ANT XXIII/7 – WWOS

Data Report: CFC and noble gas measurements

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Datafile ("ant23_7_pangaea.dat" ascii) content:

"ANT-XXIII/7"
"2006-08-24-to-2006-10-29"
Station
Cast
Bottle number
Bottle depth
Latitude
Longitude
CFC-11 [pmol/kg]
CFC-11-Flag
CFC-12 [pmol/kg]
CFC-12-Flag
Helium [nmol/kg]
Helium-Flag
δ^3He [%] = 100 x ($[^3He/^4He]_{obs}/[^3He/^4He]_{atm.} - 1$)
δ^3He-Flag
Neon [nmol/kg]
Neon-Flag

The tracer data set was carefully checked for accurate measurements and outliers. According to the WOCE standards the following flags were applied to each measurement:

flag 2 = good
flag 3 = doubtful
flag 4 = bad
flag 6 = mean of replicates
flag 9 = no measurement (then, the data value is set to -9.000)

Methods

During the expedition a total of 550 samples on 37 CTD stations were collected for chlorofluorocarbons (CFC-11 and CFC-12). The water samples from the rosette system were collected into 100 ml glass ampoules and sealed off after a CFC free headspace of pure nitrogen had been applied. Furthermore, 310 samples from 30 stations were collected for helium isotopes (^{3}He, ^{4}He) and neon (Ne). The water samples from the niskin bottles were stored in clamped off copper tubes.

Noble gases (^{3}He, ^{4}He, ^{20}Ne)

The water samples for helium isotopes and neon from the CTD-bottle-system are tapped in copper tubes, preventing air contamination and bubbles during the filling of the tubes and squeezed at both ends to keep them gas tight during transportation and storage.

In the IUP Bremen noble gas lab the samples are processed in a first step with a UHV (ultra high vacuum) gas extraction system. The required vacuum conditions are achieved by a rotary pump and an oil diffusion pump. To maintain contamination-free samples, the extraction system is checked for leaks on each sample separately. Sample gases are transferred via water vapour into a glass ampoule kept at liquid nitrogen temperature. Quality checks of this sample preparation line are done on a routine basis. This includes special vacuum checks and preparing accurately defined samples for internal control measurement.

For analysis of the noble gas isotopes the glass ampoules are connected to a fully automated UHV mass spectrometric system equipped with a two stage cryo system. Every 2 to 4 samples the system is calibrated with atmospheric air standards (reproducibility <0.2%). Also measurement of line blanks and linearity are done. The performance of the Bremen facility is described in Sültenfuß et al. (2009).

Sültenfuß, J., M. Rhein, and W. Roether (2009). The Bremen Mass Spectrometric Facility for the measurement of helium isotopes, neon, and tritium in water. Isotopes in Environmental and Health Studies, 45(2), 1-13, DOI: 10.1080/10256010902871929

Error estimate for absolute noble gases concentrations:

$\Delta(^4He)$	< 0.8 %
$\Delta(Ne)$	< 0.8 %
$\Delta(\delta^3He)$	< 0.4 %

Chlorofluorocarbons (CFC-11, CFC-12)

The Chlorofluorocarbon (CFC-11 and CFC-12) water samples from the CTD-bottle-system are stored in glass ampoules without contact to the atmosphere during the tapping. Immediately after sampling the ampoules are flame sealed after a CFC free headspace of pure nitrogen had been applied.

The loss of CFCs into the headspace is considered by a careful equilibration between liquid and gas phase under controlled conditions before the sealed ampoules are opened and a precise measurement of the volume of the headspace. The determination of CFC concentrations in the IUP Bremen gas chromatography lab is accomplished by purge and trap sample pre-treatment followed by gas chromatographic (GC) separation on a capillary column and electron capture detection (ECD). The system is calibrated by analyzing several different volumes of a known standard gas. CFC concentrations are calibrated on SIO98 scale (Prinn et al., 2000). A more detailed description of the measurement system is given by Bulsiewicz et at. (1998).

Bulsiewicz, K., H. Rose, O. Klatt, A. Putzka, W. Roether (1998). A capillary-column chromatographic system for efficient chlorofluoromethane measurement in ocean waters. Journal of Geophysical Research, Vol. 103 (C8), 15959-15970, DOI: 10.1029/98JC00140.

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, A. McCulloch (2000). A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. Journal of Geophysical Research, Vol. 105, 17.751-17.792, DOI: 10.1029/2000JD900141.

Accuracy (i.e. uncertainties of calibrated sample volume, calibration curve, extraction efficiency, standard and working gas; water blank):

CFC-12 < 1.7 %
CFC-11 < 2.9 %

Precision (i.e. mean error from 22 replicate samples):

CFC-12 < 0.005 pmol/kg or < 0.8 % (which ever is greater)

We do not give a value for the precision of CFC-12. Offline sample chromatograms regularly show a negative peak in the vicinity of the CFC-11 peak, which decreases the accuracy of CFC-11 in comparison to CFC-12, and which does not allow giving an objective estimate of a precision for CFC-11.

Noble gas and CFC data were used in Hellmer et al., 2011.

Hellmer, H. H., O. Huhn, D. Gomis, and R. Timmermann, 2011. On the freshening of the northwestern Weddell Sea continental shelf. Ocean Science, 7, 305-316, doi:10.5194/os-7-305-2011, 2011. In press: http://www.ocean-sci.net/7/305/2011/os-7-305-2011.html.

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