WHP Operations and Methods – July 1991

Chlorofluorocarbons, ^{3}He-tritium and Small Volume Radiocarbon

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1. Introduction

A number of laboratories have developed analytical systems for measuring anthropogenic tracers such as dissolved chlorofluorocarbons (CFCs), ^{3}He-tritium, and radiocarbon in seawater samples, and have active programs to study the distribution of these substances in the ocean. It is likely that, in the near future, additional laboratories will undertake programs to measure these tracers in the ocean.

Improvements in sampling techniques and analytical methods may increase the sensitivity of these measurements and allow more accurate measurements of the distributions of these geochemical tracers to be made. Efforts are also underway at several laboratories to develop improved techniques for measuring radiocarbon in small volume seawater samples using accelerator mass spectrometry (AMS).

As the number of laboratories involved in making measurements increases and analytical techniques continue to improve, there is a need to insure that the resulting measurements are consistently of the highest possible accuracy. This is especially critical in programs such as WOCE, where global geochemical tracer data sets will be obtained by the combined efforts of a number of groups collecting and analysing samples at different locations and times. The results from these efforts will serve as a baseline for future time-series studies of these tracers.

Discussions of procedures for measuring CFCs, helium-tritium, and small volume radiocarbon during the WOCE Hydrographic Programme (WHP) are given in the report by the Working Group on Standard Methods and Algorithms. In the following sections, the methods presently used for the preparation, maintenance and use of standards for calibrating oceanographic measurements of dissolved CFCs, ^{3}He-tritium and radiocarbon are discussed. Recommendations are given for procedures to help insure that the standards and calibration techniques used by groups involved in geochemical sampling during WOCE are of the highest possible quality.

2. Chlorofluorocarbons

The accuracy and precision of dissolved Freon-11^{TM} (F-11) and Freon-12^{TM} (F-12) measurements in the WHP should be better than ± 1%, with blanks of less than 0.005 pmol/kg seawater (1 pmol =1 picomole=10^{-12} mole) (Joyce, 1988). Under optimal conditions, existing techniques for CFC analyses can meet these guidelines. (Bullister and Weiss, 1988).

2.1 CFC Standards

During WOCE, efforts should be made to insure that the standards used to calibrate dissolved CFC measurements are of the highest possible accuracy. The following discussion describes the standards and methods presently used for CFC calibration and suggests means for improving the existing calibration system.

The concentrations of dissolved F-11 and F-12 in air and seawater samples are determined on board ship using electron capture gas chromatography. Oceanic and atmospheric F-11 and F-12 measurements are calibrated using gas phase working standard mixtures. Measured volumes of gas, introduced from a gravimetrically calibrated sample valve at known pressure and temperature are injected into the extraction system, and the CFCs are concentrated in a cold trap prior to injection into the chromatograph for analysis. The trapping and injection procedure is identical to the procedure used to trap and inject CFCs extracted for seawater samples and dried air samples.

The working standards used aboard ship are whole air, which has been dried and compressed to high pressure (140 *atm*), in specially treated aluminum cylinders. During the drying procedure, F-11 is sometimes partially removed. In such cases, a few cm^3 of gas containing F-11 at parts-per-thousand mole fraction are added to the tanks to bring them back to near-atmospheric values.

The working standards are calibrated against primary standards, prepared in the laboratory by volumetric dilution. The standards scale commonly used for oceanic measurements was prepared by R. F. Weiss and J. L. Bullister at the Scripps Institution of Oceanography (the SIO calibration scale). The current estimate of the accuracy [1] of the SIO concentration scale is 1.5% for F-11, and 0.3% for F-12. This scale has been intercalibrated with the Atmospheric Lifetime Experiment (ALE)/GAGE calibration scale used for many atmospheric studies, which has an estimated accuracy of 5% for both gases. The agreement is within expected combined accuracies (Weiss *et al.*, 1985).

