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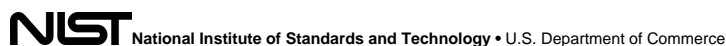
Comparison of halocarbon measurements in an atmospheric dry whole air sample

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Abstract

The growing awareness of climate change/global warming, and continuing concerns regarding stratospheric ozone depletion, will require continued measurements and standards for many compounds, in particular halocarbons that are linked to these issues. In order to track atmospheric mole fractions and assess the impact of policy on emission rates, it is necessary to demonstrate measurement equivalence at the highest levels of accuracy for assigned values of standards. Precise measurements of these species aid in determining small changes in their atmospheric

abundance. A common source of standards/scales and/or well-documented agreement of different scales used to calibrate the measurement instrumentation are key to understanding many sets of data reported by researchers. This report describes the results of a comparison study among National Metrology Institutes and atmospheric research laboratories for the chlorofluorocarbons (CFCs) dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and 1,1,2-trichlorotrifluoroethane (CFC-113); the hydrochlorofluorocarbons (HCFCs) chlorodifluoromethane (HCFC-22) and 1-chloro-1,1-difluoroethane (HCFC-142b); and the hydrofluorocarbon (HFC) 1,1,1,2-tetrafluoroethane (HFC-134a), all in a dried whole air sample. The objective of this study is to compare calibration standards/scales and the measurement capabilities of the participants for these halocarbons at trace atmospheric levels. The results of this study show agreement among four independent calibration scales to better than 2.5% in almost all cases, with many of the reported agreements being better than 1.0%.

1. Introduction

Stratospheric ozone depletion has been linked to the presence of halogenated trace gases that include chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) (Montzka et al., 2011). CFCs and HCFCs together with HFCs are strong greenhouse gases (Forster et al., 2007; Prinn et al., 1998). Research groups around the globe continuously measure halocarbons and monitor their growth/decline in the atmosphere (Blake et al., 2003; Montzka et al., 1996, 1999; O'Doherty et al., 2004; Artuso et al., 2010; Prinn et al., 2000). Measurements from the National Oceanic and Atmospheric Administration (NOAA) can be found at www.esrl.noaa.gov/gmd; from the Advanced Global Atmospheric Gases Experiment (AGAGE) at http://agage.eas.gatech.edu/ and http://agage.mit.edu, and from the University of California Irvine (UCI) at http://cdiac.ornl.gov/trends/otheratg/blake/blake.html and http://ps.uci.edu/~rowlandblake/. These measurements of the atmospheric abundance of halocarbons assist in efforts to determine their sources and sinks, their global distributions, and how these change over time in response to natural and anthropogenic processes.

Factors such as sampling or analytical methods/techniques may cause differences in abundance reported by researchers. However, the most important and influential factors usually are the calibration standards or scales used to determine those abundances. Gravimetric preparations of gas phase volatile organic compound (VOC) standards, including hydrocarbons and halocarbons, that are either in the gas or liquid phase at room temperature, have been reported (Montzka et al., 1993; Happell and Wallace, 1997; Rhoderick and Dorko, 2004; Rhoderick, 2006; Rhoderick et al., 2010). Additional literature cites the gravimetric preparation of standards/scales for methane and nitrous oxide which use the same or similar preparation techniques (Dlugokencky et al., 2005; Hall et al., 2007; Rhoderick et al., 2012; Kelley et al., 2014). In order to track and control the global and regional emissions of these species, and relate data from different laboratories, it is necessary to demonstrate measurement compatibility at the lowest levels of uncertainty. This requires reliable, accurate and precise measurements maintained over time. While there are agreed upon uncertainty requirements for precision measurements for some key atmospheric gases such as carbon dioxide, methane, carbon monoxide and nitrous oxide

(World Meteorological Organization, 2013), there are no agreed-upon levels for halocarbons. However, those preparing their standards always strive to improve their accuracy and reduce the uncertainties, as well as reducing measurement uncertainties. By reducing uncertainties, trends assessment becomes easier and more reliable from the measurement data.

These factors are of particular importance to the atmospheric monitoring and measurement communities such as the NOAA Global Monitoring Division (GMD), AGAGE and UCI. Their main objectives are to: 1) maintain adequate stability of their laboratories' internal calibration scales and thereby ensure that the atmospheric records they produce are internally consistent for determination of trends and gradients in atmospheric mole fractions over decades, and 2) maintain close links with other laboratories so that atmospheric data may be reliably merged across multiple laboratories and methods for interpretation, including atmospheric models.

Most nations have a National Metrology Institute (NMI) whose mission is to promote innovation and industrial competitiveness through the advancement of measurement science, standards and technology to improve the quality of life and economic security of that nation; https://net.nist.gov/fo/nistmission, http://www.bipm.org/en/worldwide-metrology/. NMIs have established a quality system through which each NMI establishes credentials related to their individual needs. Through this process the NMIs demonstrate equivalence to each other's measurement processes and reference standards and therefore measurement accuracy is important. This established equivalence allows users around the world to obtain reference materials and calibrations from another country's NMI, if needed, thus supporting global commerce. Through the Consultative Committee for Amount of Substance — Metrology in Chemistry (CCQM), the NMIs participate in key comparisons in order to demonstrate the equivalence of measurement capabilities. Degrees of equivalence are calculated from these key comparisons in order to support NMI Calibration and Measurement Capabilities (CMCs). For each key comparison a Key Comparison Reference Value (KCRV) is calculated and the degrees of equivalence calculated relative to the KCRV. Only CCQM member participants may participate in a key comparison. The NMIs have much experience with the preparation of gas standards, but very little, if any experience analyzing whole air samples.

There have been several reported comparisons between researchers in the halocarbon measurement community (Rasmussen, 1978; Jones et al., 2011; Hall et al., 2014). Additionally an important role of the quadrennially-published World Meteorological Organization (WMO) Ozone Assessment Reports allow for comparison results for ozone-depleting substances and their substitute gases within the atmospheric measurement community (Montzka et al., 2011). However, there have been very few opportunities between the NMI's and measurement/monitoring communities to compare standards and scales (Rhoderick and Dorko, 2004; Hall et al., 2014). Therefore, this comparison was developed to include other laboratories and agencies regularly measuring these halocarbons in the atmosphere. This study evaluates and compares the reported results of participants, representing NMIs and the atmospheric community on a smaller scale than many reported studies, to a comparison reference value. This report describes the results of a comparison

for several of the most abundant halocarbons at atmospheric mole fraction levels including the chlorofluorocarbons (CFCs) dichlorodifluoromethane (CFC-12; $\approx$ 530 pmol mol^{-1}), trichlorofluoromethane (CFC-11; $\approx$ 240 pmol mol^{-1}), and 1,1,2-trichlorotrifluoroethane (CFC-113; $\approx$ 75 pmol mol^{-1}); the hydrochlorofluorocarbons (HCFCs) chlorodifluoromethane (HCFC-22; $\approx$ 225 pmol mol^{-1}) and 1-chloro-1,1-difluoroethane (HCFC-142b; $\approx$ 22 pmol mol^{-1}); and the hydrofluorocarbon (HFC) 1,1,1,2-tetrafluoroethane (HFC-134a; $\approx$ 65 pmol mol^{-1}) in a real, dry, air sample. This study is viewed as an assessment of how each participant compares to each other.

