SAMPLING AND MEASUREMENT OF CHLOROFLUOROCARBONS AND SULFUR HEXAFLUORIDE IN SEAWATER

J.L. Bullister[1] and T. Tanhua[2]

[1] National Oceanic and Atmospheric Administration Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA, 98115 U.S.A. e-mail: John.L.Bullister@noaa.gov

[2] Leibniz Institute of Marine Sciences (IFM-GEOMAR) Düsternbrooker Weg 20, 24105 Kiel, Germany. e-mail: ttanhua@ifm-geomar.de

1. INTRODUCTION

A number of laboratories throughout the world have developed analytical systems for measuring dissolved chlorofluorocarbons (CFCs) in seawater and have active programs to study the distribution of these substances in the ocean. New groups will likely become involved in making these measurements in the future. To maximize the scientific value of these studies, there is a clear need to insure that the measurements made by all groups are intercomparable and of the highest possible accuracy and precision. This is especially critical for ongoing programs such as the CLIVAR Repeat Hydrography Program, where global geochemical tracer data sets will be obtained by the combined efforts of a number of groups collecting and analyzing samples at different locations and times. The results from these efforts will be compared to earlier studies to detect changes in water mass ventilation rates, carbon uptake, oxygen utilization rates and other ocean processes, and serve as a baseline for future time-series studies utilizing these tracers.

Recommendations for CFC standardization as well as requirements for the precision and accuracy of CFC measurements in seawater during the World Ocean Circulation Experiment (WOCE) in the 1990s are given in Joyce (1994) and Joyce and Corry (1994).

The two CFCs which have been measured most extensively in the ocean are CFC-11 and CFC-12. Measurements of these two compounds were included on a significant number of hydrographic studies since the early 1980s and on essentially all WOCE Hydrographic Program (WHP) one-time hydrographic sections in the 1990s. In many cases, the resolution of the CFC-11 and CFC-12 sampling along the sections was similar to that achieved for other hydrographic parameters such as dissolved oxygen, nutrients, dissolved inorganic carbon and other critical carbon system parameters. Many thousands of stations were sampled for CFC-11 and CFC-12 during the WHP one time survey program and this large data set allows the distributions of these compounds to be mapped on a global scale. Other halocarbons (in particular: CFC-113 and carbon tetrachloride) have been proposed as transient tracers but measurements of these compounds were included on a much smaller set of hydrographic stations during this period. There is strong evidence for non-conservative behavior for dissolved CFC-113 (Roether, et al., 2001) and CCl_4 (Huhn, et al., 2001; Krysell, et al., 1994; Lee, et al., 1999; Waugh, et al., 2004) in the ocean, particularly in the upper waters, which may limit the usefulness of these compounds as time-dependent (transient) tracers for some applications.

Following the initial release CFC-11 and CFC-12 in the atmosphere in the early 1930s, the concentrations of these compounds (and the CFC-12/CFC-11 ratio) in the atmosphere increased monotonically for the following ~5 decades. Because of stringent restrictions on the production and release of CFCs enacted in the 1980s, the rates of increase of CFC-11 and CFC-12 in the atmosphere have slowed. The atmospheric concentration of CFC-11 began to slowly decline about 1995, and that of CFC-12 about 2005. These changes have subsequently complicated the direct use of measured dissolved CFC-11 and CFC-12 partial pressures (*p*CFC11, *p*CFC12) and *p*CFC12/*p*CFC11 ratios in seawater for estimating the 'ages' of water masses. In contrast, since the 1950s the concentration of sulfur hexafluoride (SF_6) has increased rapidly and monotonically in the atmosphere, along with the SF_6/CFC-12 and SF_6/CFC-11 ratios. This makes SF_6 potentially a very useful additional transient tracer for studying ocean circulation process in conjunction the CFCs. Progress in the analysis of this compound in seawater (Law, et al., 1994; Vollmer and Weiss, 2002; Bullister and Wisegarver, 2008) has allowed this compound to be measured more routinely on oceanographic expeditions and this compound has been recognized as a core measurement (along with CFC-11 and CFC-12) as part of the CLIVAR Repeat Hydrography and other ongoing programs. It is likely that, in the near future, additional laboratories will undertake programs to measure both CFCs and SF_6 more routinely on hydrographic surveys.