The SIO primary standards are prepared using gravimetrically calibrated volumes and a precision manometer to prepare mixtures of F-11, F-12 and nitrous oxide in roughly their atmospheric ratios (approximately 1:2:1500, respectively). The virial equation of state is used to reduce the measured volumes, temperatures, and pressures to numbers of moles for each of the pure components. A small aliquot of this mixture is introduced into an evacuated aluminum high-pressure cylinder, and the cylinder is then pressurized to pressures as high as 140 *atm* using “zero air,” an artificial mixture of oxygen and nitrogen in roughly atmospheric proportions that is free of F-11, F-12, and nitrous oxide to within measurable detection limits. The resultant mixture is then measured for its nitrous oxide content using the methods and calibrations described by Weiss (1981); and by Weiss, Keeling, and Craig (1981). CFC concentrations are determined from these measured nitrous oxide values, multiplied by the known ratios of nitrous oxide to F-11 and F-12 in the prepared mixtures. Primary standards are prepared at similar concentrations, but with a range of

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[1] “accuracy” of CFC standards refers to an assessment of the possible bias resulting from an exhaustive consideration of the magnitude of possible contributions to this bias, rather than to a composite of bias and reproducibility.

total pressures, in order to exclude the possibility of adsorption effects inside the cylinders playing a significant role in the results.

Care must be exercised in the choice of high-pressure containers used to store CFC standards to insure that the materials used in the walls, valves and fittings do not alter the composition of the standard gas. The walls of some types of gas cylinders (including steel cylinders) can adsorb CFCs from the gas phase, thereby gradually altering the concentrations of the remaining gases. Adsorption of even trace amount of CFCs can lead to significant errors, since the initial mole fractions of F-11 and F-12 in standards used for calibrating dissolved CFC measurements are extremely low (100–300 parts in 10^{12}). The rates of these reactions may be influenced by many factors, including water vapor, temperature, 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 50 atm) standards may be especially susceptible to losses of F-11 and F-12 due to wall adsorption effects. Only containers which have been thoroughly tested for their long-term stability should be used to hold primary or working CFC standards. Spectra-Seal^{TM} aluminum cylinders (supplied by Airco, Inc., Murray Hill, NJ) have been used by several groups for storing CFC standards. Primary and working standards, prepared in these cylinders at the Scripps Institution of Oceanography (SIO) have shown no measurable changes in F-11 or F-12 concentrations over a period of more than five years.

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.

2.2 Calibration Procedures

The response of the electron capture detector to CFCs is significantly non-linear. In order to accurately determine the amounts of F-11 and F-12 in seawater samples, multipoint calibration curves must be run that span the range of CFCs extracted from seawater samples. Since CFCs are held in a trap prior to injection, a single standard gas can be used to calibrate the sensitivities and non-linearities of these measurements. This is done by trapping multiple injections of the same standard gas, or by having several sampling volumes of different sizes. Successive injections can then be made with various known amounts of F-11 and F-12, 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 from a seawater sample. For multiple injections of standards, the effects of losses of F-11 or F-12 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 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.

2.3 Recommendations

At present, there is no formal program for the intercomparison of CFC standards used by groups involved in oceanic studies. Several groups have had individual gas cylinders intercompared with CFC standards prepared at SIO or by investigators in the ALE program, but there is no established mechanism for the re-calibration of these sub-standards at regular intervals.

During WOCE, all laboratories involved in CFC studies should thoroughly document the calibration method used and report concentrations on a scale which has been directly inter-calibrated with established calibration scales. The calibration scale should be endorsed by the international oceanographic organizations to ensure its continuity and general use for reporting dissolved CFC concentrations. Each laboratory should maintain reference standard cylinders which are compared to with primary standards at regular (at least yearly) intervals, and used only for in-laboratory calibration of working standards. The reference standards should be re-certified *versus* primary standards at regular intervals. Working standards should be re-compared with reference standards at least twice a year, and before and after every oceanographic expedition in which they are used.

Independent techniques for preparing primary CFC standards should be developed at several laboratories. All laboratories preparing primary CFC standards should thoroughly document the methods used, along with estimates of the absolute accuracy of the calibration scale and results from inter-calibrations with existing calibration scales. Techniques for producing primary standards should be improved, especially for F-11, where the present accuracy is estimated to be only about 1.5%. New primary standards should be prepared on a regular basis, and revised calibration information reported.

