 2002), to estimate the rates of the uptake of anthropogenic CO_2 in the ocean (e.g., McNeil et al., 2003; Sabine et al., 2004) and to test and evaluate a variety of numerical ocean models (e.g., Dutay et al., 2002).

Because of restrictions enacted in the 1980s on the production and release of CFCs, the atmospheric levels of CFC11 and CFC12 have stopped increasing, and the CFC11/

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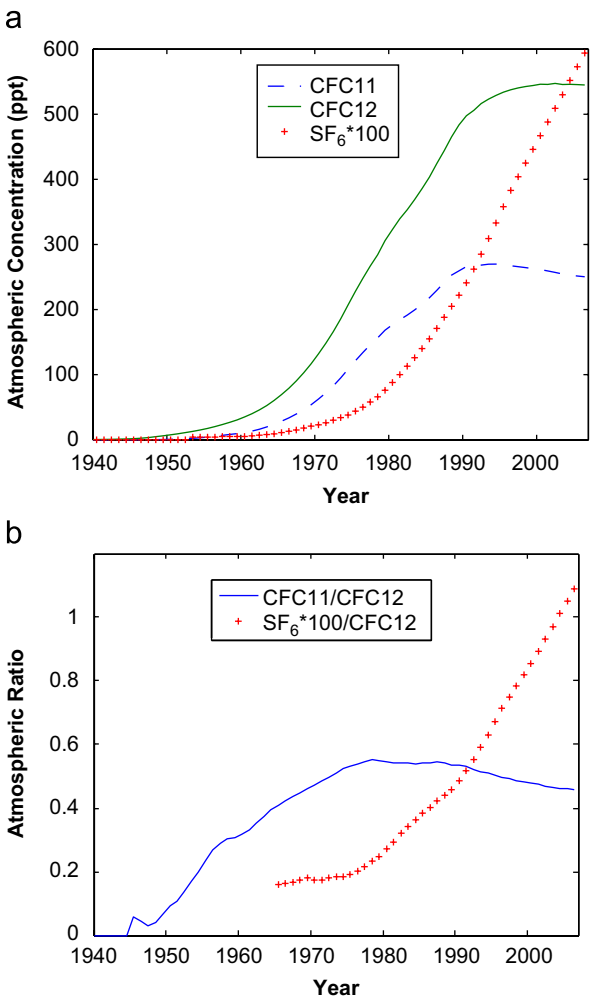

Fig. 1. (a) Concentrations of CFC11, CFC12 and SF_6 in the troposphere of the Northern hemisphere as functions of time. SF_6 concentrations are multiplied by 100. Concentrations are mole fraction (in parts-per-trillion (ppt)). Data sources and calibration scales used are discussed in Bullister et al. (2006). (b) CFC11/CFC12 and SF_6/CFC12 concentration ratios in the troposphere as functions of time. The SF_6 tropospheric concentrations are multiplied by 100.

CFC12 ratio in the atmosphere has not remained unique as a function of time (Fig. 1a and b), making methods to utilize these tracers to estimate the 'age' of water masses more problematic.

In contrast to CFC11 and CFC12, significant production and release of sulfur hexafluoride (SF_6) have occurred only since the 1970s (Fig. 1a) and the concentration of SF_6 and the SF_6/CFC12 ratio (Fig. 1b) in the atmosphere have continued to increase rapidly during the past two decades. Several recent studies have included SF_6 together with the CFCs as ocean tracers (e.g., Watson and Liddicoat, 1985; Law and Watson, 2001; Watanabe et al. 2003; Tanhua et al., 2004; Bullister et al., 2006) and have demonstrated the enhanced value of routinely including SF_6 along with CFC11 and CFC12 measurements on future hydrographic sections.

Atmospheric SF_6 concentrations in 2007 were about 6 ppt (dry gas mole fraction in parts-per-trillion or parts in 10^{12}), about a factor of 100 times lower than CFC12 and 50 times lower than CFC11 (Fig. 1a). In addition, the solubility of SF_6 in seawater (Bullister et al., 2002) is significantly lower than that of CFC11 and CFC12, so modern equilibrium concentrations of dissolved SF_6 in cold near surface seawater are in the range of 1–2 fmol kg^{-1} (1 fmol = 1×10^{-15} mol), a factor of about 1000 times lower than those of dissolved CFC12 and CFC11, typically 1–6 pmol kg^{-1} (1 pmol = 1×10^{-12} mol). Because of its extremely low atmospheric concentration and solubility in seawater, the routine analysis of dissolved SF_6 in small volumes of seawater is challenging.

2. Previous work

A number of techniques have been described for analyzing dissolved SF_6 in seawater (e.g., Watson and Liddicoat, 1985; Wanninkhof et al., 1991; Upstill-Goddard et al., 1991; Law et al., 1994; Vollmer and Weiss, 2002; Watanabe. et al., 2003; Tanhua et al., 2004). All of these analytical techniques, except that of Vollmer and Weiss, 2002, measured dissolved SF_6 alone, and measurements of CFCs were made on a separate water sample with a different analytical system.

The development of analytical techniques for measuring dissolved SF_6 in seawater was in part spurred by the potential value of SF_6 as a transient tracer, but also for the need for rapid analysis of relatively high dissolved SF_6 concentrations, in order to track plumes of this compound as part of deliberate SF_6 tracer release experiments in the ocean. A discussion of a number of these ocean tracer release experiments using SF_6 is given in Watson and Ledwell (2000).

The first reported measurements of dissolved SF_6 in seawater (Watson and Liddicoat, 1985) utilized about 1 l of seawater, and analyzed the headspace gas which had been equilibrated with the seawater sample. Wanninkhof et al. (1991) describe a method for the rapid analysis of dissolved SF_6 in seawater samples. For low concentration samples, they analyzed the headspace gas which had been equilibrated with a 500 cm^3 water sample. The minimum detection limit with this technique was ~0.03 fmol kg^{-1} for a 500 ml sample, with precisions of ~2% for higher (>1.0 fmol kg^{-1}) concentration samples. Upstill-Goddard et al. (1991) discuss the development of an SF_6 analytical technique for the rapid analysis of relatively high dissolved SF_6 concentrations. Such rapid analysis allows detailed real-time mapping of SF_6 concentrations in evolving 'patches' as part of deliberate SF_6 tracer release experiments. Law et al. (1994) developed an automated system for SF_6 analysis which allowed for analysis of water samples by either vacuum extraction followed by purging (sparging) of dissolved gases in the seawater samples, or for analysis of dissolved gases in the headspace gas equilibrated in a syringe. Using the vacuum extraction technique, they estimated a detection limit for SF_6 of ~0.03 fmol kg^{-1}, and a precision of 1.4% or ~0.007 fmol kg^{-1} (whichever is greater). Tanhua et al.

(2004) used a vacuum and purging technique with 350 cm^3 seawater samples. SF_6 analytical errors were estimated as 3.1% or 0.06 fmol kg^{-1}, with a limit of detection of 0.05 fmol kg^{-1}.

