Text S2. NOAA Measurement Report

NOAA Measurement report: Halocarbons in Dry Whole Air

Laboratory : NOAA

Cylinder number : AAL073358

nominal composition: Various from 20 x 10-12 to 550 x 10-12 (pmol/mol; ppt)

Summary Results:

|  |  |  |  |
| --- | --- | --- | --- |
|  Gas Mixture Component | Result(assigned value)pmol/mol (ppt) | Coveragefactor | Assigned expandedUncertaintypmol/mol (ppt) |
| Dichlorodifluoromethane (CFC-12)Trichlorofluoromethane (CFC-11)1,1,2-Trichlorotrifluoroethane (CFC-113)1,1,1,2-Tetrafluoroethane (HFC-134a)Chlorodifluoromethane (HCFC-22)1,1-Difluoro-1-chloroethane (HCFC-142b) | 530.5241.075.465.3224.722.07 | k=2 (all) | 3.72.71.70.72.90.29 |

Reference Method:

*Describe your instrument(s) (principles, make, type, configuration, data collection etc.):*

CFC-12 and CFC-11 were measured by gas chromatography (GC) with packed columns and electron capture detection (ECD). The GC was custom-built. Data collection was performed by computer interface. Peak integration was performed using custom software.

Other compounds were measured using an Agilent GC with mass selective detection (MS). Air samples (~200 ml) were pre-concentrated in a section of uncoated fused silica capillary column, and flash-heated onto a DB-5 column.

All samples were compared to working standards consisting of dried natural air in Aculife-treated aluminum cylinders.

Calibration Standards:

*Describe your Calibration Standards for the measurements (preparation method, purity analyses,*

*estimated uncertainty etc.):*

Primary standards are prepared using gravimetric methods. Aliquots (10-200 mg) of reagent-grade material are weighed out in glass capillary tubes or single-valve stainless steel transfer volumes (5-50 mL). Once the masses of the aliquots are determined, aliquots are expanded into an evacuated cylinder. For liquid aliquots, the glass capillaries are broken and heated to aid transfer. For gaseous aliquots, the stainless steel volumes are repeatedly flushed to the evacuated cylinder using zero grade air. The cylinder is then pressurized with zero-grade synthetic air.

For serial dilution to ppt-levels, aliquots of higher-concentration standards are weighed out using the stainless steel transfer volumes in a method similar to that described above.

Generally, Aculife-treated aluminum cylinders are used for the high-concentration standards (ppb, ppm) and daughter standards are made in Aculife-treated aluminum or electro-polished stainless steel cylinders. Reagent purity was determined by GCMS in our laboratory or taken from manufacturer’s specifications.

Instrument Calibration:

*Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):*

For GC-ECD and GC-MS analysis, sets of gravimetric standards were compared to working standards containing natural air. The ECD response was fit with a second order polynomial. A linear MS response was used, with the average molar response from the sets of gravimetric standards used to assign mole fractions to the working standard.

Sample Handling:

*How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).:*

For GC-ECD analysis, a high-purity regulator (Parker Veriflo) was attached to the cylinder, flushed, and let equilibrate overnight.

For GC-MS analysis, a CGA-590 fitting was attached to a restriction to allow a pre-determined flowrate and a high-pressure solenoid valve (NO REGULATOR).

Uncertainty:

*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.*

For each gas, five components were included in the uncertainty estimate. All are considered independent, and added in quadrature. We recognize that some uncertainties may not be independent, but assume independence regardless. We also recognize that some uncertainties might not be normally distributed, but we assume normal distribution. Often the largest contributors to uncertainty are normally distributed variables, such as analytical repeatability and weighing uncertainties. An uncertainty table for each gas is included below.

1. Uncertainty table: **CFC-12**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 0.8 | normal | 0.001508 |
| Zero-grade air | 0.2 | normal | 0.000377 |
| Gravimetric Standards | 0.42 | normal | 0.000792 |
| Reagent purity | 1.56 | normal | 0.0030 |
| Long-term stability | 0 | normal | 0 |
|  |  | **total** | 0.00347 |

Coverage factor: k=2

Expanded uncertainty: 0.69%, 3.7 ppt

1. Uncertainty table: **CFC-11**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 0.8 | normal | 0.00332 |
| Zero-grade air | 0 | normal | 0 |
| Gravimetric Standards | 0.73 | normal | 0.00303 |
| Reagent purity | 0.75 | normal | 0.0030 |
| Long-term stability | 0.4 | normal | 0.00166 |
|  |  | **total** | 0.00565 |

Coverage factor: k=2

Expanded uncertainty: 1.13 %, 2.7 ppt

1. Uncertainty table: **CFC-113**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 0.1 | normal | 0.00133 |
| Zero-grade air | 0 | normal | 0 |
| Gravimetric Standards | 0.8 | normal | 0.00106 |
| Reagent purity | 0.23 | normal | 0.0030 |
| Long-term stability | 0 | normal | 0 |
|  |  | **total** | 0.0111 |

Coverage factor: k=2

Expanded uncertainty: 2.2%, 1.7 ppt

1. Uncertainty table: **HCFC-22**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 1.1 | normal | 0.005 |
| Zero-grade air | 0.2 | normal | 0.00089 |
| Gravimetric Standards | 0.8 | normal | 0.00356 |
| Reagent purity | 0.45 | normal | 0.002 |
| Long-term stability | 0 | normal | 0 |
|  |  | **total** | 0.00652 |

Coverage factor: k=2

Expanded uncertainty: 1.3%, 2.9 ppt

1. Uncertainty table: **HCFC-142b**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 0.1 | normal | 0.004525 |
| Zero-grade air | 0 | normal | 0 |
| Gravimetric Standards | 0.1 | normal | 0.004525 |
| Reagent purity | 0.022 | normal | 0.001 |
| Long-term stability | 0 | normal | 0 |
|  |  | **total** | 0.006477 |

Coverage factor: k=2

Expanded uncertainty: 1.30%, 0.29 ppt

1. Uncertainty table: **HCFC-134a**

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt) | Assumed distribution | Fractional uncertainty |
| Analytical precision | 0.2 | normal | 0.003063 |
| Zero-grade air | 0 | normal | 0 |
| Gravimetric Standards | 0.3 | normal | 0.004594 |
| Reagent purity | 0.07 | normal | 0.001 |
| Long-term stability | 0 | normal | 0 |
|  |  | **total** | 0.005611 |

Coverage factor: k=2

Expanded uncertainty: 1.12%, 0.7 ppt