2021 A22 Chlorofluorocarbon (CFC), Sulfur Hexafluoride (SF6), and Nitrous Oxide (N2O)\* Measurements

PI: Mark J. Warner, University of Washington ([warner@u.washington.edu](mailto:warner@u.washington.edu)), Seattle, WA

Samplers and Analysts: Mark J. Warner, School of Oceanography, University of Washington

Bonnie X. Chang, CICOSE, University of Washington, Seattle, WA

Lillian Henderson, University of Miami, Miami, FL

\* Note that N2O measurements are a Level 3 measurement. The concentrations were measured on the same water samples collected for the Level 1 CFC/SF6 measurements. The N2O analysis is still under development. Please contact the PI for any use of these data.

Samples for the analysis of dissolved CFC-11, CFC-12, SF6, and N2O were collected from approximately 1417 of the Niskin water samples during the expedition. When taken, water samples for tracer analysis were the first samples drawn from the 10-liter bottles. Care was taken to co-ordinate the sampling of the tracers 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, partial pressure of CO2, dissolved inorganic carbon, and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the tracer samples were collected from the Niskin bottle petcock into 250-cc ground glass syringes through plastic 3-way stopcocks. The syringes were stored in the dark in a large ice chest in the laboratory at 3.5° - 6° C until 30-45 minutes before analysis to reduce the degassing and bubble formation in the sample. At that time, they were transferred to a water bath at approximately 35° C to warm the samples prior to analysis in order to increase the stripping efficiency.

Concentrations of CFC-11, CFC-12, SF6, and N2O in air samples, seawater and gas standards were measured by shipboard electron capture gas chromatography (EC-GC). This system from the University of Washington was located in a portable laboratory on the fantail. Samples were introduced into the EC-GC via a purge and trap system. Approximately 200-ml water samples were purged with nitrogen and the compounds of interest were trapped on a Porapak Q/Carboxen 1000/Molecular Sieve 5A trap cooled by an immersion bath to >-55oC. During the purging of the sample (6 minutes at 170 ml min-1 flow), the gas stream was stripped of any water vapor via a Nafion trap in line with an ascarite/magnesium perchlorate dessicant tube prior to transfer to the trap. The trap was then isolated and heated by direct resistance to 175oC. The desorbed contents of the trap were back-flushed and transferred onto the analytical pre-columns. The first precolumn was a 40-cm length of 1/8-in tubing packed with 80/100 mesh Porasil B. This precolumn was used to separate the CFC-11 from the other gases. The second pre-column was 13 cm of 1/8-in tubing packed with 80/100 mesh molecular sieve 5A. This pre-column separated the N2O from CFC-12 and SF6. Three analytical columns in three gas chromatographs with electron capture detectors were used in the analysis. CFC-11 was separated from other compounds (e.g. CFC-113 and CCl4) by a column consisting of 36 cm of Porasil B and 150 cm of Carbograph 1AC maintained at 80°C. CFC-12 and SF6 were analyzed using a column consisting of 2.33 m of molecular sieve 5A and 1.5 m of Carbograph 1AC maintained at 80°C. The analytical column for N2O was 30 cm of molecular sieve 5A in a 120°C oven. The carrier gas for this column was instrumental grade P-5 gas (95% Ar / 5% CH4) that was directed onto the second precolumn and into the third column for the N2O analyses. The detectors for the CFC-11, and for CFC-12 and SF6 analyses were operated at 300ºC. The detector for N2O was maintained at 320 ºC.

The analytical system was calibrated frequently using a standard gas of known gas composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure were recorded so that the amount of gas injected could be calculated. CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (UW WRS 32399) into the analytical instrument. A full range of calibration points were run at the beginning and end of the cruise, as well as during long transits/weather delays when possible. The procedures used to transfer the standard gas to the trap, precolumns, main chromatographic columns and EC detectors were similar to those used for analyzing water samples. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 2 hours) to monitor short-term changes in detector sensitivity. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for samples was 740 sec.

For atmospheric sampling, an ~100 meter length of 3/8-in OD Dekaron tubing was run from the portable laboratory to the bow of the ship. A flow of air was drawn through this line to the main laboratory using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm. using a back-pressure regulator. A tee allowed a flow (100 ml min-1) of the compressed air to be directed to the gas sample valves of the CFC/SF6/N2O analytical system, while the bulk flow of the air (>7 l min-1) was vented through the back-pressure regulator. Air samples were generally analyzed when the relative wind direction was within 50 degrees of the bow of the ship to reduce the possibility of shipboard contamination. The pump was run for approximately 30 minutes prior to analysis to insure that the air inlet lines and pump were thoroughly flushed. The average atmospheric concentrations determined during the cruise (from sets of 3 or 4 measurements analyzed when possible) were 221.9 +/- 1.8 parts per trillion (ppt) for CFC-11 (n=27), 496.6+/- 1.8 ppt for CFC-12 (N=40), 10.8 +/- 0.2 ppt for SF6 (N=15), and 332.9 +/- 2.0 parts per billion for N2O (N=19).

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et. al., 2000). Concentrations in air and standard gas are reported in units of mole fraction in dry gas, and are typically in the parts per trillion (ppt) range for CFCs and SF6 and parts per billion (ppb) for N2O. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg-1), SF6 in femtomoles per kilogram seawater (fmol kg-1), and N2O in nanomoles per kilogram seawater (nmol kg-1). Estimated limit of detection is 1 fmol kg-1 for CFC-11, 1 fmol kg-1 for CFC-12 and 0.01 fmol kg-1 for SF6.

The efficiency of the purging process was evaluated by re-stripping water samples and comparing the residual concentrations to initial values. These re-strip values were less than 1% for CFC-11 and essentially zero for CFC-12 and SF6. Based on the re-strips of numerous samples where the stripper blank was low and relatively constant, the mean values for N2O were approximately 5-10% during the cruise.

On this expedition, based on the analysis of 40 duplicate samples (i.e. two syringe samples collected from the same Niskin), we estimate precisions (1 standard deviation) of 0.65% or 0.0012 pmol kg-1 (whichever is greater) for dissolved CFC-11, 0.36% or 0.00058 pmol kg-1 for CFC-12 measurements, 0.017 fmol kg-1 or 1.98% for SF6, and 0.67% or 0.096 nmol kg-1 for N2O.

Analytical Difficulties/Acknowledgments:

During A20, two immersion coolers failed – the first lost coolant through a leak during transport to the start of A20; the second had its low-stage compressor fail during the transit after the completion of the measurement program of A20. Without an immersion cooler for the trapping process, we would have only been able to measure CFC-12 for A22. Thanks to the efforts of Dana Greeley, Eric Wisegarver, the shipping department at NOAA-PMEL and the tracer measurement lab at NOAA-PMEL, a spare working immersion cooler was located, tested, and shipped to St. Thomas in advance of the departure for A22. We were only able to make high-precision measurements during this cruise due to the efforts, above and beyond, of the people listed above. These individuals deserve the credit for the quality of the reported data.

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