Vollmer and Weiss (2002) describe a method for the simultaneous measurement of SF_6, CFC11, CFC12 and CFC113 in seawater samples. In this method, seawater is collected and sealed in ~350 cm^3 glass ampoules and typically analyzed later in a shore-based laboratory. Unlike methods which collect and analyze only the headspace gas, and which require corrections to be applied for the remaining dissolved gas fraction, the Vollmer and Weiss (2002) technique transfers both the headspace and, via subsequent purging, the remaining dissolved gases to the cold trap. Because of the relatively low removal efficiency for extracting the remaining dissolved gases in the ampoules by their purging process, the seawater in each ampoule is purged, trapped and analyzed at least twice to correct for residual gas. During each analysis, the CFC12 and SF_6 initially collected in the first cold trap are transferred to a second smaller cold trap to sharpen the chromatographic peaks. The estimated detection limit for SF_6 using this technique is ~0.015 fmol kg^{-1}. Because of persistent blanks, likely arising in the ampoule opening and extraction process, the CFC12 and CFC11 detection limits were estimated to be in the range of ~0.014 and ~0.010 pmol kg^{-1}, respectively.

3. Methods

3.1. Sampling

The techniques described below allow for the rapid shipboard measurement of CFC11, CFC12 and SF_6 in the same seawater sample. Water column samples for dissolved CFC11, CFC12 and SF_6 analysis ('CFC/SF_6 samples') are collected on oceanographic expeditions in low contamination 10 l PVC bottles designed at NOAA–PMEL. These bottles use a modified end-cap designed to minimize the contact of the water sample with the end-cap O-rings after closing. Stainless steel (SS) springs covered with a nylon powder coat are used to close and hold the end-caps in position. To minimize the possible uptake of elevated levels of atmospheric SF_6 and CFCs into the bottle walls and elastomers during storage between oceanographic cruises, the bottles are kept outside in a clean-air environment. The bottles are flushed and filled with purified nitrogen before shipment. Care is taken to avoid exposure of these bottles to high levels of CFCs and SF_6 in shipboard air while at sea. These bottles have been used on a number of oceanographic expeditions and have been found to introduce exceptionally low levels of CFC11, CFC12 and SF_6 contamination blanks into seawater samples.

Seawater samples with low concentrations of CFC and SF_6 are extremely sensitive to contamination by contact with shipboard air once the bottles are opened for sampling. On oceanographic expeditions where a variety of parameters are to be measured from these sample bottles, CFC/SF_6 samples are typically the first collected in order to minimize the time that air in the bottle headspace contacts the seawater. Care is taken to coordinate the sampling of CFC/SF_6 with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, ^{3}He, and carbon system samples are collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC/SF_6 samples are drawn directly through the stopcocks of the 10 l bottles into 250 ml precision glass syringes equipped with three-way plastic stopcocks. During the sampling process, the glass syringes are rinsed several times by partially filling with seawater and then expelling the water from the syringe. Care is taken to exclude any bubbles when filling the syringes. After final filling, the syringe valve is closed and the syringes are immersed in a water bath at ~0 °C. The cold-water bath minimizes the formation of bubbles (and possible induced supersaturation of the dissolved gases in the seawater in the syringes) due to warming during storage. For example, if a 250 cm^3 seawater sample, with a salinity of ~35, initially at equilibrium with atmosphere at 4 °C is allowed to warm to 25 °C, a ~0.5 cm^3 bubble (consisting primarily of nitrogen) can form in the syringe. Because of the extremely low solubility of SF_6 at equilibrium, ~33% of the initial dissolved SF_6 in the sample would enter the 0.5 cm^3 bubble, significantly altering the concentration of dissolved SF_6 remaining in the seawater. Because of their higher solubilities, the relative losses of dissolved CFC11 and CFC12 into the bubble would be significantly lower (~1% and ~4%, respectively).

3.2. Sample processing

Diagrams of the system used for CFC and SF_6 sample extraction and analysis are shown in Fig. 2a–e. Table 1 lists the major components of the analytical system.

The carrier gas and purge gas streams are supplied from a high-pressure compressed gas cylinder containing ultra high purity nitrogen. Before initial use, each gas cylinder is analyzed for possible CFC11, CFC12 and SF_6 contamination by trapping and analyzing a large aliquot (~200 cm^3) of the gas on the system. The large sample volume analyzed provides good sensitivity to even ultra-trace levels of contamination. Contaminated nitrogen cylinders are rejected. The ultra high purity nitrogen gas is further purified by passing through sets of MS13X traps (Fig. 2a). The MS13X columns are back flushed at approximately 3 day intervals to remove accumulated impurities.

3.3. Water sample processing

Prior to analysis, each syringe is transferred from the 0 °C cold bath into a ~25 °C water bath, and held for ~30–40 min to allow the seawater sample to warm to this constant temperature. CFC and SF_6 solubility is decreased and purging efficiency increased for these dissolved gases at this higher temperature, allowing more rapid and efficient purging of the gases from the water sample into

the cold trap. Although this temperature increase can cause the dissolved nitrogen in some seawater samples to become supersaturated, the kinetics of bubble formation in seawater held in the syringes is slow enough that no bubbles are typically observed to form during this brief warming period.

3.4. Transfer

To initiate the analysis of a seawater sample, the syringe valve is inserted into a fitting connected to V11 on the side arm of the $\sim$200 cm^3 water purge chamber, following the methods described in Bullister and Weiss

