Text S4: SIO Measurement Report

1. SIO Measurement report: Halocarbons in Dry Whole Air
2. Laboratory: Scripps Institution of Oceanography, R.F. Weiss, C.M. Harth, J. Mühle
3. Cylinder number: AAL073358
4. NOMINAL COMPOSITION: Various dry air mole fractions from 20 X 10-12 to 550 X 10-12 (pmol/mol; ppt)

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| --- | --- | --- | --- | --- |
| Measurement No. 1 | Date | Result (pmol/mol) | stand. deviation 1σ (% relative) | # of sub- measurements |
| Dichlorodifluoromethane (CFC-12) | 4/30/2012 | 533.23 | 0.045 | 13 |
| Trichlorofluoromethane (CFC-11) | 4/30/2012 | 239.63 | 0.19 | 14 |
| 1,1,2-Trichlorotrifluoroethane (CFC-113) | 4/26/2012 | 75.12 | 0.18 | 12 |
| 1,1,1,2-Tetrafluoroethane (HFC-134a) | 4/26/2012 | 64.89 | 0.17 | 12 |
| Difluorochloromethane (HCFC-22) | 4/26/2012 | 224.05 | 0.24 | 12 |
| 1,1-Difluoro-1-chloroethane (HCFC-142b) | 4/26/2012 | 22.36 | 0.45 | 11 |

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| Measurement No. 2 | Date | Result (pmol/mol) | stand. deviation 1σ (% relative) | # of sub- measurements |
| Dichlorodifluoromethane (CFC-12) | 5/1/2012 | 533.07 | 0.052 | 14 |
| Trichlorofluoromethane (CFC-11) | 5/1/2012 | 239.82 | 0.27 | 16 |
| 1,1,2-Trichlorotrifluoroethane (CFC-113) | 4/28/2012 | 75.23 | 0.15 | 10 |
| 1,1,1,2-Tetrafluoroethane (HFC-134a) | 4/28/2012 | 64.98 | 0.20 | 10 |
| Difluorochloromethane (HCFC-22) | 4/28/2012 | 223.89 | 0.21 | 9 |
| 1,1-Difluoro-1-chloroethane (HCFC-142b) | 4/28/2012 | 22.49 | 0.97 | 11 |

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| Measurement No. 3 | Date | Result (pmol/mol) | stand. deviation 1σ (% relative) | # of sub- measurements |
| Dichlorodifluoromethane (CFC-12) | 5/2/2012 | 533.35 | 0.053 | 15 |
| Trichlorofluoromethane (CFC-11) | 5/2/2012 | 240.02 | 0.36 | 15 |
| 1,1,2-Trichlorotrifluoroethane (CFC-113) | 5/3/2012 | 75.15 | 0.19 | 11 |
| 1,1,1,2-Tetrafluoroethane (HFC-134a) | 5/3/2012 | 64.79 | 0.13 | 11 |
| Difluorochloromethane (HCFC-22) | 5/3/2012 | 223.26 | 0.12 | 9 |
| 1,1-Difluoro-1-chloroethane (HCFC-142b) | 5/3/2012 | 22.55 | 0.61 | 11 |

1. Summary Results:

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| --- | --- | --- | --- | --- | --- |
| Gas Mixture Component | Result (assigned value) pmol/mol (ppt) | Coverage factor  (*k*) | Assigned Expanded Uncertainty pmol/mol (ppt) | | |
| Precision | Accuracy | U(xi) |
| Dichlorodifluoromethane (CFC-12) | 533.2 | 2 | 0.29 | 5.96 | 5.97 |
| Trichlorofluoromethane (CFC-11) | 239.8 | 2 | 0.39 | 2.77 | 2.80 |
| 1,1,2-Trichlorotrifluoroethane (CFC-113) | 75.17 | 2 | 0.11 | 1.17 | 1.18 |
| 1,1,1,2-Tetrafluoroethane (HFC-134a) | 64.88 | 2 | 0.19 | 1.04 | 1.06 |
| Difluorochloromethane (HCFC-22) | 223.7 | 2 | 0.84 | 2.54 | 2.68 |
| 1,1-Difluoro-1-chloroethane (HCFC-142b) | 22.47 | 2 | 0.20 | 0.46 | 0.50 |

