Text S1: NIST Measurement Report

NIST Measurement report: Halocarbons in Dry Whole Air

Laboratory : National Institute of Standards and Technology (NIST)

Cylinder number : AAL073358

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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 1 | Date | Result  (pmol/mol) | stand. deviation  (% relative) | # of sub-  measurements |
| 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) | 06-Feb-12  31-Oct-11  13-Dec-11  01-Feb-12  01-Feb-12  01-Feb-12 | 530.9  240.21  77.63  64.45  219.54  21.78 | 1.4  0.80  0.19  1.08  1.42  0.27 | 3  3  3  3  3  3 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 2 | Date | Result  (pmol/mol) | stand. deviation  (% relative) | # of sub-  measurements |
| 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) | 07-Feb-12  01-Nov-11  13-Dec-11  02-Feb-12  02-Feb-12  02-Feb-12 | 528.92  241.94  77.69  63.03  221.95  21.80 | 0.56  0.37  0.19  1.12  1.44  0.27 | 3  3  3  3  3  3 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 3 | Date | Result  (pmol/mol) | stand. deviation  (% relative) | # of sub-  measurements |
| 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) | 09-Feb-12  03-Nov-11  14-Dec-11  06-Feb-12  06-Feb-12  06-Feb-12 | 528.87  240.06  77.68  62.66  222.42  21.72 | 0.92  0.30  0.19  1.11  1.44  0.27 | 3  3  3  3  3  3 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 4 | Date | Result  (pmol/mol) | stand. deviation  (% relative) | # of sub-  measurements |
| 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) | 03-Nov-11 | 240.06 | 0.30 | 3 |

Summary Results:

|  |  |  |  |
| --- | --- | --- | --- |
| Gas Mixture Component | Result  (assigned value)  pmol/mol (ppt) | Coverage  factor | Assigned expanded  Uncertainty  pmol/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) | 529.6  240.7  77.68  63.4  221.5  21.77 | 2  2  2  2  2  2 | 3.4  0.8  0.38  2.2  3.0  0.54 |

Reference Method:

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

An HP 5890 Gas Chromatograph (NIST #: 597806) equipped with an electron capture detector (ECD) operated at 320°C was used to analyze CFC-12, CFC-11 and CFC-113.

CFC-12 and CFC-11: A 0.914 m x 3.81 cm stainless steel column packed with Porapak Q, 60°C for 10 min then to 120°C at 60°C/min held 2 min then to 60°C at 60°C/min; 30 mL/min nitrogen carrier flow rate; 5 mL sample injected onto column;

CFC-113: A 0.914 m x 0.32 cm stainless steel column packed with Porapak Q, 150°C for 10; 30 mL/min nitrogen carrier flow rate; 5 mL sample injected onto column.

An Agilent 6890 Gas Chromatograph (NIST #: 607135) equipped with an flame ionization detector (FID) operated at 250°C was used to analyze HFC-134a, HCFC-22 and HCFC-142b. A 30m x 0.32mm capillary column coated with GS-GASPRO at 40°C for 8 min to 160°C at 10°C/min to 220°C at 20°C/min; 1.5 mL/min helium column flow rate with 43.5 mL/min helium make-up flow. 1500 mL of sample was collected using an Entech 7100 automatic preconcentrator (NIST #: 620102) and cryofocused on the head on the capillary column.

HP Chemstation data system was used for peak area integration with the data transferred to Excel via macro program.

Calibration Standards:

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

estimated uncertainty etc.):

Primary standards were prepared by gravimetry starting from pure components. Each pure halocarbon was analyzed for purity by preparing an individual lower concentration standard using ultra high purity nitrogen as the matrix gas. The UHP nitrogen was analyzed for the presence of each halocarbon using GC/ECD. The matrix synthetic air used to prepare the atmospheric level standards was analyzed for each halocarbon by collecting 1500 mL and analyzing by GC/ECD. The purity of the halocarbons is as follows: CFC-12 99.98 %; CFC-11 99.95 %; CFC-113 99.98 %; HFC-134a 99.9 %; HCFC-22 99.9 %; HCFC-142b 99.9 %.

The uncertainty in the primary gravimetric standards follow and are given as relative % and represent a *k=*1 value: CFC-12 ± 0.1 %; CFC-11 ± 0.1 %; CFC-113 ± 0.4 %; HFC-134a ± 2.0 %; HCFC-22 ± 0.3 %; HCFC-142b ± 2.2 %.