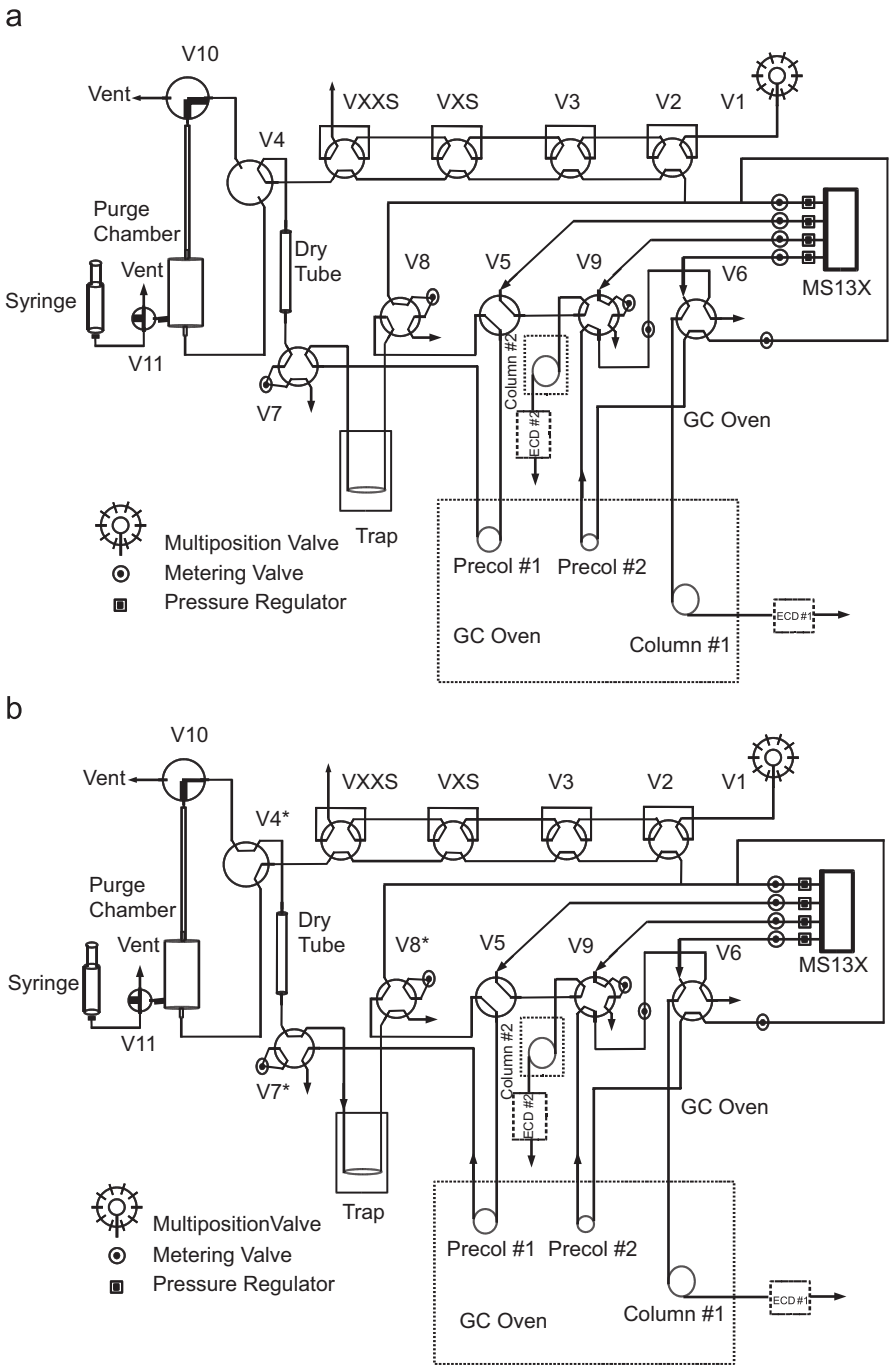

Fig. 2. (a) Schematic of the CFC/SF_6 extraction and analytical system in the 'standby' mode. A listing of components is given in Table 1. Tubing connecting the MS13X traps, valves V1–V10, VXS and VXXS is stainless steel (SS). Tubing connecting V11 to the purge chamber and syringe is 1/8″ nylon. Temperature-controlled zones are indicated by the dotted lines. Arrows in (a–e) indicate direction of gas flow though the trap and precolumns. (b) CFC/SF_6 system in 'trapping' mode. The asterisk '*' symbol next to valve numbers in this and (c–e) indicate changes in valve rotor positions from the previous figure. (c) CFC/SF_6 system in 'Inject 1' mode. (d) CFC/SF_6 system in 'Inject 2' mode. (e) CFC/SF_6 system in 'Back flush precolumn 2 mode'.

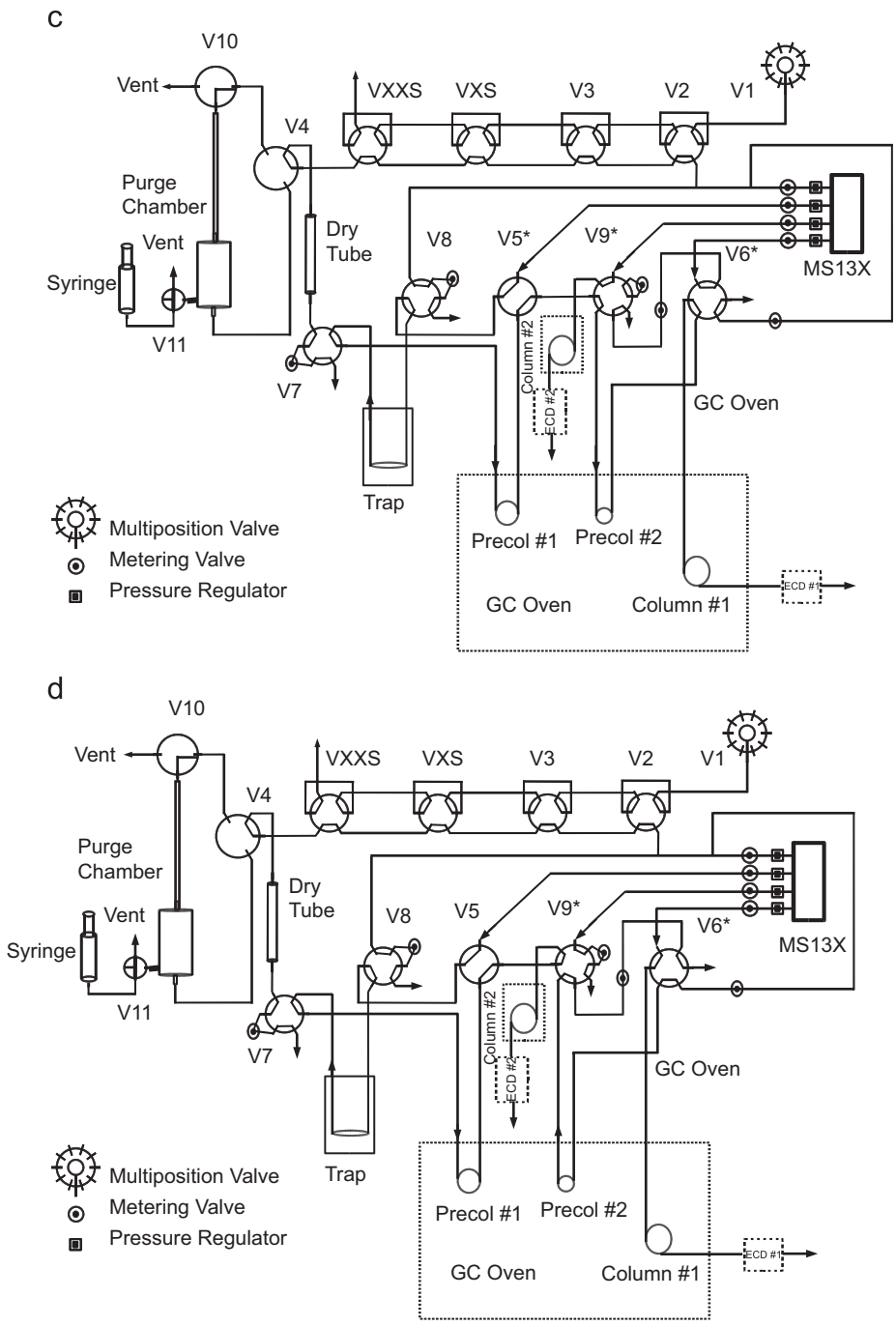

Fig. 2. (*Continued*)

(1988). The syringe valve is manually opened and ~40 cm^3 of water sample flushed through the side arm of the purge chamber (Fig. 2a). The vent valve (V10) of the purge chamber is then manually opened and valve V11 manually switched to direct the syringe water to the purge chamber, and an aliquot of ~200 cm^3 of the syringe seawater sample is transferred from the syringe to the water purge chamber. This process is done quickly to minimize any gas exchange with the nitrogen headspace in the purge chamber. Valves V10 and V11 are then manually switched to isolate the purge chamber containing the water sample. The exact volume of the transferred water is read from the calibrated burette on the neck of the purge chamber.