2. METHODS

CFC-11, CFC-12 and SF_6 (subsequently referred to together as CFC:SF_6) are measured using electron capture-gas chromatography. A number of studies have been published which discuss techniques for the rapid shipboard analyses of CFCs in seawater and air (e.g. Bullister and Weiss, 1988; Bulsiewicz et al., 1998). Typically both air and seawater samples should be analyzed on board ship soon after sampling, using purge and trap techniques. Air samples should be analyzed routinely at intervals of 1 day or so as a check their consistency with expected background atmospheric levels and on the saturation state of surface seawater. For CFC analyses, water samples are typically collected in ~100 cc volume precision ground glass syringes to minimize the contact of the water samples with the atmosphere. An aliquot of the water (typically ~30-40 cc) is transferred from the syringe/ampoule to a glass sparging chamber, where a flow of a CFC-free gas (typically nitrogen) is passed through the sample. Dissolved CFCs enter this gas flow which are collected and concentrated on a cryogenic trap. After enough gas is passed through the water sample to remove essentially all (typically > 99%) of the dissolved CFCs, the trap is heated and the CFCs swept into a chromatographic precolumn and main column. CFC-11 and CFC-12 are separated on these columns, and elute separately into the electron capture detector (ECD). The resultant chromatographic peaks are digitally integrated and stored. Various amounts of standard gas of known CFC composition (see below) are injected and analyzed on the same system as a means to calibrate the water and air measurements.

As an alternate to collecting the seawater samples in syringes, seawater can be collected in various styles of glass ampoules (Bulsiewicz et al., 1998; Vollmer and Weiss, 2002). These ampoules can be sealed temporarily using a variety of plugs or valves and analyzed on board ship soon after collection. The ampoules can also be sealed by fusing the glass tip of the ampoule , which allows the samples to be analyzed much later ashore. There are both advantages as well as significant disadvantages for shore-based analysis. Sealing ampoules on board ship for later analyses ashore does not require an analytical system to be brought and operated on board ship. However, the sealing process itself can be labor-intensive and the method still requires a significant amount of time ashore to analyze the samples. Unlike ship-board based analysis, with shore-based analysis any sampling problems, contaminants etc. can remain undetected until after the cruise is completed and all samples have been collected, so no corrective actions can be taken to reduce or eliminate these problems during the cruise.

For SF_6 studies (where dissolved concentrations in surface waters can be a factor of 1000 times lower than for the CFCs), a larger volume of water (200-500 cc) is typically used. Both purging and vacuum extraction techniques (Law et al., 1994; Vollmer and Weiss, 2002; Tanhua et al., 2005; Bullister and Wisegarver, 2008) have been used to extract SF_6 from the water samples.

3. CALIBRATION

3.1 Standards and analytical accuracy

A precision of better than 1% or 0.005 pmol kg^{-1} (1 pmol =1 picomole=10^{-12} mole), whichever is greater, with overall accuracies of about 2% or 0.010 pmol kg^{-1} was recommended for dissolved CFC-11 and CFC-12 measurement during the WHP (Joyce, 1994). Under optimal conditions, existing techniques for CFC analyses (e.g. Bullister and Weiss, 1988) can meet these guidelines. Guidelines for accuracy and precision of dissolved SF_6 measurements were not included in Joyce (1988). Based on recent analytical methods (e.g. Bullister and Wisegarver, 2008) and expected improvements in these methods in the near future, we propose a target precision for SF_6 of 1.5% or 0.02 fmol kg^{-1} (1 fmol =1 femtomole=10^{-15} mole), whichever is greater, with overall accuracies about 3% or 0.04 fmol kg^{-1}.