1. Reference Method:
2. Describe your instrument(s) (principles, make, type, configuration, data collection etc.): CFC-11 and CFC-12 were measured on a custom gas chromatographic (GC) system with electron capture detector (ECD) (Prinn et al., A History of Chemically and Radiatively Important Gases in Air deduced from ALE/GAGE/AGAGE, J. Geophys. Res., 105, 17,751-17,792, 2000). All other compounds were measured on a custom GC system with mass spectrometric detector (MSD) (Miller et al., Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons, and Sulfur Compounds, Analytical Chemistry, doi: 10.1021/ac702084k, 2008).
3. Calibration Standards:
4. Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.): In-house gravimetric multiple primary calibration mixtures at near ambient concentrations, prepared by a “bootstrap” method using gravimetric mixtures ratioed to CO2 and N2O. See cited Prinn et al. (2000) and Miller et al. (2008) for discussion and details.

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| --- | --- | --- | --- | --- |
|  | Primary Scale | Number of Primary Standards in Scale | Relative Standard Deviation of Scale 2σ (Internal Agreement) | Quoted Reagent Purity |
| CFC-12 | SIO-05 | 27 | 0.50% | ≥ 99.97% |
| CFC-11 | SIO-05 | 23 | 0.58% | ≥ 99.9% |
| CFC-113 | SIO-05 | 17 | 0.42% | ≥ 99.9% |
| HFC-134a | SIO-05 | 13 | 0.56% | ≥ 99.9% |
| HCFC-22 | SIO-05 | 20 | 0.54% | ≥ 99.9% |
| HCFC-142b | SIO-05 | 13 | 0.42% | ≥ 99.4% |

1. Instrument Calibration:
2. Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.): Fitting of primary calibrations in sensitivity space. Please see cited Prinn et al. (2000) and Miller et al. (2008) references.
3. Sample Handling:
4. How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).: Cylinders were stored at room temperature for several days, and were transferred to the instruments using high purity single stage stainless steel (SS) pressure regulators (see Prinn et al., 2000 and Miller et al., 2008) and chromatographic grade 1/16” SS tubing using compression type fittings (Swagelok and/or VICI).
5. Uncertainty:
6. There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.
7. a) Uncertainty table:

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| --- | --- | --- | --- | --- | --- | --- |
| **Uncertainty source**  ***XI*** | **Gas Mixture Component** | **Estimate *xI pmol/mol (ppt)*** | **Assumed distribution** | **Standard uncertainty *u(xi)*** | **Sensitivity coefficient c*I*** | **Contribution to standard uncertainty *uI(y)*** |
| Xp, k=2 | CFC-12 | 0.29 | Normal |  |  |  |
| CFC-11 | 0.39 |
| Propagation from | CFC-113 | 0.11 |
| Primaries to Final | HFC-134a | 0.19 |
| Analysis | HCFC-22 | 0.84 |
| HCFC-142b | 0.20 |
| Xs, k=2  Primary Standard Preparation (Internal Agreement)\*\* | CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b | 2.67  1.39  0.32  0.36  1.21  0.09 | Normal |  |  |  |
| Xa, k=1 | CFC-12 | 5.33 | Normal |  |  |  |
| Estimated |
| Analytical | CFC-11 | 2.40 |
| Interference | CFC-113 | 1.13 | (except |
| Uncertainty | HFC-134a | 0.97 | reagent |
| (including | HCFC-22 | 2.24 | impurity |
| reagent | HCFC-142b | 0.45 | component) |
| impurity) |

1. Coverage factor: 2