2. Experimental

2.1 Sample mixture for the comparison

The single gas mixture circulated as the comparison study sample was prepared by the Global Monitoring Division, Earth System Research Laboratory, NOAA, in Boulder, Colorado, US. Whole air was sampled, dried and pumped at Niwot Ridge, Colorado, into a new, nominal 30 L, aluminum cylinder that had been treated with the Aculife IV™ process (Air Liquide America Gases, Plumsteadville, Pennsylvania, US) to passivate the cylinder walls. Previous unpublished data has shown that many halocarbons are unstable in untreated aluminum cylinders. Some data demonstrating two years storage of several halogenated trace gases in nitrogen contained in Aculife IV™ treated aluminum cylinders have been reported (Miller and Rhoderick, 1995). The mole fraction of CFC-12, CFC-11 and CFC-113 in that stability study were at slightly higher pmol/mol (ppt) levels (9 to 35%) than the levels in this current sample. Although data have not been published, the National Institute of Standards and Technology (NIST) have observed stability for these three species, in a dry air matrix, for 15 years in similarly-treated cylinder types. (The samples must be dried as moisture will destroy the treatment). The cylinder was pressurized to nominal 12.5 Mpa. The Niwot Ridge facility is used by NOAA to prepare cylinder mixtures of dried whole air for various uses, including supplying mixtures for calibration of greenhouse and related trace gas measurements for laboratories which do not prepare their own primary standards.

2.2 Stability study of the comparison sample

NIST analyzed the comparison sample two times to determine its stability over the comparison time scale. Initially, NOAA analyzed 3 of the halocarbons followed by an analysis of all 6, and then a final analysis after each participant had analyzed the sample. These multiple analyses were used to demonstrate stability of the halocarbons in the mixture over the time period of this comparison. The mole fractions and expanded uncertainties (U) for those analyses are given in Table 1. Expanded uncertainties are calculated using the equation:

$$U = k u_c \quad (1)$$

where u_c is the uncertainty of known measurement results including those in the calibration standards and k is the coverage factor. The data in this study are reported using $k=2$ which implies a level of confidence of approximately 95% (http://physics.nist.gov/cuu/Uncertainty/coverage.html). The stability data are also displayed graphically in Figure S1. CFC-12,

CFC-11, and HCFC-22 stability data statistically indicate that there has been no drift over time for each laboratory's individual set of data points, as all error bars overlap. While the NIST and NOAA data for CFC-113 indicate a small bias in reported values, the individual sets of data show stability, as all error bars overlap for each data set. NOAA reported values were determined using gas chromatography with either electron capture detection (GC-ECD) and or coupled to a mass spectrometer (GC-MS) showing a slight bias between the two instrumental methods. However, each data set for the two methods indicates stability. Of note is that the NOAA uncertainties shown in Table 1, k=2, are only based on their measurement precision and not measurement reproducibility, which would be a more appropriate uncertainty for detecting drift based on few samples. However, each limited data set by itself appears to indicate no drift of the halocarbons in the comparison sample. (Throughout the text k=2 represents the approximate 95% uncertainty confidence interval.)

The NIST $k=2$ error bars for the two HFC-134a stability values overlap which indicates that the HFC-134a has remained stable. Even though the uncertainties overlap the difference between the two NIST data points is 2.3 pmol/mol. This suggests the HFC-134a has increased in the cylinder which is not a likely scenario based on past experience with similar mixtures at low nmol mol^{-1} levels. However, both NOAA data points and the second NIST value agree within the $k=2$ error bars, thus suggesting stability. An explanation for the larger difference between the 1st and 2nd NIST data points is most likely related to instrumental issues. The 1st NIST data point was determined using GC-FID-preconcentration of the sample. The HCF-134a eluted on the tail of a rather large unknown peak in the chromatogram making the peak area determination difficult. The 2nd NIST measurement was taken using a GC-MSD system which was not available for the 1st analysis. While the standard uncertainty, 1.8 pmol/mol, is much larger for the measurement by GC-MSD, the column used for this measurement yielded better separation of HFC-134a from the other halocarbons, so the 2nd NIST stability data point is most likely a more accurate representation of the mole fraction of the HFC-134a in the comparison sample.

The HCFC-142b stability data show results very similar to HFC-134a in that the 1st NIST data point was determined using GC with a flame-ionization detector (GC-FID) and preconcentration, and the 2nd data point using GC-MSD. In both cases the HCFC-142b peak was baseline-to-baseline separated with no interferences. Even though the 2nd NIST data point is 0.7 pmol/mol (3.2% relative) higher than the 1st, it is not a likely scenario that HCFC-142b is increasing. Peaks for the first NIST data points for both the HFC-134a and HCFC-142b were very small, making peak area determinations relatively imprecise compared to other gases. The two NOAA data points are in agreement, suggesting stability.

2.3 Comparison of dry whole air sample

Participating laboratories in this comparison, listed in Table 2, analyzed the dry, whole air sample contained in aluminum cylinder AAL073358, in between stability measurements by NIST and NOAA. A time table for the comparison is shown in Table S1. Each laboratory was allowed appropriate time as needed for measurements and shipping of the cylinder to the next participant. Each laboratory was requested to provide their value determination and uncertainty for each halocarbon as a mole fraction from at least 3 individual determinations.

An uncertainty budget, description of their analysis procedure, and their calibration methods were also requested. These individual measurement reports can be found in the Supplemental Materials: Text S1, Text S2, Text S3, Text S4, and Text S5. We note here that the pressure in sample cylinder AAL073358 after all laboratories analysis and all stability measurements were completed was ≈ 4.8 Mpa (700 psi).

Instrumentation and methods development for the measurement of halocarbons has been previously documented (Montzka et al., 1993; Simmonds et al., 1995; Miller et al., 2008). Methods used for this comparison were solely at the laboratories discretion, and reflect their normal measurement procedures as listed in Table 3.

3. Results

A small group of participants were selected for this initial "pilot" study coordinated by NIST in order to keep it manageable as only one sample was being circulated. Two NMIs, the Korea Research Institute of Standards and Science (KRISS) and NIST, and three atmospheric research laboratories, NOAA, Scripps Institution of Oceanography (SIO), and the Swiss Federal Laboratories for Materials Science and Technology (Empa), participated in this halocarbons comparison. Each participant develops and perpetuates their own calibration scales with the exception of Empa, as they use the SIO scales used by AGAGE and other projects for the species under discussion. Since the comparison was to be used to determine the agreement between different scales, the Empa data were not used in determining a comparison 'halocarbon (x) reference value (RV)' (x_{RV}). However, their data are extremely useful since they are using the SIO scales and those results should be comparable within scale propagation uncertainties. Additionally SIO and Empa use the same type of instrument for analysis, the GC/MS Medusa system (Miller et al., 2008). Therefore, any differences in reported values between these two laboratories may be due to factors such as introduction of the sample into the instrument or other artifacts.