3.5. Trapping

All subsequent procedures during the analysis (valve switching, control of solenoids for trap cooling, control of

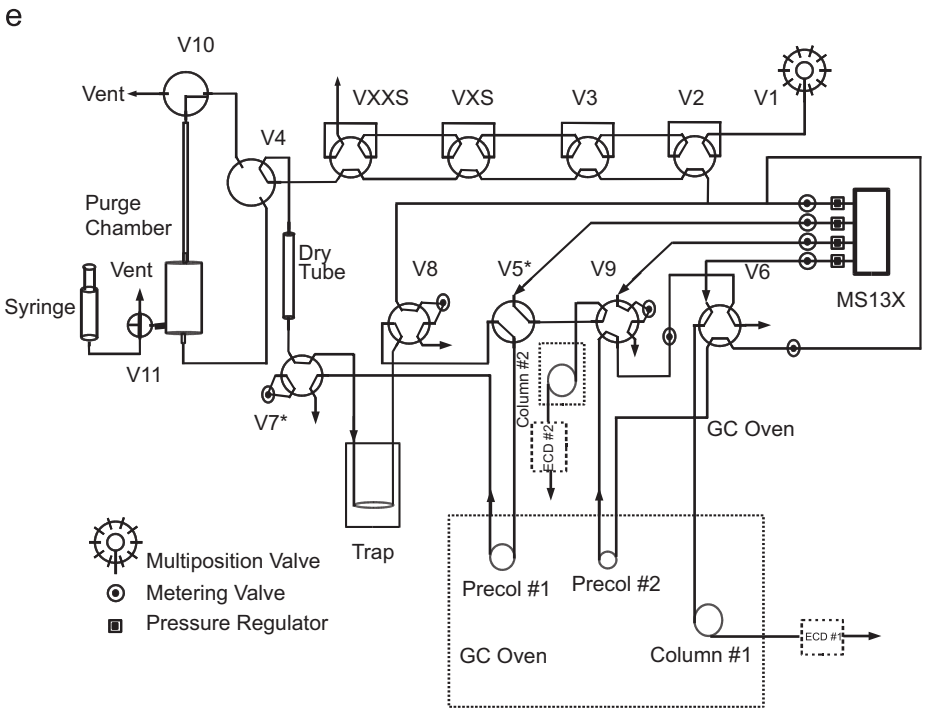

Fig. 2. (*Continued*)

relays for trap heating, data acquisition, etc.) are performed automatically via a Hewlett-Packard™ HP35900e A/D controller interfaced with a personal computer running the Linux operating system. Prior to the start of purging of the water sample (Fig. 2a), the trap is cooled by directing a flow of compressed air to rapidly push the level of a bath of ethanol (held at $<-70\,^{\circ}C$ by a Neslab™ Cryocool 100 cryogenic refrigeration system) held in an enclosure up around the trap. Once the ethanol level is raised, the flow rate of the compressed air is reduced. The timing and flow rates of the compressed air used to move the ethanol is computer controlled with the solenoid valves. After cooling the trap for 40 s, valves V4 and V7 (Fig. 2b) are switched. This directs a flow of CFC and SF_6 free purge gas through a glass frit at the bottom of the purge chamber. The dissolved gases in the seawater enter the fine stream of bubbles formed and are swept up and out of the purge chamber. After an additional 20 s, valve V8 is switched. This boosts the purging flow rate to $\sim 175\,cm^3\,min^{-1}$ by removing the first precolumn (Precol #1) from the trapping stream. By delaying the switching of valve V8, bubbles do not rise as high in the purge chamber and have less tendency to bubble over and enter the system via valve V4. The purge gas stream passes through the desiccant tube and into the cold trap, which holds the CFC11, CFC12 and SF_6, while allowing the nitrogen purge gas and some components (e.g., oxygen) in the stream to pass through. The trap is constructed of 1/16 inch (1/6″) o.d. SS tubing to minimize trap volume and chromatographic peak broadening. This tube is housed inside a 1/8″. o.d. SS tube with a Type K thermocouple welded to the exterior. Electrical leads are attached to the bulkhead fittings used to secure the trap to the lid of cold bath, while the 1/16″ trap passes through the bulkhead fittings and is plumbed to valves V7 and V8 using 1/16″ tubing. Purging and trapping occur for a period of 6 min at a flow rate of $\sim 175\,cm^3\,min^{-1}$.

3.6. Sample injection

After 6 min, the trap is isolated by switching valves V4, V7 and V8 back to the standby position shown in Fig. 2a. The ethanol level is lowered from the trap by switching solenoid valves which allow the compressed air to escape. After 30 s, the trap is then rapidly heated to $\sim 175\,^{\circ}C$ by passing a low voltage (~ 2 V) high amperage current through the wall of the 1/8″ SS tube that holds the trap. The electrical connections for the current are made directly to the two fittings on the top of the SS trap. Although this current also has an additional pathway through the 1/16″ SS tubing connecting the trap to valves V7 and V8, the relatively short length of the trap relative to that of the tubing from the trap to V7 and V8, and the higher electrical conductance of the 1/8″ versus 1/16″ SS tubing assures that most of the current passes through the trap. The trap temperature is controlled by an Omega™ 76000 PID controller based on input from a thermocouple welded to SS walls of the trap. The Omega controller is programmed to switch a solid-state relay which sends pulses of current to the step-down transformer used to generate the high-amperage current used to heat the trap.