Oceanic and atmospheric CFC-11, CFC-12 and SF_6 measurements are typically calibrated using gas phase working standard mixtures. Standards used to calibrate dissolved CFC:SF_6 measurements should be of the highest possible accuracy. The working standards used aboard ship are typically whole air containing these gases at concentrations near modern atmospheric values. These standard gases have been dried and compressed to high pressure (~140 atm) in specially treated aluminum cylinders. These working standards are calibrated against primary standards, typically prepared in the laboratory by volumetric or gravimetric dilution.

The primary standard scale commonly used for reporting oceanic CFC-11 and CFC-12 measurements was developed at the Scripps Institution of Oceanography (SIO). The SIO primary standards were initially prepared using gravimetrically calibrated volumes and a precision manometer to blend mixtures of pure CFC-11, CFC-12 and nitrous oxide at ratios close to their modern atmospheric ratios (Bullister, 1984). To prepare a primary standard, a small aliquot of this mixture was introduced into an evacuated aluminum high-pressure cylinder, and the cylinder was then filled to a pressure of ~140 atm using "zero air", an artificial mixture of oxygen and nitrogen in roughly atmospheric proportions that is free of CFC-11, CFC-12, and nitrous oxide to within detection limits. The resultant mixture was then measured for its nitrous oxide concentration. The CFC concentrations (at part-per-trillion levels) in these cylinders were determined from these measured nitrous oxide concentration, multiplied by the known ratios of nitrous oxide to CFC-11 and CFC-12 in the blended mixture.

There have been modifications to this standard preparation technique and several revisions of the SIO calibration scales for CFCs since the initial 1986 SIO-86 calibration scale was developed. These include the SIO-93 and SIO-98 calibration scales [Prinn, et al., 2000] and the recent SIO-05 scale (http://bluemoon.ucsd.edu/pub/cfchist/) The differences between the scales are of the order of a few percent or less. Conversion from the scales is done as follows:

For CFC-11:
SIO-98 = SIO-86 * 0.9835
SIO-98 = SIO-93 * 1.0082
SIO-98 = SIO-05 * 1.0050

For CFC-12:
SIO-98 = SIO-86 * 1.0230
SIO-98 = SIO-93 * 1.0053
SIO-05 = SIO-98 * 1.0000

Most of the CFC-11 and CFC-12 measurements made as part of the WHP were reported on the SIO-98 calibration scale, and it is recommended that all oceanic concentration measurements be reported and stored at data centers on this scale. It is unlikely that future revisions from the SIO-98 scale will differ by more than a few percent. Reporting and storing all CFC-11 and CFC-12 measurements archived at data centers on a fixed, common scale (SIO-98) will eliminate the need to make revisions to data sets already stored at the sites or to keep track of which data sets are reported on the various scales. If desired, it will be straightforward and unambiguous for users in the future to make a conversion of the entire CFC historical data set stored on the SIO-98 scale to another scale in one step.

In a similar fashion as for CFC-11 and CFC-12, it is desirable to report SF_6 measurements on a common calibration scale. Since a specific 1998 SIO-98 calibration scale for SF_6 was not developed, it is recommended that in the future all SF_6 concentration values be reported to data centers on the recently developed 2005 SIO-05 SF_6 calibration scale. Details on the SIO-05 SF_6 calibration scale will be provided at http://bluemoon.ucsd.edu/pub/cfchist/ in the near future. A set of gas standards has been prepared by the NOAA-PMEL-CFC group (see below) for distribution in 2010 to laboratories involved in the analysis of CFCs and SF_6 in seawater. These standards have been calibrated on the new SIO-05 SF_6 calibration scale.