3.1 Data comparison among participants maintaining own standards/scale (KRISS, NIST, NOAA, SIO)

All measurement data were reported to NIST with the reported value (x_i) and expanded uncertainty (U_{xi}) (approximate 95% confidence interval) in pmol/mol given in Table 4. A standard uncertainty (u_{xi}) of a reported value was calculated by each laboratory for a reported value. The u_{xi} includes the precision (measurement) uncertainties (p_{xi}) and accuracy (standards or calibration scale) uncertainties (a_{xi}) and is calculated using equation 2:

$$u_{xi} = \mathrm{sqrt}(p_{xi}^2 + a_{xi}^2) \quad (2)$$

The expanded uncertainty, U_{xi}, is then calculated using equation 3:

$$U_{xi} = k * u_{xi} \quad (3)$$

where the coverage factor (k) equals 2 for an approximate 95% confidence interval. The reference values (x_{RV}) for the comparison were calculated from the values reported by the

participants, excluding Empa, for each halocarbon. The x_{RV} were calculated using the DerSimonian-Laird random effects model, a simple and well-established non-iterative weighted-mean estimator that includes a between-participant variance component as well as the participant-reported uncertainties in the weights (DerSimonian and Laird, 1986). Figures 1–6 display the results of the DerSimonian-Laird model for each halocarbon excluding the Empa data. (Empa data will be compared to the SIO results later). The open circles represent the reported x_i for each participant and the vertical bars span the $k = 2$ expanded uncertainty interval, $x_i \pm U_{xi}$, reported by the participants. The horizontal black line represents the x_{RV} with the red lines representing the $k = 2$ expanded uncertainty interval of the x_{RV}, $x_{RV} \pm U(x_{RV})$. Also given in Table 4 is the difference (d_i) between the RV and the participant's value, and % relative difference between the participants reported value and the x_{RV} for each of the six halocarbons, except for Empa. The $U(x_{RV})$ are listed as both absolute pmol/mol and percent relative, $100*U(x_{RV})/x_{RV}$.

Uncertainties assigned to the halocarbon values are on the same order of magnitude for all participants with a few exceptions. Those reported by KRISS for HFC-134a, HCFC-22 and HCFC-142b are larger relative to NIST, NOAA and SIO. KRISS used a preconcentrator (Gerstel Co.) coupled to an Agilent Gas Chromatograph (7890A) equipped with an Agilent mass spectrometer (5975C) for their analyses. The large analytical uncertainties are a result mainly because of a non-uniform recovery rate of cryogenic adsorption and desorption at the preconcentrator. NIST assigned a lower uncertainty for CFC-11 and CFC-113 relative to NOAA, KRISS and SIO. The NIST method used (multi-step dilutions) resulted in a low uncertainty for the NIST gravimetric standards. Additionally, the analytical uncertainty was lower compared to the other halocarbons resulting in a lower expanded uncertainty ($k = 2$). The uncertainty for CFC-12 reported by SIO is noticeably larger relative to those reported by the other participants.

Dichlorodifluoromethane (CFC-12)—The DerSimonian-Laird model statistics results for the CFC-12 are illustrated in Figure 1. All participants reported uncertainty bars intercept the x_{RV} line (solid black) demonstrating good agreement with the x_{RV}. The SIO value is slightly outside the upper uncertainty limit of the x_{RV} (red line), however their uncertainty covers the upper and lower uncertainty bands. All participant d_i are 0.6% relative to the x_{RV} as shown in Table 4, accentuating the good agreement for CFC-12.

Trichlorofluoromethane (CFC-11)—Figure 2 shows the DerSimonian-Laird results for CFC-11. The reported values for SIO, NIST and NOAA all lie within the uncertainty bands of the x_{RV}. The KRISS value lies outside the lower x_{RV} uncertainty, but their uncertainty bands intercept the x_{RV} line indicating agreement. As with the CFC-12, all participant d_i are 0.6% relative to the x_{RV} as shown in Table 4, demonstrating the good agreement for CFC-11.

1,1,2-Trichlorotrifluoroethane (CFC-113)—The CFC-113 DerSimonian-Laird results are depicted in Figure 3 and appear to show the largest variations for any of the halocarbons in this comparison. KRISS, SIO, and NOAA data points all are within the x_{RV} uncertainty bands. All three of these participants' uncertainty bands for these points intersect the x_{RV} line

indicating agreement. The NIST value, with very small uncertainty, is the only one in question as it is not within the x_{RV} uncertainty estimates. Since the NIST CFC-113 value is significantly different it is probably biasing the *RV*. If we exclude the NIST value from the calculations, as shown in Figure S2 (NIST value in red not included in *RV* calculation), then the *RV* = (75.17 ± 0.65) pmol/mol (0.86% relative) compared to an *RV* of (75.9 ± 1.3) pmol/mol (1.7% relative) when including all 4 participants.

NIST used their CFC-113 2004 standards, prepared for the International Halocarbons in Air Comparison Experiment (IHALACE) (Hall et al., 2014), which will be discussed later, and newly prepared 2011 standards for this comparison. The 2004 and 2011 standards showed consistency predicting the CFC-113 in the comparison sample to within 0.1% using both suites. While the reported NIST uncertainty is small, all known sources of uncertainty were included in their calculations. Since NIST is predicting the CFC-113 high, it is possible that there is consistent loss in the aluminum cylinders containing the standards. However, this has not been observed by NIST in the past. It is more plausible that the analytical method is not optimized and there may be a small contribution from another component, CH_3Cl, in the sample. All participant d_i are < 2.3% relative to the x_{RV} as shown in Table 4.

1,1,1,2-Tetrafluoroethane (HFC-134a)—Results for the HFC-134a data are shown in Figure 4. The NIST (low) and KRISS (high) values both lie outside the x_{RV} uncertainty; however their uncertainties overlap the x_{RV} uncertainty bands. The low NIST value is attributed to analytical issues, in particular the sensitivity and repeatability. SIO and NOAA data points intersect the x_{RV} line with the d_i < 1.0% relative to the x_{RV} as shown in Table 4. The d_i for NIST is 2.5% and 6.0% for KRISS.

Chlorodifluoromethane (HCFC-22)—The results for HCFC-22 are in agreement as shown in Figure 5. All participants' data points and uncertainties are on or within the x_{RV} uncertainty bands. All participant d_i are   0.9% relative to the x_{RV} as shown in Table 4.

1-Chloro-1,1-difluoroethane (HCFC-142b)—The results for HCFC-142b are very similar to the HCFC-22, but with larger differences from the x_{RV}. Agreement to the x_{RV} is observed as shown in Figure 6. All participants' data points and uncertainties are on or within the x_{RV} uncertainty bands. All participant d_i are < 1.8% relative to the x_{RV} as shown in Table 4.

3.2 Comparison of Empa data to SIO scale

In the case of the Empa data in Table 4, the difference is calculated versus the SIO value: $x_{Empa} - x_{SIO}$. Since Empa uses the SIO scale (used by AGAGE and other projects for the halocarbons discussed here) their uncertainties propagate from those of the SIO scale and their own measurement uncertainties. Empa is not responsible for primary calibrations as they come from SIO via a tertiary calibration standard. Therefore, the Empa U_{xi} is computed using equation 4:

$$U_{xi} = \mathrm{sqrt}(P_{xi}^2 + P'^2_{xi} + Q_{xi}^2) \quad (4)$$

where P_{xi} is precision of the SIO calibration of the comparison tank, P'_{xi} is the precision of the SIO calibration of the tertiary standard used by Empa and Q_{xi} is the Empa measurement precision; all expanded (95% approximate confidence interval).