After 30 s of heating, valves V5, V6 and V9 are switched (Fig. 2c) and the sample gases held in the trap are back flushed onto Precol #1 for the initial separation of CFC12, CFC11 and SF_6. After the SF_6 and CFC12 have passed through Precol #1, Precol #2 and into GC column #1, valves V6 and

Table 1

MS13X: Molecular Sieve 13X columns are used for removing contaminants from the ultra high purity nitrogen supply (Fig. 2a). Pressure from the nitrogen cylinder to the MS13 X columns is set at ~14 atm using a high purity two-stage pressure regulator. Each MS13X column consists of ~300 cm length of MS13X 60–80 mesh, packed in a 1/4″ o.d. stainless steel tubing. The MS13X columns are coiled and are initially heated to ~250 °C for ~8 h with ultra high purity nitrogen flowing through before attaching to the system. After this initial conditioning, the columns are held at ~35 °C. These paired columns are attached to an 8 port Valco™ valve, allowing one of the pair to provide flow streams to the system, while the other can be back flushed to remove accumulated impurities.
Pressure regulator: Porter™ stainless-steel diaphragm pressure regulator, used to set upstream pressure for each of the nitrogen streams.
Metering valve: Nupro™ stainless steel needle valve, used to regulate flow rate of the nitrogen streams.
Purge chamber: Water purging (sparging) chamber with volume of ~250 cm^3, fitted with a medium pore size glass frit at the lower end, used to extract dissolved gases from the water samples. A long (~50 cm) 1 cm diameter neck is attached to reduce spray from bursting bubbles, generated during the purging process, from being carried out of the purge chamber and through valve V4.

Valves:
V1: A 10 port multi-position Valco valve to select gas sample streams (standard, blank, air).
V2: A 6 port Valco valve with calibrated sample loop volume of ~3.6745 cm^3.
V3: A 6 port Valco valve with calibrated sample loop volume of ~1.2020 cm^3.
V4: A custom designed 4 port Valco valve, for connecting/isolating the purge chamber from the rest of the system.
V5: A 4 port Valco valve, for switching the trap and precolumn #1 in line with valve V9.
V6: A 6 port Valco valve, for directing flow from precolumn #2 to column #1.
V7: A 6 port Valco valve, for isolating the trap at standby or while the trap is heating.
V8: A 6 port Valco valve, for back flushing the first precolumn while a sample is been trapped.
V9: An 8 port Valco valve for directing flow from valve 5 to precolumn #2.
V10: A 3 port Valco valve, manually operated, used to vent the head space of the purge chamber while it is being filled with a water sample.
V11: 3 port Hamilton™ valve for transferring water from the syringe into the purge chamber.
VXS: A 6 port Valco valve with a calibrated sample loop volume ~0.2024 cm3.
VXXS: A 6 port Valco valve with a calibrated sample loop volume ~0.0406 cm^3.
Trap: A 1/16″ o.d., 0.04″ i.d. stainless steel tube packed tightly with a ~5 cm section of Porapak Q (60–80 mesh) and a 22 cm section of 80–100 mesh Carboxen 1004, all held in place with glass wool. Output from Valve V7 flows first into the Porapak Q section of the trap.
ECD #1: Electron Capture Detector held in a Shimadzu™ GC8AI gas chromatograph (GC #1) at 340 °C.
ECD #2: Electron Capture Detector held: Shimadzu™ Mini2 gas chromatograph (GC #2) at 250 °C.
Precol #1 (Precolumn 1): ~60 cm of 1/8″ o.d. stainless steel tubing packed with 80–100 mesh Porasil B, held in place with glass wool. This precolumn is kept at 80 °C in the oven of GC #1
Precol #2 (Precolumn 2): ~5 cm of 1/8″ o.d. stainless steel tubing packed with 100–120 mesh Molecular Sieve 5 Å (MS5A), held in place with glass wool. This precolumn is kept at 80 °C in the oven of GC #1.
Column #1: ~170 cm of 1/8″ o.d. stainless steel tubing packed with 100–120 mesh MS5A, held in place with glass wool. This column is held at 80 °C in the oven of GC #1
Column #2: ~150 cm 1/8″ o.d. stainless steel tubing packed with 80–100 mesh Carbograph 1AC, held in place with glass wool. This column is held at 100 °C in the oven of GC #2.
Desiccant tube: 18 cm long, 3/8″ diameter glass tube packed with the desiccant magnesium perchlorate. The desiccant is held in place with glass wool.

V9 are switched (Fig. 2d) allowing the SF_6 and CFC12 to continue through GC column #1 and to allow the nitrous oxide, and any other late eluting gases to back flush from Precol #2. CFC11 continues through Precol #1 to GC column #2. After CFC11 has passed through Precol #1 into GC column #2, valves V5 and V7 are switched and any gases remaining in Precol #1 are back flushed and vented (Fig. 2e). The nominal flow rates through column #1 and #2 are ~32 and ~33 $cm^3\,min^{-1}$, respectively. The trap continues to be heated for ~1 min, then valve V7 is switched to return the system to the standby position (Fig. 2a) for the start of the next sample cycle.

The rates at which SF_6, CFC11 and CFC12 move out of the trap and through the various precolumns and columns are functions of trap/precolumn/column composition, cross-section and length, temperature and gas flow rates. The timing for the valve switching for injection and back flushing in Fig. 2d and e were determined empirically. Tests were performed by varying the switching times to optimize the chromatographic peak shape and separation, and to minimize baseline disruption during the elution of the key chromatographic peaks.

SF_6 and CFC12 peaks are detected on the ECD #1 of GC #1 and the CFC11 peak is detected on the ECD #2 of GC #2. The two separate analog ECD output voltages are sent to the HP35900e for analog to digital conversion. The digitized ECD output voltages are then sent to the Linux-based PC and integrated using chromatographic software developed by P. Salameh at Scripps Institution of Oceanography (SIO). The chromatographic output signals are integrated, and fit to multi-point calibration curves (Bullister and Weiss, 1988) as discussed below to determine concentrations. The typical analysis time for a water sample is 11 min.

The fraction of CFCs and SF_6 remaining in the water sample after the 6 min purging is estimated by repeating the purging, trapping and analysis of the same water sample remaining in the purge chamber. Typically, the removal efficiency is greater than 99% for all the three gases in seawater at 25 °C, purged for 6 min at a flow rate of 175 $cm^3\,min^{-1}$. Final reported concentrations are corrected for the calculated residual gas remaining in the purge chamber.

Analytical blanks are estimated by purging and trapping gas passing through an empty purge chamber for the same length of time as for the analysis of a seawater sample. A correction for these analytical blanks is applied to the water analysis.

Water sample blanks on oceanographic expeditions are estimated by several methods. Ideally, on expeditions

which occur in regions where sub-surface water is present that is likely to be essentially free of dissolved SF_6 and CFCs, blanks are estimated from the analysis of these SF_6 and CFC-free water samples. Under good conditions using the specially designed PMEL CFC/SF_6 sample bottles, these blanks can be <0.001 pmol kg^{-1} for CFC11 and CFC12 and <0.02 fmol kg^{-1} for SF_6. In regions where detectible levels of CFCs and SF_6 are present in all samples, the rate of increase of dissolved CFCs and SF_6 in seawater held in closed water sample bottles can be estimated from replicate bottles closed at the same depth in low tracer regions. These replicate bottles can be sampled as a function of time after closing, to estimate the 'grow-in' rate of the CFC/SF_6 blanks in the closed sample bottles. Typical grow in rates in these specially designed bottles are <0.001 pmol kg^{-1} h^{-1} for CFC11 and CFC12 and <0.02 fmol kg^{-1} h^{-1} for SF_6.

