Text S5: Empa Measurement Report

1. Empa Measurement report: Halocarbons in Dry Whole Air

Laboratory : Empa, Swiss Federal Laboratories for Material Science and Technology

Cylinder number : AAL073358

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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 1  **vs J-127** | 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)  Difluorochloromethane (HCFC-22)  1,1-Difluoro-1-chloroethane (HCFC-142b) | 22 June 2012 | 530.25  238.93  74.24  64.371  221.70  22.510 | 0.08  0.31  3.4  0.23  0.20  0.47 | 7  7  7  7  7  7 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 2  **vs EG-003** | 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)  Difluorochloromethane (HCFC-22)  1,1-Difluoro-1-chloroethane (HCFC-142b) | 23 June 2012 | 530.25  239.57  74.57  64.598  221.77  22.427 | 0.12  0.19  2.2  0.15  0.25  0.56 | 6  6  6  6  6  6 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Measurement  No. 3  **vs E-071B** | 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)  Difluorochloromethane (HCFC-22)  1,1-Difluoro-1-chloroethane (HCFC-142b) | 23 June 2012 | 530.81  239.53  75.72  64.719  222.45  22.526 | 0.08  0.20  2.5  0.29  0.16  0.13 | 7  7  7  7  7  7 |

Note: Please copy this table as many times as needed for reporting additional measurements.

Summary Results: Our summary results are these from the measurement of CCQM- vs J-127. We have most confidence in these numbers.

|  |  |  |  |
| --- | --- | --- | --- |
| 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)  Difluorochloromethane (HCFC-22)  1,1-Difluoro-1-chloroethane (HCFC-142b) | 530.25  238.93  74.24  64.371  221.70  22.510 |  | 10.7  5.2  7.3  2.0  4.6  0.95 |

Reference Method:

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

Medusa-GCMS technology. Trap 2 L of sample, cryofocus, separate on CP-PoraBOND Q, 0.32 mm ID x 25 m, 5 um, Varian Crompack). See e.g. Miller, B. R. et al., Anal. Chem 80(5), 1536-1545, doi:10.1021/ac702084k, 2008, or Vollmer, M. K. et al., J. Geophys. Res., 116, D08304, doi:10.1029/2010/JD015309, 2011.

The instrument used for this analysis is called empa-medusa or Medusa-20.

Calibration Standards:

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

estimated uncertainty etc.):

We used 3 different calibrations standards, with filling names J-127, EG-003, and E-071B. All three standards are whole air fillings into 35 L Essex internally electropolished ss tanks. Filling J-127 is a whole air filling from Trinidad Head, California (~2009) using an oil-free diving compressor, EG-003 is whole air filling from Jungfraujoch (~2005) using cryogenic filling techniques, and E-071B is a whole air filling from the Swiss Rigi NABEL station using an oil-free diving compressor. All three standards are linked into the SIO/AGAGE R1 calibration system, whereas J-127 is most directly linked into this system, EG-003 through transfer standards (including J-127 and other canisters) and E-071B is linked into R1 via J-127. All results are reported on SIO scales as dry air mole fractions.

Instrument Calibration:

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

The tank filling CCQM-83K was measured in an alternating mode vs the above-described standards. Each measurement takes 1 hr. Concentrations of the standards were close to those of the CCQM-83K. The measurement system is considered linear in response for the compounds reported here and the mole fractions reported here. Measurements for the compounds reported here are based on chromatography/mass spectrometry peak areas (rather than peak heights). The peak sizes of CCQM-83K are references against those of the bracketing standard results. Corrections for the trapped volume are applied, which sometimes slightly deviates from the nominal 2L.

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).:

The cylinder was moved to the laboratory, where the instrument is located. It was left there standing for a few days. Then a pressure regulator was mounted (Veriflo 1-stage, 959 TDR), and thoroughly flushed. The regulator was left pressurized for a couple of days. Then it was flushed again, and connected to the instrument inlet via a 1/16” OD ss tube. Then analysis was started. The three sets of measurements were made one after the other without interruption, and took a total of about 2 days.