Empa and SIO both use a GC/MS Medusa system for analyses. Therefore we discuss and compare here the results between SIO and Empa separately from the results discussed earlier and shown in Figures 1–6, where uncertainties for each participant maintaining their own standards and scales are based on comparable uncertainty considerations. Figure 7 compares the Empa result to SIO for each halocarbon as taken from the data in Table 4. The solid horizontal black line represents the SIO value (SIO scale) with the associated expanded uncertainties as the red lines. For comparison, the solid blue line is the x_{RV} value and the dashed blue lines represent the expanded uncertainty, $U(x_{RV})$, from Table 4. The open black circles represent the reported values for SIO and Empa with the vertical black lines being the expanded uncertainty of the reported value. In each case the Empa value lies within the expanded uncertainty of the SIO value. Empa values agree within < 1.2% for all six halocarbons illustrating consistency.

3.3 Comparison to previous studies

A bilateral comparison between NOAA and NIST, that included CFC-12 and CFC-11 (Rhoderick and Dorko, 2004), and the IHALACE comparison exercise (Hall et al., 2014), can be used to compare to the results of this study for the common participants. Since all participants' data for the IHALACE were compared to the NOAA value, the same will be done for the 2004 and current studies. The differences in values of participants to NOAA for each of these comparisons are listed in Table 5. The % relative uncertainties for the reported values in those comparisons are also given in parenthesis; the first uncertainty being that of NIST, SIO, Empa or KRISS, followed by the uncertainty for the NOAA value in each case. Differences in bold indicate that the uncertainty bounds of the submitted values do not cover the % difference of the reported values and may be significant. Additionally, inter-calibration factors to the NOAA values for each of the comparisons are given in Table S2.

In general, NIST-NOAA differences show consistent results for CFC-12 and CFC-11 compared between the agencies over a 15 yr. time period from the 2004 comparison to this work. (Measurements were actually taken during 1998–1999 followed by publication in 2004). The -1.5% difference for the CFC-12 in the IHALACE study is only slightly significant as the uncertainty bounds are minimally smaller and do not cover the difference. However, the uncertainties given for the IHALACE study are the standard deviation (sd) of the measurements. If we expanded those uncertainties as an approximate 95% confidence interval, as so done in Table 5, then they do cover the -1.5% difference. Considering both the NIST and NOAA uncertainty bounds for the CFC-11, they overlap, therefore the -0.9% difference is not significant. Considering all three studies, the average differences for CFC-12 are -0.7% and 0.4% for CFC-11, while there is a larger difference for CFC-113 (average 2.5%) but consistent. The 3.8% difference for the CFC-113 in the IHALACE study is significant as the uncertainty bounds (sd) do not cover the difference. This present study was the first between NIST-NOAA for the HCFCs and HFC-134a, resulting in differences for HCFC-22 (-1.4%), HFC-134a (-2.9%), and HCFC-142b (-1.8%). An interesting

observation is that NIST predicts lower values than NOAA for all but one of the halocarbons. Based on the associated % relative uncertainties of the reported values, there is no significant difference in the reported values.

Differences between SIO-NOAA are very consistent between the IHALACE and this comparison, with differences < 0.5% for CFC-12, CFC-11, and HCFC-22. A difference of -0.4% for the CFC-113 in the IHALACE study is consistent with the results of this comparison, considering all MS data. The differences for HFC-134a are slightly higher but still under 1.5% even though the IHALACE result is (0.8%) of opposite sign compared to the present study (-0.6%). Something to consider is that the atmospheric abundance of the HFC-134a had increased the most since the IHALACE study. Differences between SIO-NOAA are higher on average for HCFC-142b at 2.8%. The 3.7% difference for the IHALACE is significant if just considering the uncertainties given (sd) but expanding those uncertainties to 95% would result in no significant difference. These results are also consistent with SIO-NOAA differences in reported global surface mean mixing ratios in the 2011 WMO Ozone Assessment Report (Montzka et al., 2011). It is likely that the differences mentioned here also propagate to those global means, thereby reinforcing the point that calibration differences are a large part of the uncertainty related to measurements of these important trace gases as opposed to instrumental influences or sampling network differences.

Differences between Empa-NOAA for all comparisons are consistent for CFC-12 (0.1% on average), CFC-11 (-0.7%), HCFC-22 (-0.6%) and HCFC-142b (2.6%). The agreement for CFC-113 is slightly better for this study (-1.5%) compared to the IHALACE result (-2.3%). The CFC-113 difference in the IHALACE study is significant as the sd reported, even if expanded, do not cover the difference. The 3.3% difference for the HCFC-142b IHALACE comparison is significant if just considering the uncertainties from that study (sd) but expanding those uncertainties to 95%, as shown in Table 5, would result in no significant difference. Additionally, the agreement between Empa and SIO is consistently within 0.9% for all halocarbons except CFC-113 which shows a difference of 1.2%–1.8%. Those results should be expected since the Empa measurements are closely linked to the SIO scale and both use the Medusa GC/MS systems.

This study represents the first comparison that KRISS has participated in involving the measurement of halocarbons in a whole air sample. The differences are within 1.5% of the NOAA values for all halocarbons except HFC-134a (5.5%) that is relatively high compared to the other participants. NIST and KRISS, the two NMI participants, were in agreement to 0.7% for CFC-12, CFC-11, HCFC-22 and HCFC-142b, but had larger disagreements for CFC-113 (3.3%) and HFC-134a (8.7%). The NIST-NOAA agreement (-2.9%) is closer with the other participant-NOAA differences for HFC-134a, while the KRISS-NOAA difference is much larger at 5.5%. KRISS-NOAA agreement (-0.3%) is in line with SIO-NOAA (-0.3%) and Empa-NOAA (-1.5%) for CFC-113, while the NIST-NOAA agreement is much larger at 3.0%.

4. Discussion

This halocarbon comparison study has served to bring together two communities involved in supporting a broader group of scientist needing standards for measurements of atmospheric halocarbons. Each of the two communities has a different need and approach. The atmospheric community needs a stable scale based on precise measurements and continuity in order to establish trends of these gases in the atmosphere, and to relate many independent measurement sets. The NMIs need to establish degrees of equivalence between those NMIs in order to make CMC claims to support a global commerce where any NMIs standards may be used by others universally. As a requirement, accuracy is of the highest importance, as are the associated uncertainties in those standards. This study serves only as a measure of how well those two communities standards and scales for trace level halocarbons agree, and not as to what is necessarily the truth.