3.7. Gas sample processing

Gas samples for analysis are flushed through a set of four calibrated sample loops mounted in series on valves V2, V3, VXS and VXXS. The volumes of the larger sample loops (V2~3.6745 cm^3 and V3~1.2020 cm^3) are calibrated both gravimetrically (by filling with degassed, de-ionized water), and by filling with pure CO_2, which is subsequently injected and analyzed in a coulometer. The results from the two methods are in good agreement, with overall accuracy of the loop volumes estimated to be better than 0.1%. The smaller loop volumes (VXS~0.2024 cm^3 and VXXS~0.0406 cm^3) are calibrated using the CO_2/coulometer technique alone.

The procedures used to analyze gas (standard, blank gas and air) samples are similar to those for water samples. The trap is initially cooled to $-70\,^{\circ}C$. After flushing the gas sample loops (typically at a flow rate of 100 cm^3 min^{-1} for 1.5 min), the flow is stopped for 10 s, which allows the pressure and temperature in the sample loops to come to ambient. Loop temperature and pressure are automatically recorded so that the amount (in moles) of gas injected can be calculated. To initiate trapping, instead of switching the purge chamber in line (Fig. 2a), one of the four sample valves is switched, allowing the flow of purge gas to sweep the loop contents through the desiccant tube and into the cold trap. The subsequent trapping and injection procedures are the same as for water sample analysis. Additional aliquots of gas sample from any of the sample loops can be injected into the cold trap by the procedure above. The entire gas analysis procedure is automated, and a complete series of gas analysis of multiple loops of standards to generate a calibration curve can be pre-programmed for unattended operation.

For air sampling at sea, a ~100 m length of 3/8″ o.d. Dekaron™ tubing is typically run from the bow of the ship to the laboratory. A flow of air is drawn through this line into the laboratory using an Air Cadet™ pump. The air is compressed in the pump with the downstream pressure held at ~1.5 atm using a back-pressure regulator. A tee in line allows a flow of ~100 cm^3 min^{-1} of the compressed air to be directed to the gas sample valves of the CFC/SF_6 analytical systems, while the bulk flow of the air (>7000 cm^3 min^{-1}) is vented through the backpressure regulator. Air samples are typically only analyzed when the relative wind direction is within 60° of the bow of the ship to reduce the possibility of shipboard contamination.

3.8. Calibration

The analytical system is calibrated frequently using a standard gas of known CFC and SF_6 composition. Multiple injections of combinations of the four loop volumes can be made to allow the system to be calibrated over a relatively wide range of air and seawater sample concentrations. CFC and SF_6 concentrations in air and seawater samples are determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard. Typically, the response of the detector to the range of moles of CFC and SF_6 passing through the detector remains relatively constant during a cruise. Full-range calibration curves are typically run at intervals of 3 days during a cruise. Single injections of a fixed volume of standard gas at one atmosphere are run at intervals of ~90 min to monitor short-term changes in detector sensitivity.

Because of the very different solubilities for CFC11, CFC12 and SF_6 in seawater, the amounts (and ratios) of these three gases extracted from a 200 cm^3 seawater sample can be significantly different from those contained in a few cubic cm^3 of gas standard containing near-modern air concentrations of these compounds. Special 'seawater ratio' working gas standards can be prepared, where the CFC11, CFC12 and SF_6 concentrations are adjusted to better match the amounts of these compounds extracted from a ~200 cm^3 sample of modern surface seawater.

Concentrations of the CFC11 and CFC12 in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et al., 2000) and SF_6 concentrations relative to the GMD 2000 calibration scale (http://www.cmdl.noaa.gov/hats). Concentrations in air and standard gas are reported in units of mole fraction CFC or SF_6 in dry gas, and are typically in the parts per trillion (ppt) range. For seawater samples, the water volume analyzed (in cm^3) is converted to mass (kg) units, based on the density of the water sample during analysis. Final concentrations are reported in units of pmol kg^{-1} for dissolved CFCs and in fmol kg^{-1} for SF_6.

3.9. Sample chromatograms

Fig. 3a shows a typical chromatogram from analysis of a ~3 cm^3 sample of clean marine air collected and measured on board ship at Station 88 (located at 28° 19.08′S 95°0.50′E) in the south Indian Ocean in March 2007 during the CLIVAR I8SI9N expedition. In Fig. 3b, the *y*-axis of the chromatogram is expanded by roughly a

factor of five to highlight the SF_6 peak and chromatographic baseline noise level.

Fig. 3c and d show similar chromatograms for a typical analysis of ~190 cm^3 of surface seawater collected at the same station. Fig. 3e shows the chromatogram for the analysis of a low concentration sample (CFC12~0.113 pmol kg^{-1}, SF_6 ~0.037 fmol kg^{-1}), collected at Station 88 at a depth of ~1000 m and analyzed under moderate wave height and swell conditions. The chromatographic baseline is relatively noisy compared to the SF_6 peak height and integrated peak area, and limits the precision and detection limit for low SF_6 concentration samples. The baseline noise level is typically observed to be variable and to some extent related to the intensity of ship-motion. The noise level of the GC/ECD system used has been observed to decrease by a factor of two or so under calm conditions, and increase by a factor of two or more with increased ship-motion during periods of very rough weather, negatively impacting the precision of the SF_6 measurements and the limits of detection for this compound. The baseline shown in Fig. 3e reflects moderate sea conditions and can be appreciably better during periods of calm weather. In contrast, the CFC12 (and CFC11, not shown) chromatographic peak height and area for this sample are robust relative to the level of baseline noise.

3.10. Accuracy and precision

Based on the analysis of replicate water samples, we estimate precisions (1 S.D.) of approximately 1% or 0.002 pmol kg^{-1}(whichever is greater) for both dissolved CFC11 and CFC12 measurements. Overall accuracy, including that of the calibration scale is estimated to be ~2% or 0.004 pmol kg^{-1}, whichever is greater. In part, because of the larger volume of seawater analyzed using this method versus that of Bullister and Weiss (1988), the extremely low contamination levels introduced by the sample bottles, and the clean sample transfer and storage techniques used, we estimate that the limit of detection for CFC11 and CFC12 in seawater samples using this method can be of the order of ~0.001 pmol kg^{-1}, substantially lower than that using previous methods. It should be possible under good conditions to measure to this low concentration level more-or-less routinely on future oceanographic expeditions.

The estimated precision for dissolved SF_6 measurements is ~1–2% or ~0.02 fmol kg^{-1}, (whichever is greater). Overall accuracy including that of the calibration scale is estimated to be ~3% or ~0.03 fmol kg^{-1}, whichever is greater, with a limit of detection of ~0.01 fmol kg^{-1} under good sea-state conditions.