Relatively few dissolved SF_6 concentration measurements have been reported to data centers as of 2010. Some earlier SF_6 measurements (e.g. Bullister et al., 2006) have been reported on the NOAA-GMD 2000 scale, which has subsequently been revised to the NOAA-GMD 2006 scale (http://www.esrl.noaa.gov/gmd/ccl/sf6_scale.html). SF_6 concentrations reported on the NOAA-GMD 2000 scale (SF_6-NOAA-GMD-2000) can be converted to SF_6 concentrations reported on the NOAA-GMD 2006 scale (SF_6-NOAA-GMD-2006) as follows:

$Y = 4.8546 * e^{-3} * X^2 + 9.3479e^{-1} * X + 0.21664$
Where:
$Y = SF_6$-NOAA-GMD-2006
$X = SF_6$-NOAA-GMD-2000

A series of comparisons between the NOAA-GMD and SIO calibration scales has been completed recently as part of the IHALACE program:
(http://www.esrl.noaa.gov/gmd/hats/ihalace/index.html).

Preliminary results from this program indicate very good agreement between the NOAA-GMD-2006 and SIO-05 scales for SF_6 and these results should be published in late 2010. The few dissolved SF_6 data sets now archived at data centers and reported on other calibration scales should be converted to the SIO-05 SF_6 scale once this information becomes available.

Care must be exercised in the choice of high-pressure containers used to store standards to insure that the materials used in the walls, valves and fittings do not alter the composition of the standard gas. Adsorption or release of even trace amount of these gases can lead to significant errors, since the mole fractions in standards used for calibrating dissolved CFC and SF_6 measurements are extremely low. The walls of some types of gas cylinders (including steel cylinders) may adsorb/release CFCs or other components from the gas phase, thereby gradually altering the concentrations of the remaining gases. The rates of these absorption/release reactions may be influenced by many factors, including temperature, the presence or absence of water vapor, partial pressures of the components making up the standard gas, the materials used in the construction of the cylinder, the surface area of the inner wall, and the presence of surface films (including rust, corrosion products, oils, etc.) on the inner walls of the cylinder. Low pressure (less than 30 atm.) standards may be especially susceptible to changes due to low total amounts of these compounds in the cylinder, and the enhanced significance of any wall effects on the contents.

Only containers which have been thoroughly tested for their long-term stability should be used to hold primary or working CFC:SF_6 standards. Spectra-Seal^{TM} aluminum cylinders (supplied by Airco, Inc., Murray Hill, NJ) were used initially by several groups for storing CFC standards. Primary and working standards, prepared in these cylinders at the Scripps Institution of Oceanography did not show measurable changes in CFC-11 or CFC-12 concentrations over a period of more than five years. More recently, specially treated aluminum Aculife^{TM} cylinders (supplied by Scott Specialty Gases) and stainless steel cylinders (supplied by Essex Cryogenics of Missouri) have been used successfully for holding pressurized CFC-11 and CFC-12 and other trace gas standards.

Extreme care should be exercised during the use of a standard cylinder to prevent possible contamination of the contents. Pressure regulators should be thoroughly purged when attached to a cylinder to prevent traces of CFCs in the regulator from entering the cylinder. Pressure regulators attached to the cylinder should not contain elastomer materials which are exposed to the standard gas. Cylinder valves should be tightly closed when not in use.

3.2 Calibration Procedures

The response of the electron capture detector to CFC-11, CFC-12 and SF_6 is significantly non-linear. In order to accurately determine the amounts of these compounds in seawater samples, multipoint calibration curves should be run that span the range of amounts extracted from seawater samples. Since CFCs and SF_6 are collected and held in a trap prior to injection, a single standard gas can be used to calibrate the sensitivities and non-linearities of these measurements.

Measured volumes of gas, introduced from a carefully calibrated sample loop at known pressure and temperature can be injected into the extraction system, where the CFCs and SF_6 are concentrated in a cold trap prior to injection into the chromatograph for analysis. The trapping and injection procedures are similar to the procedure used to trap and inject CFCs and SF_6 extracted from seawater samples and dry air samples.