The atmospheric community has much more experience in actual measurements of whole air samples, and has refined their analytical instrumentation and methods. The NMIs have many years of experience developing and analyzing standards, in "clean synthetic air", of some of these halocarbons at trace levels, but not the level of experience measuring whole air samples. Whole air samples are much more complex than synthetic air in that they include a matrix of many compounds including permanent gases, hydrocarbons, halocarbons, volatile organic compounds and unknowns. This makes for a very complex chromatographic/mass spectral analysis where it can and is difficult to separate many components. Considering these factors, the results of this pilot study/comparison indicate rather good agreement between the participants. All reported participants values or associated uncertainties, $k=2$, lie within or at least intercept the DerSimonian-Laird $x_{RV}k=2$ uncertainty limits for 97% of the data. All participant differences from the x_{RV} are within 2.5% except one and 66% are within 1.0%. This demonstrates that the different methods and techniques used to prepare standards/scales, and the measurement systems and techniques used to assign mole fractions to halocarbons in a dry whole air sample are consistent within the uncertainties reported. The only participant that does not make their own standards for the discussed species is Empa; it uses the SIO scales. Their values are in agreement within the uncertainties of the SIO data demonstrating that the analytical systems are in good control. The Empa uncertainties are large for all the halocarbons making it difficult to draw any conclusions on scale transfer.

While most of the differences are not significant based on the k=2 uncertainties, changes are probably significant from study to study for some. For example, the NOAA CFC-12 scale is stable to about 0.3% over time, so even though the overall uncertainty is 0.7%, they expect to be able to reproduce results on a given scale to ∼1.8 ppt (0.3%), (95% confidence interval). On this basis, the NIST-NOAA differences that move from -0.4% to -1.5% to -0.2% could be significant, depending on stability of the NIST scale. So, to compare results from one study to the next, one would have to assume that there have been no scale changes (or all are consistent) and also know the long-term reproducibilities. This is a topic which is better addressed in separate paper closely assessing these long-term reproducibilities.

NIST has prepared and analyzed standards for all of the halocarbons studied here for more than 30 years but at nmol/mol (ppb) to μmol/mol (ppm) levels. NIST has experience preparing and analyzing standards for CFC-12 and CFC-11 at atmospheric levels, but not for HFC-134a, HCFC-22 and HCFC-142b. Some of the differences for NIST and KRISS are most probably due to lack of experience in analyzing halocarbons at the very low pmol/mol (ppt) levels. Continued efforts should assist in honing those capabilities resulting in improved agreement. Anticipated future comparisons coordinated by NIST will reach out to other willing participants.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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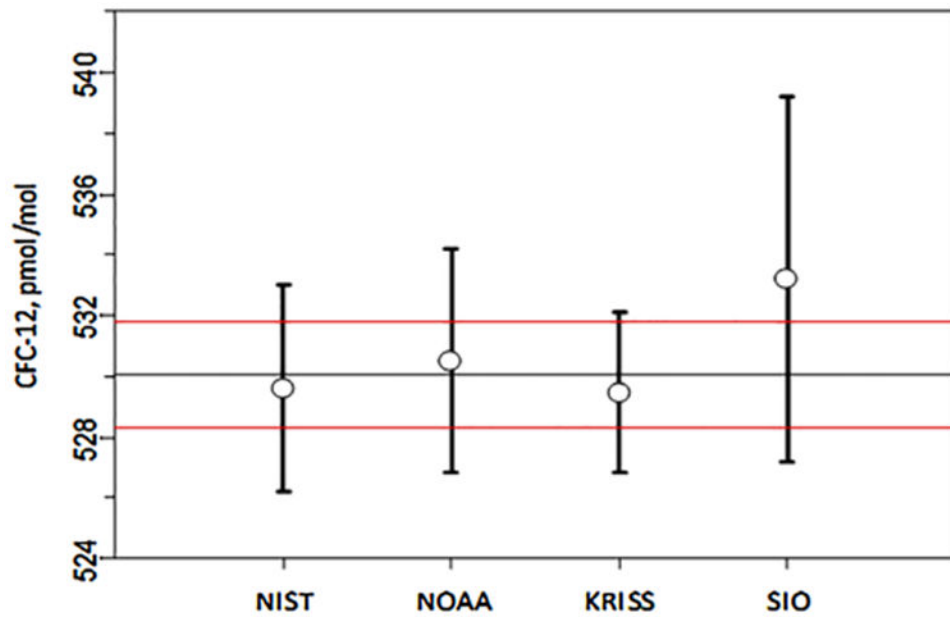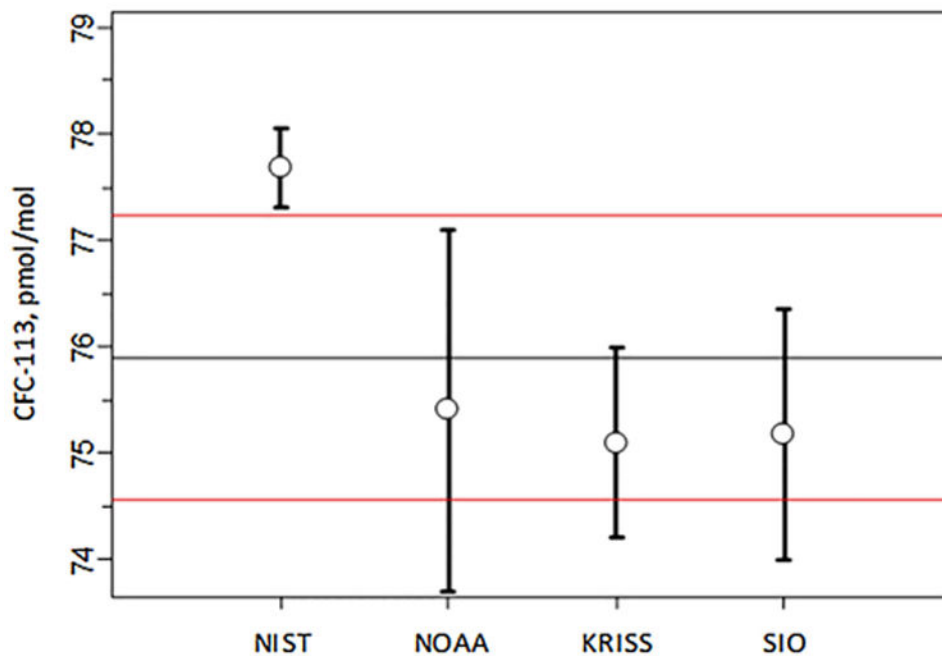
Figure 1. Results for dichlorodifluoro-methane (CFC-12)
CFC-12 laboratory reported values in relationship to the DerSimonian-Laird reference value
(RV) represented by the solid black line. The error bar represents the expanded uncertainty,
k=2, reported by participants.
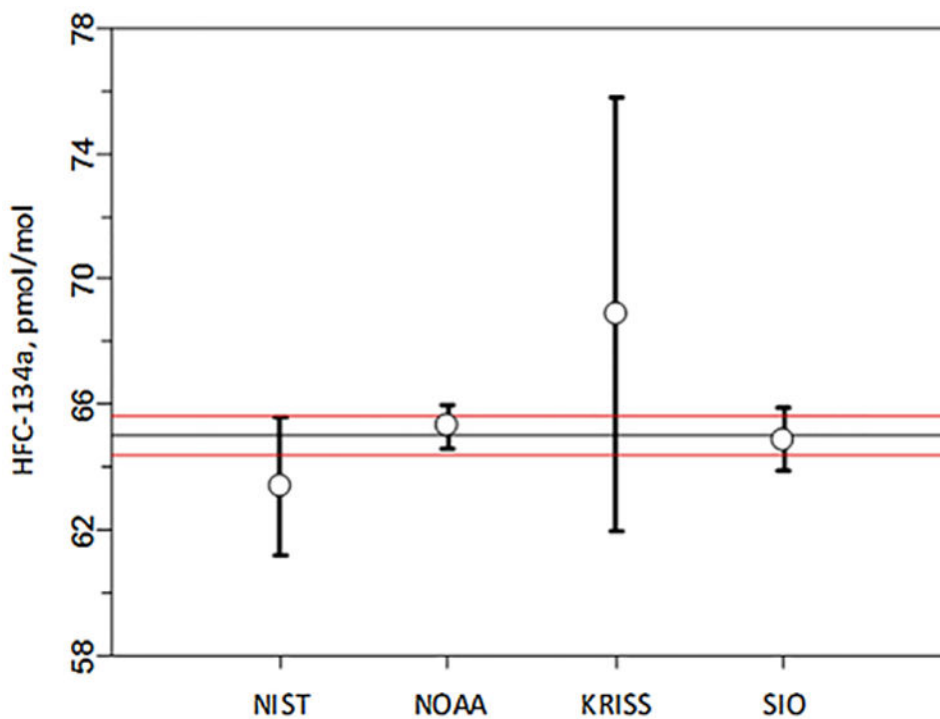doi: 10.12952/journal.elementa.000075.f001
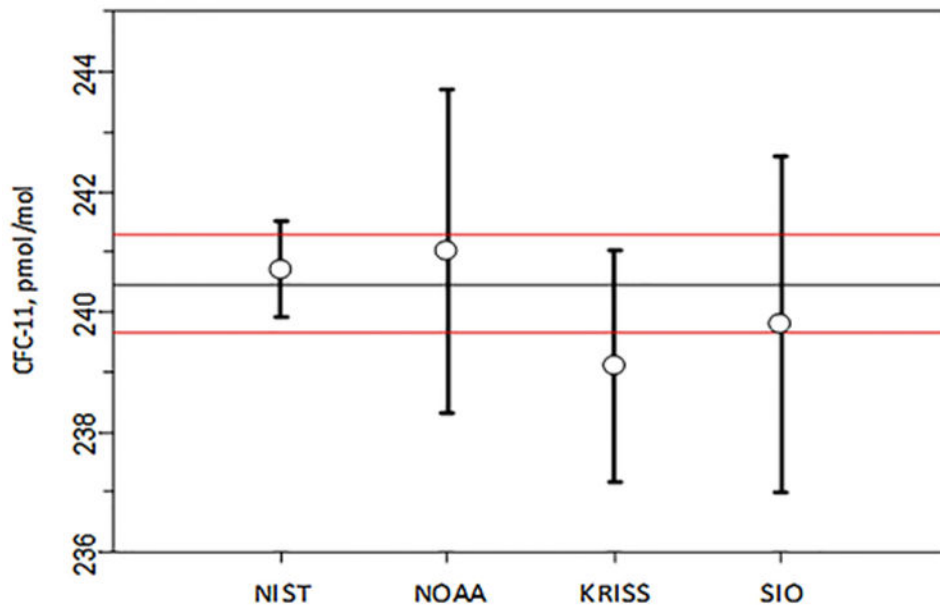
Figure 2. Results for trichlorofluoro-methane (CFC-11)
CFC-11 laboratory reported values in relationship to the DerSimonian-Laird reference value
(RV) represented by the solid black line. The error bar represents the expanded uncertainty,
k=2, reported by participants.
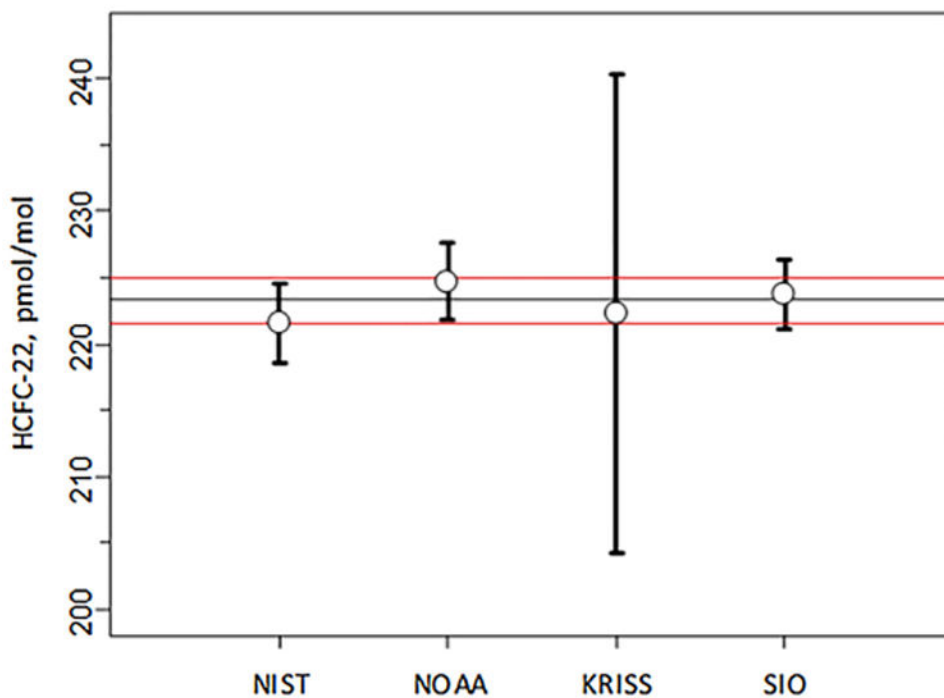doi: 10.12952/journal.elementa.000075.f002