4. Discussion

The methods described have been tested at sea on visits to the Hawaii Ocean Time-series (HOT) site (Bullister et al., 2006) and recently as part of the CLIVAR repeat hydrography program. Fig. 4a and b show preliminary sections of dissolved CFC12 and SF_6 data, measured along CLIVAR repeat section I8SI9N in February–April 2007. The highest concentrations of CFC12 and SF_6 were observed in cold, near-surface water along the southern end of the section, and were of the order 3.4 pmol kg^{-1} for CFC12 and 2.4 fmol kg^{-1} for SF_6. The lowest contour intervals shown are 0.005 pmol kg^{-1} for CFC12 and 0.02 fmol kg^{-1} for SF_6. A number of interesting oceanographic features are evident in these sections including the presence of these compounds at abyssal depths in Antarctic Bottom Water along the southern end of the section, the penetration of a measurable deep CFC12 signal to at least 20°S, and the strong ventilation signal in intermediate and mode waters to mid latitudes. A detailed analysis and discussion of these results will be presented elsewhere.

The typical highest CFC11 and CFC12 concentrations present in modern cold surface seawater are roughly 6 and 3 pmol kg^{-1}, respectively. The limits of detection for these compounds in seawater using this technique (~0.001 pmol kg^{-1}) yields a dynamic range at present of more than 1000:1 for measurements of these compounds in the ocean. This signal-to-noise is significantly higher than the comparable span for SF_6 measurements in seawater, which currently have a range of only about 200:1 (with the highest value of ~2 fmol kg^{-1} in cold surface water versus the limit of detection of ~0.01–0.02 fmol kg^{-1}). SF_6 measurements in seawater samples using this technique are limited by the extraordinarily small amounts of SF_6 initially in the samples, and the correspondingly small size of the chromatographic peak for this compound relative to the background noise level of the GC/ECD system. A determination of the cause of the ship-motion related background chromatographic baseline noise and a reduction of this may lead to significant future improvements in the limit of detection for dissolved SF_6.

Attempts have been made to shield the ECD signal cable to reduce electronic interference. Several other models of gas chromatographs with ECD have been tested, but did not demonstrate significantly greater sensitivity than the model used in this study. Research into alternate ECDs and methods for reducing background chromatographic baseline noise is continuing.

An increase in the chromatographic peak signal-to-noise ratio may be possible by changing conditions in the ECD cell or with further improvements in the trapping and separation techniques. This might also include investigating alternate trap and column materials and temperatures, and by reducing the volumes of the cold trap, precolumns and chromatographic columns.

Analysis of larger volumes of seawater to increase the SF_6 signal is possible. Bullister et al. (2002) discuss a technique of equilibration and subsequent gas headspace analysis using ~4 l seawater samples, but such a large volume of seawater is typically not available in multi-parameter oceanographic studies. Using the purge and trap technique discussed here, there are limitations on the ability to retain SF_6 in the present cold trap for the longer period of time which may be needed to extract the CFCs and SF_6 from larger samples. Experiments were performed using the trap design outlined in Table 1, varying the