The amount of standard trapped can be varied by injecting several sampling loops of different volumes, by trapping multiple injections of the same standard gas, or by injecting the loop volumes at different pressures. Successive injections can then be made with various known amounts of CFC-11, CFC-12 and SF_6, thus producing a calibration of non-linearity for each gas. Examples of equations for fitting calibration data are given in Bullister and Weiss (1988). The trapping times required for multiple injections of standard gas can be longer than that required for a single injection of standard and for the extraction of CFCs and SF_6 from a seawater sample. For multiple injections of standards, the effects of losses of CFC-11, CFC-12 or SF_6 by migration through the trap, broadening of the chromatographic peaks due to long trapping times, and the accumulation of analytical blanks should be evaluated.

During processing of seawater samples, the response (sensitivity) of the system should be checked at approximately hourly intervals by injection of a fixed volume of standard gas. Complete calibration curves should be run at approximately daily intervals, and before and after any procedures which might change the response of the system (baking of columns, opening of the system to the atmosphere, etc.). Blanks, standards and complete calibration curves should be run more frequently during periods when the response of the analytical instrument is drifting.

4. SAMPLE CONTAMINATION AND EVALUATION OF SAMPLING BLANKS

Because of the large gradients that can exist between the CFC and SF_6 content of the modern atmosphere and the low concentrations (and partial pressures) of CFCs and SF_6 in much of the sub-surface ocean, dissolved CFC and SF_6 samples can be easily contaminated by contact with air. Contamination problems can be especially severe if the shipboard air contains high levels of CFCs and SF_6.

CFC:SF6 samples should normally be the first samples collected from the sample bottles. On oceanographic expeditions, a sampling order should be established and carefully coordinated so that other dissolved gas samples (e.g. dissolved oxygen, helium) and samples that can be significantly impacted by gas exchange (e.g. DIC, pH, $p\mathrm{CO}_2$) are collected as soon as possible after the bottles are opened and the CFC:SF_6 samples collected.

Replicate seawater samples (two or more samples collected from the same sample bottle) should be analyzed frequently to estimate analytical precision. Near surface samples should be run at every station if possible to determine the degree of surface water saturation. Air samples should be run daily if possible to determine possible atmospheric gradients, the degree of saturation of the surface waters and as a check on the analytical system.

The dissolved CFC:SF_6 concentrations in seawater held in sealed PVC 'Niskin' bottles commonly used on oceanographic expeditions can change with time. This is likely due to the slow release of trace levels of CFC:SF_6 from the bottle walls and O-rings. The CFC:SF_6 contaminants released into the water sample prior to sub-sampling into the syringes/ampoules are referred to as the 'bottle blanks' These contamination problems are typically most significant in low-concentration water samples.

The problem with contamination of the Niskin bottles may be reduced by carefully cleaning the bottles with a weak solvent, e.g., iso-propanol before the cruise. The O-rings should be cleaned and then heated to moderate temperatures for an extended period of time in a vacuum-oven before initial use to partially remove any contaminant gases present in the O-ring material.

The amount of CFC:SF_6 contamination often appears to be a function of previous exposure of the bottles to high levels of atmospheric CFC:SF_6 (e.g. by storing the bottles indoors in some cases). The release of contaminants may also be related to temperature, with higher rates of CFC:SF_6 release at higher temperatures. Specially designed bottles have been produced by some groups (e.g. at NOAA-PMEL- Bullister and Wisegarver, 2008) to minimize the contact of O-rings with the seawater and may reduce the level of this contamination.

CFC:SF_6 bottle blanks can be estimated in several ways. The most direct way is to close replicate bottles in regions of the water column thought to be tracer free (based on other transient tracer measurements) and then measuring the CFC:SF_6 content of samples from each bottle. Because bottle blanks can drift during a cruise, if possible, test casts should be made at several locations during a cruise, with all bottles closed at the same depth in low CFC:SF_6 water. This information can be used to make an estimate of the blank for each bottle as a function of time during the cruise.