Figure 3. Results for 1,1,2-Trichlorotrifluo-roethane (CFC-113)
CFC-113 laboratory reported values in relationship to the DerSimonian-Laird reference value (RV) represented by the solid black line. The error bar represents the expanded uncertainty, *k=2*, reported by participants.
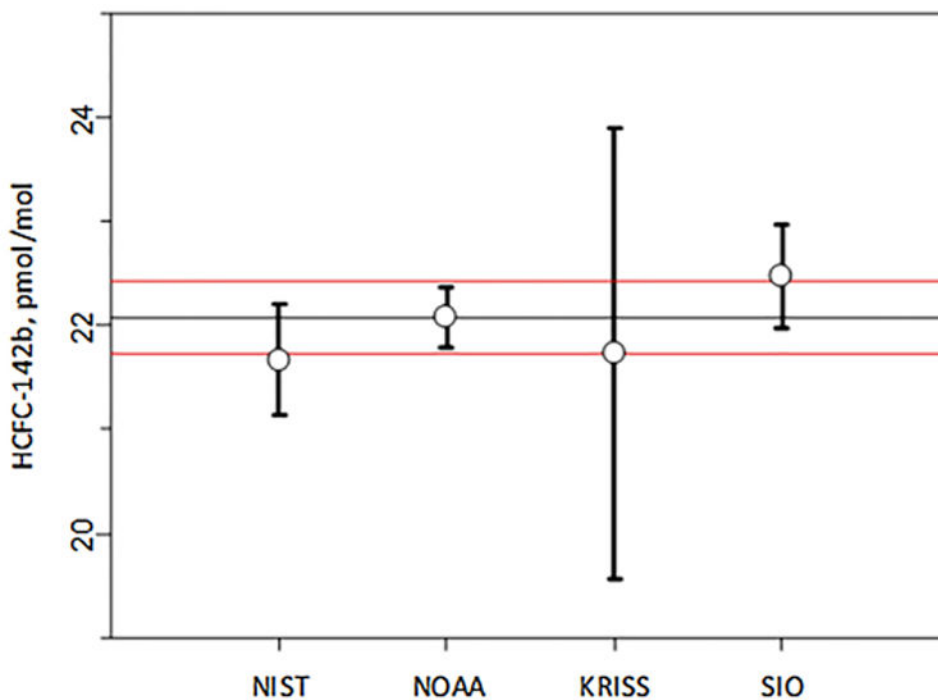doi: 10.12952/journal.elementa.000075.f003