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.

We distinguish between three types of uncertainties. First the uncertainty associated with the preparation of the primary scale (at SIO). Secondly, the uncertainty associated with the propagation of the primary reference material to the standard used for the quantification of the unknown filling. And third, the uncertainty of the measurement, which consist of the random uncertainty (reported precision above) and some systematic uncertainty (such as mass-flow controllers, pressure gauges, potential nonlinearities, mass-spectrometric interferences etc). The three uncertainties are aggregated assuming independency. The separation into the three different types of uncertainties will also later allow for comparison with the results provided by SIO --- because we report on the same calibration scale as SIO, some of the uncertainties have to be omitted in such a comparison, and, essentially the SIO-Empa direct result comparison will reduce to the second and third type mentioned here.

1. Uncertainty of scale: To calculate this part, we combined two types of uncertainties that were reported by SIO, i.e. their 'Primary standard preparation' and their 'Estimated analytical interference uncertainty'. We combined these two by assuming them independen, i.e. we took the square root of the sums of the squares. For several compounds, this is the most significant uncertainty, e.g. HCFC-142b.
2. Propagation uncertainty: The propagation uncertainty is the uncertainty related to the measurement of transfer standards at SIO and transfer standards at Empa. This uncertainty is the higher the more indirect a working standard is linked into the SIO R1 calibration system. In our case, this uncertainty is lowest for J-127, followed by EG-003, and E-071B. For simplicity, we have only considered the measurement set vs J-127 in our final reported results. Hence we apply that transfer uncertainty. This transfer uncertainty is approximated by the uncertainty of tank measurements because compound concentrations are similar, and measurement procedures are similar too. However the propagation uncertainty may be considered somewhat lower, because the measurements of J-127 vs other relevant tanks at SIO was done with more replicate measurement than our CCQM-. Nevertheless for the sake of simplicity we assume it to be equal the measurement uncertainty. We use 2 sigma
3. Measurement uncertainty: Is the uncertainty given in the results tables above. While in the

result tables above, they are in 1-sigma, we here use 2 sigma.

Overall expanded uncertainty: We combine the three above uncertainties by considering them as independent uncertainties (square root of sums of squares), and then multiply that number by two.

1. Uncertainty table:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Uncertainty source  *XI* | Compound | Estimate  *xI* | Assumed distribution | Standard uncertainty  *u(xi)* | Sensitivity coefficient  c*I* | Contribution to standard uncertainty  *uI(y)* |
| 1)  Estimated Analytical Interference Uncertainty (including reagent impurity).  We requested this information from SIO, is their sqrt-combined uncertainties of the SIO reported (19 April 2014) Primary Standard Preparation and Estimated Analytical interference. | CFC-12  CFC-11  CFC-113  HFC-134a  HCFC-22  HCFC-142b | 1.12 %  1.16 %  1.56 %  1.60 %  1.14 %  2.04 % |  |  |  |  |
| 2)  Propagation uncertainty (from primary scale to Empa instrument working standards, 2 sigma) | CFC-12  CFC-11  CFC-113  HFC-134a  HCFC-22  HCFC-142b | 0.16 %  0.62 %  6.8 %  0.46 %  0.40 %  0.94 % |  |  |  |  |
| 3)  Measurement uncertainty, 2 sigma | CFC-12  CFC-11  CFC-113  HFC-134a  HCFC-22  HCFC-142b | 0.16 %  0.62 %  6.8 %  0.46 %  0.40 %  0.94 % |  |  |  |  |
| Overall expanded uncertainty  SQRT of sum of squared 1)-3) | CFC-12  CFC-11  CFC-113  HFC-134a  HCFC-22  HCFC-142b | 1.14 %  1.45 %  9.74 %  1.72 %  1.27 %  2.43 % |  |  |  |  |
|  |  |  |  |  |  |  |

Coverage factor:

Expanded uncertainty:see above table