If low concentration or CFC-free and SF_6-free water is not available along a section, an alternative way to obtain a rough estimate of the bottle blanks is to determine the 'grow in' rate of CFC:SF_6 as a function of the time that a water sample is stored in the bottle. Replicate bottle can be closed in a region of the water column with low levels of CFC:SF_6. One of the bottles is sampled immediately upon return to deck, while the others are held closed for various lengths of time (up to 4-6 hours) before sampling. The CFC:SF_6 concentrations can be plotted as a function of the time between when the bottles were initially closed and when the samples were drawn. Extrapolating this trend to the initial (zero) time of closing gives an indication of the typical rate at which CFC:SF_6 contaminants can enter the sample and can be used to estimate a bottle blank.

The stripping efficiency for water samples can be estimated by re-purging a water sample following the initial extraction. The amount of CFC:SF_6 collected on the second extraction is an indication of the fraction remaining and a correction for this residual CFC:SF_6 should be applied to the concentration value obtained from the first extraction. Ideally the stripping efficiencies for all components should be greater than about 99% to minimize the size of the required corrections.

5. DATA QUALITY EVALUATION

Following all recommendations for measurements and corrections stated in this document should provide the best possible data. However, it is necessary to do a careful data quality evaluation to find random and systematic biases in the data.

Primary quality control (QC) is a process in which data are objectively studied in order to identify outliers and obvious errors. These outliers are either flagged, and/or the sources of the errors are sought. A first step is to plot the profiles of CFC:SF_6 partial pressure vs. depth. The profiles should be reasonably smooth and outliers can normally be spotted easily. A comparison of the CFC:SF_6 profiles with those of other properties (e.g. oxygen) can often help determine if apparent outliers are unique to the CFC:SF_6 measurement (and likely due to a bad analysis) or are seen in other property fields. A second step in the DQE is to plot the partial pressure of CFC-12 vs. CFC-11. Another useful exercise is to check the saturation for near surface samples, which normally should be close to 100% (beware though of very deep mixed layers or rapid cooling/warming of surface layers that tend to shift the equilibrium away from 100%). However, there are reports that the surface saturations might be dependent on the rate of atmospheric increase (Azetsu-Scott et al., 2005; Azetsu-Scott et al., 2003) such that contemporary (2010) CFC-12 values tend to have higher saturation than CFC-values measured in the early 1990's when CFC-12 was increasing rapidly in the atmosphere. Similarly, the saturation of SF_6 has been observed to be lower than that of CFC-12 and CFC-11 in some recent studies (Tanhua et al., 2008), again possibly reflecting the differences in recent atmospheric growth rates between SF_6 and the two CFCs.

Secondary QC is a process in which the data are objectively studied in order to quantify systematic errors in the reported values. This can be done by comparing results from two independent cruises to the same area, i.e. crossover analysis (Johnson et al., 2001). Normally this is done in the deeper part of the water column to avoid short time variability. The crossover analysis for CFC:SF_6 is complicated by the fact that these are transient tracers and that the deep water concentrations very often are so low that direct comparison is meaningless. However, in certain areas of the ocean, meaningful comparisons can be made between cruises that were occupied within a few years of each other.

6. RECOMMENDATIONS

6.1 Standards

Each laboratory should maintain at least two reference cylinders of standard gas. At least one of these should have its CFC:SF_6 concentrations calibrated directly versus a primary standard. These reference standards should be compared with each other on a regular basis to check for relative drift in CFC:SF_6 concentrations. To check for absolute drift in CFC:SF_6 concentrations, at regular intervals at least one of the reference standards should be compared with a standard from another laboratory or be re-certified by comparing it to primary standard. Working standards should be re-calibrated relative to the reference standards yearly and before and after every oceanographic expedition in which they are used. Because of the risk of loss or contamination of reference standards if taken to sea, only working standards should be used for routine calibration of samples on cruises.

At present, there is no formal program for the inter-comparison of CFC and SF_6 standards used by groups involved in oceanic studies. To facilitate this, a set of gas cylinders should be prepared in a central laboratory and filled with standard gas having the same CFC and SF_6 concentrations. The concentration values should be close to that of modern air. These cylinders can serve as the laboratory reference standards.