Figure 4. Results for 1,1,1,2-tetrafluoro-ethane (HFC-134a)
HFC-134a laboratory reported values in relationship to the DerSimonian-Laird reference value (RV) represented by the solid black line. The error bar represents the expanded uncertainty, *k=2*, reported by participants.
doi: 10.12952/journal.elementa.000075.f004

Figure 5. Results for chlorodifluoro-methane (HCFC-22)
HCFC-22 laboratory reported values in relationship to the DerSimonian-Laird reference value (RV) represented by the solid black line. The error bar represents the expanded uncertainty, *k*=2, reported by participants.
doi: 10.12952/journal.elementa.000075.f005

Figure 6. Results for 1-chloro-1,1-difluoro ethane (HCFC-142b)
HCFC-142b laboratory reported values in relationship to the DerSimonian-Laird reference value (RV) represented by the solid black line. The error bar represents the expanded uncertainty, *k*=2, reported by participants.
doi: 10.12952/journal.elementa.000075.f006
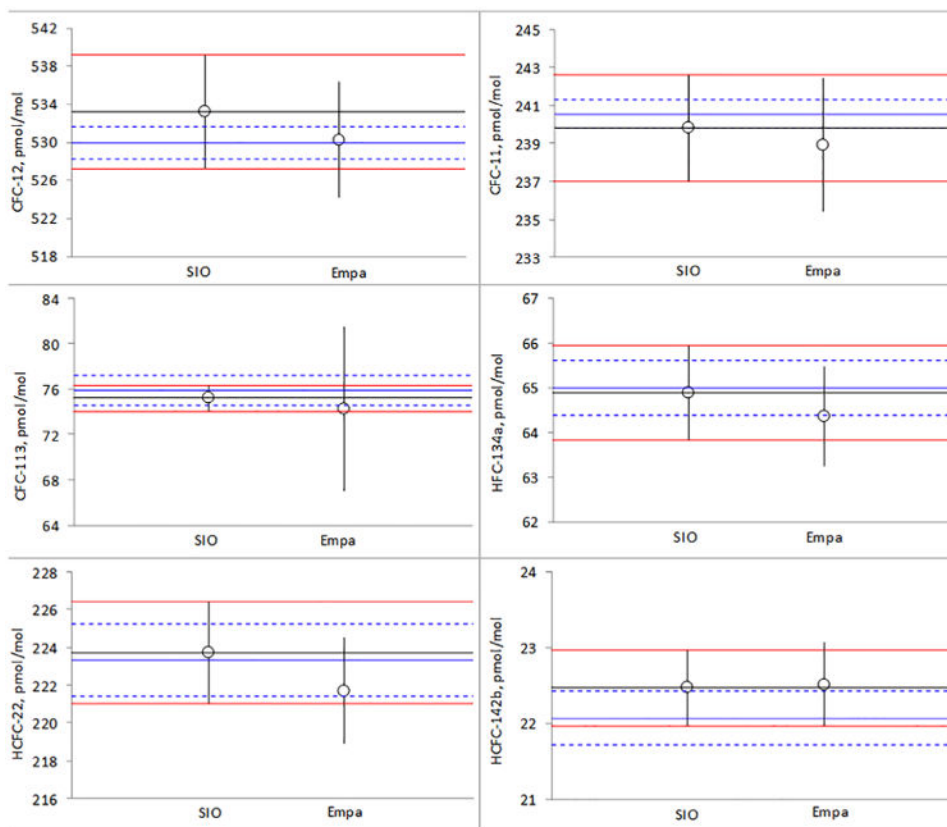
Figure 7. Comparison of Empa reported mole fractions and uncertainties to the SIO scale result
SIO scale result (solid black line) with *k =2* expanded uncertainty (red lines). Vertical black error bars represents the expanded uncertainty, *k = 2*, reported by participants. The solid blue line is the x_{RV} value and the dashed blue lines represent the expanded uncertainty, U(x_{RV}). doi: 10.12952/journal.elementa.000075.f007

Table 1

NIST and NOAA stability data for comparison mixture AAL073358

| Halocarbon | NOAA | | | | NIST | | | | NOAA | |
| | October 2010 | | January 2011 | | February 2012[a] | | December 2012[b] | | February 2013 | |
	pmol/mol	U^c	pmol/mol	U^c	pmol/mol	U^c	pmol/mol	U^c	pmol/mol	U^c
Dichlorodifluoromethane (CFC-12)	530.5[d]	1.6	530.5[d]	1.6	529.6	3.4	530.0	4.4	529.9[d]	1.0
Trichlorofluoromethane (CFC-11)	241.0[d]	1.6	241.0[d]	1.4	240.7	0.8	240.6	2.4	241.7[d]	1.6
1,1,2-Trichlorotrifluoroethane (CFC-113)	76.6[d]	0.4	76.6[d], 75.30[e]	0.2, 0.21	77.68	0.38	77.4	1.6	76.3[d], 74.99[e]	0.4, 0.14
1,1,1,2-Tetrafluoroethane (HFC-134a)			65.3[e]	0.4	63.4	2.2	65.7	3.6	65.0[e]	0.4
Chlorodifluoromethane (HCFC-22)			224.7[e]	0.4	221.5	3.0	221.9	3.0	223.4[e]	0.3
1-Chloro-1,1-Difluoroethane (HCFC-142b)			22.07[e]	0.10	21.67	0.54	22.37	1.00	21.99[e]	0.12

[a] Measurement for CFC-12, CFC-11 and CFC-113 made using GC-ECD. Measurement for HFC-134a, HCFC-22 and HCFC-142b made using GC-FID-preconcentration of sample.

[b] Measurement for CFC-12 and CFC-11 made using GC-ECD. Measurement for CFC-113, HFC-134a, HCFC-22 and HCFC-142b made using GC-MSD-preconcentration of sample.

[c] Uncertainty, U, is $k = 2$ (approximate 95% confidence interval).

[d] NOAA value was determined by GC-ECD.

[e] NOAA value was determined by GC- MS.