All dissolved CFC measurements should be reported in units of moles per kilogram of seawater. The accuracy of the determination of the mass of the seawater samples should be reported. If water volume is measured during processing of a sample, then the temperature and salinity of the seawater sample at the time of measurements must be used to calculate the mass of the seawater sample. Measurements of CFCs in marine air should be made at least twice daily during oceanographic expeditions, and reported as mole fraction CFC in dry air.

Suitable methods are not available at present for preparing, storing and analysing low-level dissolved CFC standards for inter-comparison purposes. Such standards (analogous to seawater standards used for calibration of salinometers) could provide a means to check the performance of CFC analytical systems during expeditions. Dissolved CFC standards could also be exchanged routinely among groups involved in oceanographic measurements of CFCs, and be used as reference materials for new groups undertaking the study of CFCs in the ocean. Efforts should be made to develop techniques for preparing, storing, and analysing such dissolved CFC "reference" materials.

Comparisons of dissolved CFCs measurements can also be accomplished by means of intercalibration cruises. An intercomparison cruise was organized for groups planning to make F-11 and F-12 measurements during WOCE. Water column samples were obtained on this cruise (in December, 1989 in a region southwest of San Diego), which spanned a wide range of dissolved CFC concentrations. This intercomparison cruise has provided an opportunity to compare gas phase standards and to determine if systematic differences exist among the laboratories now measuring dissolved CFCs.

In addition to F-11 and F-12, other CFCs such as F-113 (Wisegarver and Gammon, 1988), and halocarbons such as carbon tetrachloride (Krysell and Wallace, 1988), can be used as time-dependent tracers in the ocean. Calibration procedures, similar to those proposed for F-11 and F-12, should also be established for these tracers.

3. Small Volume Radiocarbon Measurements

For the WHP, accuracies of ± 5–10‰ are recommended for small volume radiocarbon measurements using accelerator mass spectrometry (AMS) (Joyce, 1988). Recent work has demonstrated that precisions of better than ± 10‰ (Kromer *et al.*, 1987; Schlosser *et al.*, 1987) can be obtained for analysis of seawater samples. Efforts are being made at several laboratories to develop methods for the rapid and automated analysis of seawater samples at accuracies which meet or exceed the WHP recommendations. A discussion of techniques for radiocarbon measurements in seawater by AMS is given by Schlosser *et al.* (1987); and Kromer *et al.* (1987). A discussion of possible errors due to mass fractionation during sample processing and analysis is given by Bonani *et al.* (1987).

3.1 Standardization

Measurements of radiocarbon in seawater samples are reported as per mille deviations from 95% of the activity of the 1950 decay-corrected NBS oxalic acid standard. Recommended methods of reporting radiocarbon measurements, based on the NBS scale, are discussed by Stuiver and Polach, (1977). Secondary standard materials, calibrated *versus* this internationally accepted standard reference material, are used by all laboratories involved in seawater radiocarbon studies, and provide a common basis by which all seawater radiocarbon measurements can be directly compared.

3.2 Intercalibration

At sea, small volume seawater samples for AMS radiocarbon analysis can be transferred into specially cleaned and evacuated glass bulbs for long-term storage. The samples are poisoned with mercuric chloride to avoid changes in the CO_2 concentration by microbial activity. Good agreement has been shown between these samples and large volume seawater samples processed using conventional techniques and analysed using low-level counting (Kromer *et al.*, 1987).

The ability to collect and store seawater samples for radiocarbon analysis will allow replicate samples to be distributed to laboratories for inter-comparison studies. For intercalibrations, replicate small volume samples should be collected from a large volume sampler, and the remaining water processed using high precision, low-level counting. The replicate samples can then be distributed to different laboratories for AMS measurement, and the results compared with the large volume data. Distribution of such samples will allow differences in seawater sample processing techniques to be evaluated on a relatively routine basis and to insure that a consistent set of seawater radiocarbon data can be obtained during WOCE by the combined efforts of a number of separate laboratories.