The standard gas in the cylinders should be tested initially for uniformity and calibrated for both CFC-11 and CFC-12 *vs.* a primary standard on the SIO-98 scale. The SF_6 content should be calibrated versus the SIO-05 SF_6 scale. The cylinders should be initially held for a period of ~6 months to check for possible drift in CFC and SF_6 concentrations. One cylinder from this set should be distributed to each CFC lab as a reference standard and used only for calibration of other cylinders (including working standards) and for re-calibration checks with other labs. The preparation of a set of these reference standards has been initiated at the NOAA-PMEL CFC laboratory, and it is anticipated that cylinders will be available for distribution in 2010.

The solubility of SF_6 in seawater (Bullister and Wisegarver, 2004) is about a factor of 10 lower than that of CFC-12 and about a factor of 40 lower that of CFC-11 (Warner and Weiss, 1988). Therefore, the ratios of SF_6 to CFC-11 and of SF_6 to CFC-12 in modern seawater are distinctly different from those in modern air. In order to more easily generate calibration curves that better fit the range of CFC:SF_6 concentrations in seawater samples, it may be desirable in some cases to prepare working 'seawater ratio' standards where the CFC-11, CFC-12 and SF_6 concentrations and ratios differ from modern atmospheric ones, and are designed to better match those in seawater.

6.2 Data reporting

A data quality flag should be provided for each CFC:SF_6 concentration measurement These flags should follow WOCE guidelines (Joyce and Corry, 1994).

Detailed documentation should be provided with each CFC:SF_6 data set and accompany the data sets stored at national and international data centers. The documentation should include names of the principal investigators and CFC analysts, a reference to the analytical methods used and a discussion of modifications and problems encountered. The IDs of the standard cylinder(s) used on the cruise and the CFC:SF_6 concentrations of the standards should be reported. The data sets should be reported on the SIO-98 scale for CFC-11 and CFC-12 and on the SIO-05 scale for SF_6, and this information specifically stated in the data report. The methods used for estimating bottle blanks should be discussed and the values applied as bottle blank corrections to the data set should be explicitly stated. The method and accuracy of the determination of the mass of the seawater samples should be reported. If water volume is measured during sample processing, then the temperature and salinity of the seawater sample at the time of measurements must be used to calculate the actual mass of the seawater sample.

The measurement team should apply all final corrections (bottle blanks, stripping efficiency, adjustment to the appropriate calibration scale) to the data set before supplying it to the data centers. All dissolved CFC:SF_6 measurements should be reported in units of picomole (or femtomole) per kilogram of seawater. Estimated accuracy and precision of the measurements should be reported, along with tables of replicate measurements.

Measurements of CFC and SF_6 concentrations (in units of mole fraction CFC in dry air) in marine air made during the cruise, along with measurement time and location, should be listed in a table in the data report.

7. REFERENCES

Azetsu-Scott, K., E. P. Jones, and R. M. Gershey. 2005. Distribution and ventilation of water masses in the Labrador Sea inferred from CFCs and carbon tetrachloride. *Mar. Chem.* 94, 55-66.

Azetsu-Scott, K., E. P. Jones, I. Yashayaev, and R. M. Gershey. 2003. Time series study of CFC concentrations in the Labrador Sea during deep and shallow convection regimes (1991-2000). *J. Geophys. Res.*, 108, 3354, doi:10.1029/2002JC001317.

Bullister, J. L. 1984. Atmospheric chlorofluoromethanes as tracers of ocean circulation and mixing: measurement and calibration techniques and studies in the Greenland and Norwegian seas. Ph.D. Thesis, Univ. of California.

Bullister, J. L., and R. F. Weiss. 1988. Determination of $CC1_3F$ and $CC1_2F_2$ in seawater and air. *Deep Sea Res.* 35(5), 839-853.

Bullister, J. L., and D. P. Wisegarver. 2008. The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater. *Deep-Sea Res. I* 55, 1063-1074.

Bullister, J.L., D.P. Wisegarver, and F.A. Menzia. 2002. The solubility of sulfur hexafluoride in water and seawater. *Deep-Sea Res. I* 49(1), 175–187.