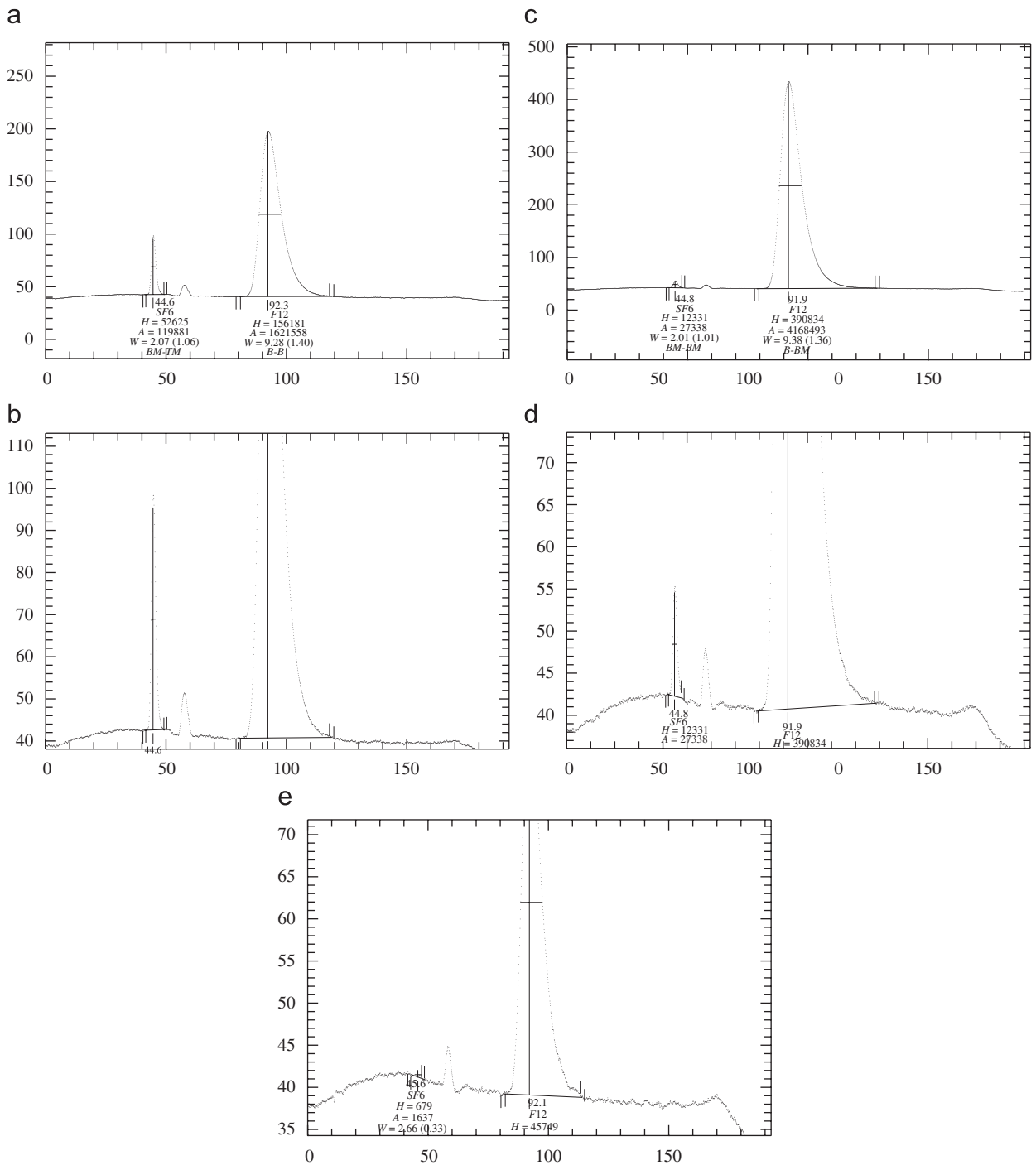

Fig. 3. (a) Example chromatogram of SF_6 and CFC12 from the analysis of a clean marine air sample collected at Station 88 on the I8SI9N expedition in the south Indian Ocean in 2007. Horizontal axis is retention time (in seconds), vertical axis is arbitrary detector voltage. Retention times for SF_6 and CFC12 peaks are ~44.6 and 93.2 s, respectively. Approximate concentrations of the air sample are: CFC12 = 538 ppt, SF_6 = 5.7 ppt. (b) Same sample as a, with expanded vertical axes to show details of the SF_6 peak and chromatographic baseline. (c) Example chromatogram of SF_6 and CFC12 from the analysis of a ~190 cm^3 surface seawater sample, collected at Station 88, with temperature = 22.4 °C and salinity = 36.125. Approximate concentrations are CFC12 = 1.25 pmol kg^{-1}, SF_6 = 0.97 fmol kg^{-1}. (d) Same sample as (c), with expanded vertical axes to show details of SF_6 peak and chromatographic baseline. (e) Example chromatogram of SF_6 and CFC12 from the analysis of a deep (~1000 m) ~190 cm^3 seawater sample, collected at Station 88, with temperature = 4.24 °C and salinity = 34.428. Approximate concentrations are CFC12 = 0.113 pmol kg^{-1}, SF_6 = 0.037 fmol kg^{-1} (corresponding to approximately 0.01 fmol SF_6).

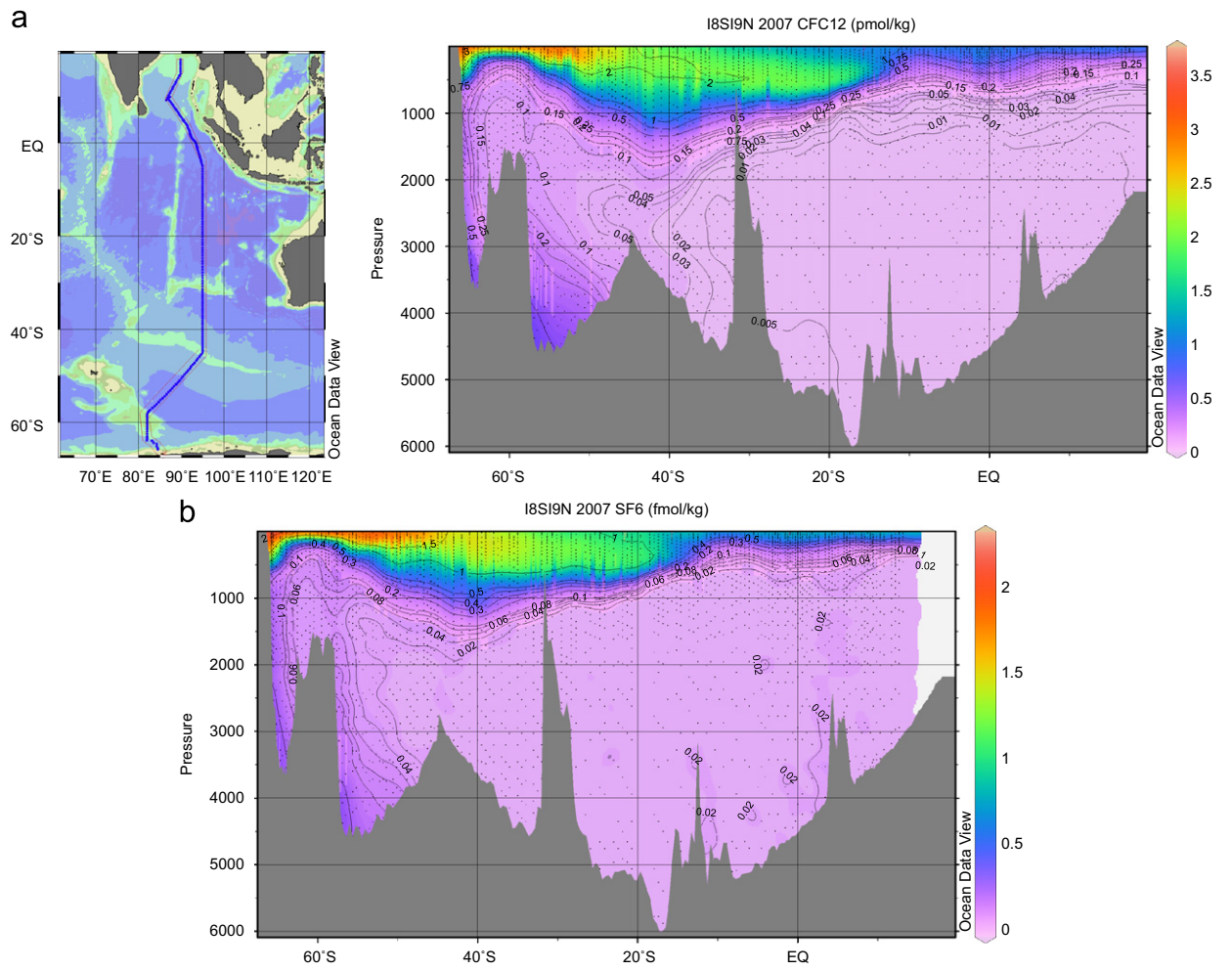

Fig. 4. (a) Section of dissolved CFC12 along the I8SI9N hydrographic section in the south Indian Ocean collected from 15 February–27 April 2007 using the analytical procedures described in this paper. Concentrations are in pmol kg^{-1} seawater. Dots indicate locations where seawater samples were collected for CFC/SF_6 analysis. (b) Section of dissolved SF_6 along section in south Indian Ocean as in (a). Concentrations are in fmol kg^{-1} seawater.

purge times from 1 to 20 min. The rapid decrease in SF_6 peak area after about 10 min of trapping indicates that the SF_6 has migrated through the cold trap and begun to break through the trap and be lost after that time interval. Further research into alternate traps and trapping methods (including vacuum-assisted extraction) may allow improved extraction of SF_6 and other gases from larger volume water samples.

5. Conclusions

The described techniques allow for the rapid, automated shipboard analysis of CFCs and SF_6 from the same, relatively small seawater sample. Significant improvements in the sensitivity for low-concentration CFC11 and CFC12 measurements are possible when combined with low-blank sample bottles, which may allow the extension of the useful range of these measurements further into the interior of the ocean. The rapid sampling and analysis times allows SF_6/CFC data to be collected on hydrographic cruises with spatial resolutions similar to that for other key hydrographic parameters such as dissolved inorganic carbon (DIC), nutrients and dissolved oxygen. The recent and continuing rapid increases in SF_6 in the atmosphere will make this compound of great importance as an ocean transient tracer. In particular, in upper ocean outcropping waters, where CFC11 and CFC12 no longer record an unambiguous 'date' due to their declining levels in the atmosphere, SF_6 provides a new dating tool that is increasing at a quasi-linear rate in the atmosphere. Further improvements in methods for analyzing SF_6 in seawater are needed to take full advantage of the potential of this compound as an ocean tracer.

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