Further studies are needed to insure that small volume, poisoned samples can be stored for extended periods of time (greater than one year). At present, small volume samples from the 1986 Winter Weddell Sea Project are being processed in Heidelberg (Schlosser, personal communication) and will be compared with large volume samples from the same Gerard samplers analysed using high precision, low-level counting. This experiment should evaluate the suitability of long-term storage of poisoned samples for AMS radiocarbon measurement.

4. Helium-Tritium Measurements

For tritium concentration measurements during the WHP, recommendations are for an accuracy of ± 1% and precision of ± 0.5%, with a detection limit of 0.05 tritium units (TU) in the upper ocean in the Northern Hemisphere, and 0.005 TU elsewhere. For helium, an accuracy of ± 1.5‰ in the $^3He/^4He$ isotopic ratio; and ± 0.5% in total helium is recommended (Joyce, 1988). Techniques have been developed for measuring helium and tritium (by the ^3He ingrowth method) which meet the WHP recommendations for precision and accuracy. A discussion of these techniques is given in Jenkins *et al.* (1985) and Bayer *et al.* (1989).

4.1 Helium and Tritium Standards

Air is used as the primary standard for ^3He and ^4He measurements, and for tritium determinations made using the ^3He ingrowth technique. Helium concentrations, and $^3He/^4He$ ratios are reported relative to air. Tritium is reported in TU units. A discussion of a uniform scale for reporting tritium concentrations is given by Taylor and Roether (1982).

For calibration purposes, clean air is collected in a large volume (10 liters or greater) reservoir and pressure, temperature and relative humidity are measured. Care must be taken while collecting the air to ensure that the sample is not contaminated due to release of helium from nearby industrial or laboratory sources. Before use as reference standards, newly collected air samples should be carefully compared with existing air standards.

For ^{3}He and ^{4}He calibration purposes, small volume aliquots (typically in the range of about 1 cm^3) are taken from the large air standard reservoir and introduced into the analytical line in the same manner as unknown samples. The aliquot volumes are carefully calibrated and chosen to contain similar amounts of helium as typical seawater samples.

The accuracy of the helium concentration measurements depends upon the accuracy by which the amount of helium standard introduced into the system is known (a function of standard concentration, aliquot volume, pressure, and temperature). Gas samples should be purified so that interference from other gases (*e.g.*, neon) will not affect the results.

The amount of ^{3}He produced from tritium decay during storage of seawater samples can be much lower (several orders of magnitude) than the ^{3}He initially present in a seawater sample. To calibrate the "ingrown" ^{3}He following the initial degassing of a seawater sample, very small quantities of air standard must be used. To calibrate these measurements, a small aliquot of standard from an air reservoir is expanded into a large, fixed volume, and an aliquot from the fixed volume is then introduced into the analytical instrument after purification. This process allows samples with a wide range of helium concentrations to be calibrated using the same air standard.

During sample processing, air standards should be run frequently to check for drifts in the sensitivity of the instrument. Non-linearities should be checked by introducing various quantities of air standard which span the range of sample sizes.

Production of ^{3}He by cosmic rays during storage may need to be accounted for in the "lower level" samples in the ^{3}He regrowth technique. Unshielded samples at sea level can suffer artifacts equivalent to 0.020 TU (W. Jenkins, personal communication).

Tritium measurements can also be made by low-level beta counting. These measurements are calibrated using an internationally adopted standard material (National Bureau of Standards–Standard Reference Material No. 4926). This standard water is available to all laboratories and can be processed and analysed using the same procedures as with seawater samples. A discussion of this tritium standard and its use is give by Mann *et al.* (1982).

4.2 Intercalibration

Intercalibration among the laboratories making helium and tritium measurements can be accomplished in several ways. Aliquots of air standards can be exchanged and analyzed to ensure the uniformity of the basic calibration scale. Replicate water samples can be collected in standard copper sampling tubes and distributed among the groups involved in seawater measurements. Such 'unknown' samples could cover the range of helium and tritium concentrations typically present in the ocean and provide a test for the calibration methods used by various laboratories. Direct intercalibration can be made between tritium measurements made on samples using the ^{3}He ingrowth technique and measurements made by low-level beta counting techniques.

5. References

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