Bullister, J.L., D.P. Wisegarver, and R.E. Sonnerup. 2006. Sulfur hexafluoride as a transient tracer in the north Pacific Ocean. *Geophys. Res. Lett.* 33, L18603, doi: 10.1029/2006GL026514.

Bulsiewicz, K., H. Rose, O. Klatt, A. Putzka, and W. Roether. 1998. A capillary-column chromatographic system for efficient chlorofluorocarbon measurements in ocean waters. *J. Geophys. Res.* 103, 15959-15970.

Huhn, O., W. Roether, P. Beining, and H. Rose. 2001. Validity limits of carbon tetrachloride as an ocean tracer. *Deep-Sea Res. I* 48, 2025-2049.

Johnson, G. C., P. E. Robbins, and G. E. Hufford. 2001. Systematic adjustments of hydrographic sections for internal consistency. *J. Atmos. Ocean. Technol.*, *18*, 1234-1244.

Joyce, T., ed. 1994. WHPO 91-1, WOCE Operations Manual Volume 3 : The Observational Programme, Section 3.1 : WOCE Hydrographic Programme Part 3.1.3 : WHP Operations and Methods, WOCE Report No. 68/91 November 1994, Revision 1 Woods Hole, Mass., USA.

Joyce, T. and C. Corry, eds. 1994. *Requirements for WOCE Hydrographic Programme Data Reporting.* WHPO Publication 90-1 Revision 2, WOCE Report 67/91, Woods Hole, Mass., USA, May 1994.

Krysell, M., E. Fogelqvist, and T. Tanhua. 1994. Apparent removal of the transient tracer carbon tetrachloride from anoxic seawater. *Geophys. Res. Letters* 21, 2511-2514.

Krysell, M., and D. W. R. Wallace. 1988. Arctic Ocean Ventilation Studied using a suite of Anthropogenic Halocarbon Tracers. *Science* 242, 746-748.

Law, C. S., A. J. Watson, and M. I. Liddicoat. 1994. Automated vacuum analysis of sulphur hexafluoride in seawater: Derivation of the atmospheric trend (1970-1993) and potential as a transient tracer. *Mar. Chem.* 48, 57-69.

Lee, B.-S., J. L. Bullister, and F. A. Whitney. 1999. Chlorofluorocarbon CFC-11 and carbon tetrachloride removal in Saanich Inlet, an intermittently anoxic basin. *Mar. Chem.* 66, 171-185.

Prinn, R. G., R. F. Weiss, P. J. Fraser, P. G. Simmonds, D. M. Cunnold, F. N. Alyea, S. O'Doherty, P. Salameh, B. R. Miller, J. Huang, R. H. J. Wang, D. E. Hartley, C. Harth, L. P. Steele, G.

Sturrock, P. M. Midgley, and A. McCulloch. 2000. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.* 105, 17751-17792.

Roether, W., B. Klein, and K. Bulsiewicz. 2001. Apparent loss of CFC-113 in the upper ocean. *J. Geophys. Res.* 106, 2679-2688.

Tanhua, T., K. Bulsiewicz, and M. Rhein. 2005. Spreading of overflow water from the Greenland to the Labrador Sea. *Geophys. Res. Letters* 32, L10615.

Tanhua, T., D. W. Waugh, and D. W. R. Wallace. 2008. Use of SF_6 to estimate anthropogenic carbon in the upper ocean. *J. Geophys. Res.-Oceans* 113, C04037.

Vollmer, M. K., and R. F. Weiss. 2002. Simultaneous determination of sulfur hexafluoride and three chlorofluorocarbons in water and air. *Mar. Chem.* 78, 137-148.

Warner M. J., and R. F. Weiss. 1985. Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res.* 32, 1485-1497.

Waugh, D. W., T. M. Hall, and T. W. N. Haine. 2004. Transport Times and Anthropogenic Carbon in the Subpolar North Atlantic Ocean. *Deep Sea Research I* 51, 1471-1491.