Instrument Calibration:

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

The gravimetric standards used for the determination of halocarbons in the sample, AAL073358, are given below:

PSM --------------------------Gravimetric Concentration, pmol/mol (ppt)a-----------------

Cylinder # Year CFC-12 CFC-11 CFC-113 HCFC-22 HCFC-142b HFC-134a

CAL014823 1998 467.9 (0.6) 334.7 (0.3)

CAL014810 1998 425.4 (0.6) 251.9 (0.3)

CAL014821 1998 375.3 (0.6) 271.1 (0.3)

CAL014139 1998 281.3 (0.6) 165.8 (0.3)

CAL014101 1998 276.2 (0.6) 204.7 (0.3)

AAL070499 2004 65.11 (0.1)

AAL070466 2004 87.66 (0.1)

FF4236 2012 51.22 (0.15) 69.55 (0.6)

FF4270 2012 455.9 (1.0) 20.59 (0.15) 27.95 (0.6)

FF4266 2012 237.85 (1.0)

FF4204 2012 540.2 ± 0.5

aRelative combined uncertainty, in ( ), with the coverage factor *k=*1 (68 % confidence interval).

The sample was used as a control; it was analyzed first followed by two primary gravimetric standards, followed by the sample, and continued until all standards had been analyzed. This allowed for drift in the complete analysis sequence to be corrected due to temperature/pressure conditions. Three injections were made of each standard, or sample, before moving to the next sample. A ratio was calculated for each gravimetric standard to the sample from the peak area data. The CFC-12 and CFC-11 concentrations were determined for each days data using a generalized least squares regression and a 2nd order fit. The gravimetric standards for the other halocarbons bracketed the concentration in the sample. The concentration was determined against each standard and an average calculated. The final concentration was determined by using the ratio data from each days analysis and fitting to the generalized least squares regression to a linear fit; rather than taking an average of all days concentration determinations. The CFC-113, HFC-134a, HCFC-22 and HCFC-142b were determined by bracketing with PSMs.

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).:

All standards and the sample were brought into the lab and set next to the GC to be used. They were allowed to stabilize over 2 days. Stainless steel 2-stage, low dead volume, regulators were used and the sample lines were 3.8 cm stainless steel. The samples, for CFC-12, CFC-11 and CFC-113 analysis, were flushed through the sample loop at 40 mL/min flow but then dropped to ambient pressure 5 seconds before automatic injection onto the GC column. In the case of HFC-134a, HCFC-22 and HCFC-142b, the sample was preconcentrated in stainless steel traps then cryofocused on the head of the capillary column.

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.

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 0.6 | normal | 0.222 |
| Analytical precision | 1.4 | normal | 0.519 |
| Sample to Grav Stds | 0.7 | normal | 0.259 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 3.4 pmol/mol

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 0.3 | normal | 0.429 |
| Analytical precision | 0.1 | normal | 0.143 |
| Sample to Grav Stds | 0.3 | normal | 0.429 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 0.8 pmol/mol

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 0.1 | normal | 0.00429 |
| Analytical precision | 0.1 | normal | 0.143 |
| Sample to Grav Stds | 0.13 | normal | 0.394 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 0.38 pmol/mol

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 0.6 | normal | 0.00429 |
| Analytical precision | 0.8 | normal | 0.143 |
| Sample to Grav Stds | 0.5 | normal | 0.394 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 2.2 pmol/mol

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 1.0 | normal | 0.00429 |
| Analytical precision | 1.0 | normal | 0.143 |
| Sample to Grav Stds | 0.5 | normal | 0.394 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 3.0 pmol/mol

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

|  |  |  |  |
| --- | --- | --- | --- |
| Uncertainty component | Estimate (ppt)  *u*(*k=1*) | Assumed distribution | Contribution to standard uncertainty, *ui*(y) |
| Gravimetric Standards | 0.15 | normal | 0.00429 |
| Analytical precision | 0.10 | normal | 0.143 |
| Sample to Grav Stds | 0.20 | normal | 0.394 |
|  |  |  |  |

Coverage factor: *k=*2

Expanded uncertainty: 0.54 pmol/mol