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Table 2

Participating laboratories

Acronym	Country	Institute
NIST (NMI)	US	National Institute of Standards and Technology, Materials Measurement Laboratory, Chemical Sciences Division, Gas Metrology Group Gaithersburg, MD, United States
NOAA	US	National Oceanographic and Atmospheric Administration, Earth System Research Laboratory (ESRL), Global Monitoring Division (GMD), Boulder, CO, United States
KRISS (NMI)	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
SIO	US	Scripps Institution of Oceanography, La Jolla, CA, United States
Empa	CH	Swiss Federal Laboratories for Materials Science and Technology, Dubendorf, Switzerland

Table 3

Measurement and calibration methods used by participating laboratories

Laboratory	Measurement method[a]	Calibration method	Traceability
NIST	GC-ECD, GC-MS, GC-FID	GLS, 2nd order polynomial, linear, or bracketing	Own gravimetric standards
NOAA	GC-ECD, GC-MSD	2nd order polynomial or linear	Own gravimetric standards
KRISS	GC-ECD, GC-MSD	One point calibration	Own gravimetric standards
SIO	GC-ECD (GC-MD)[b], GC-MSD (Medusa)	Primary calibration in sensitivity space	Own gravimetric standards ("bootstrap" method ratioed to CO_2 and N_2O)
Empa	Medusa-GC-MS technology (Empa-medusa or Medusa-20)	Bracketing	Whole air linked to SIO/AGAGE R1 scale

[a]Details about which measurement methods were used for specific halocarbons can be found in the individual Measurement Reports under Supplemental Materials: Text S1, Text S2, Text S3, Text S4, Text S5.

[b]This is a multi-detector GC containing 2 ECDs and one FID.

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Table 4

Differences between DerSimonian-Laird statistical determined reference values (x_{RV}) and participant's values for halocarbons in comparison mixture

	DerSimonian-Laird Estimates		Participants Reported Values, Uncertainty, and Difference (d_i) from the Reference Value (RV) in pmol/mol[a]				
	x_{RV}	$U(x_{RV})^b$	NIST	NOAA	KRISS	SIO	Empa
Halocarbon	**pmol/mol**	**pmol/mol Relative**	$x_i U(x_i)^b d_i^c$	$x_i U(x_i)^b d_i^c$	$x_i U(x_i)^b d_i^c$	$x_i U(x_i)^b d_i^c$	$x_i U(x_i)^f x_{Empa}−x_{SIO}^g$
CFC-12	530.0	1.7 (0.32%)	529.6 3.4 **-0.4** (0.1%)	530.5^d 3.7 **0.5** (0.1%)	529.44 2.64 **-0.6** (0.1%)	533.2 6.0 **3.2** (0.6%)	530.25 6.04 **-2.95** (0.5%)
CFC-11	240.5	0.8 (0.33%)	240.7 0.8 **0.2** (0.1%)	241.0^d 2.7 **0.5** (0.2%)	239.09 1.91 **-1.4** (0.6%)	239.8 2.8 **-0.7** (0.3%)	238.93 3.5 **-0.87** (0.4%)
CFC-113	75.9	1.3 (1.7%)	77.68 0.38 **1.8** (2.3%)	75.4^e 1.7 **-0.5** (0.7%)	75.1 0.9 **-0.8** (1.1%)	75.17 1.18 **-0.7** (1.0%)	74.24 7.2 **-0.93** (1.2%)
HFC-134a	65.0	0.61 (1.0%)	63.4 2.2 **-1.6** (2.5%)	65.3^e 0.7 **0.3** (0.5%)	68.9 6.9 **3.9** (6.0%)	64.88 1.06 **-0.1** (0.2%)	64.37 1.11 **-0.51** (0.8%)
HCFC-22	223.3	1.9 (0.85%)	221.5 3.0 **-1.8** (0.8%)	224.7^e 2.9 **1.4** (0.6%)	222.29 18 **-1.0** (0.4%)	223.7 2.7 **0.4** (0.21%)	221.7 2.8 **-2.0** (0.9%)
HCFC-142b	22.07	0.35 (1.6%)	21.67 0.54 **-0.40** (1.8%)	22.07^e 0.29 **0.00** (0.0%)	21.73 2.17 **-0.34** (1.5%)	22.47 0.50 **0.40** (1.8%)	22.51 0.55 **0.04** (0.2%)

[a] The d_i is followed by the percent d_i relative to the reference value in parenthesis.

[b] k = 2 expanded uncertainty; approximate 95% confidence interval.

[c] The difference, d_i, is calculated from $x_i − x_{RV}$, given in pmol/mol and bold. The percent difference relative to the reference value follows in parenthesis.

[d] Determined by GC-ECD.

[e] Determined by GC-MS.

[f] The Empa uncertainty does not include an uncertainty for the accuracy of calibration standard uncertainty k =2 expanded uncertainty (approximate 95% confidence interval). See Section 3.2 for explanation.

[g] Difference of Empa from AGAGE (SIO) scale.

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Table 5

Percent differences of NIST, SIO, Empa and KRISS relative to NOAA values in several comparisons, including the % relative uncertainty of the reported values in same order

Comparison	Differences from NOAA values[a]			
	NIST-NOAA	SIO-NOAA	Empa-NOAA	KRISS-NOAA
CFC-12 (2004)	-0.4% (± 1.1%; ± 0.3%)			
CFC-12 (IHALACE)[b]	**-1.5% (± 0.6%; ± 0.6%)[c]**	0.3% (± 0.2%; ± 0.6%)	0.2% (± 0.6%; ± 0.6%)	
CFC-12 (this work)	-0.2% (± 0.6%; ± 0.7%)	0.5% (± 1.2%; ± 0.7%)	0.0% (± 1.1%; ± 0.7%)	-0.2% (± 0.5%; ± 0.7%)
CFC-112004	-0.9% (± 0.7%; ± 0.7%)			
CFC-11 (IHALACE)[b]	-0.1% (± 0.8%; ± 0.3%)	-0.5% (± 0.1%; ± 0.3%)	-0.6% (± 0.2%; ± 0.4%)	
CFC-11 (this work)	-0.1% (± 0.3%; ± 1.1%)	-0.5% (± 1.2%; ± 1.1%)	-0.9% (± 1.5%; ± 1.1%)	-0.8% (± 0.8%; ± 1.1%)
CFC-113 (IHALACE)[b]	**3.8% (± 1.0%; ± 0.8%)[c]**	-0.4% (± 0.2%; ± 0.8%)	-2.3% (± 2.0%; ± 3.2%)	
CFC-113 (this work)	**3.0% (± 0.5%; ± 2.2%)[c]**	-0.3% (± 1.6%; ± 2.2%)	-1.5% (± 9.7%; ± 2.2%)	-0.3% (± 1.2%; ± 2.2%)
HFC-134a (IHALACE)[b]		0.8% (± 0.3%; ± 0.6%)	0.2% (± 0.1%; ± 0.6%)	
HFC-134a (this work)	-2.9% (± 3.5%; ± 1.1%)	-0.6% (± 1.6%; ± 1.1%)	-1.4% (± 1.7%; ± 1.1%)	-5.5% (± 10%; ± 1.1%)
HCFC-22 (IHALACE)[b]		-0.7% (± 0.3%; ± 0.4%)	0.0% (± 0.7%; ± 0.4%)	
HCFC-22 (this work)	-1.4% (± 1.4%; ± 1.3%)	-0.4% (± 1.2%; ± 1.3%)	-1.3% (± 1.3%; ± 1.3%)	-1.1% (± 8.1%; ± 1.3%)
HCFC-142b (IHALACE)[b]		**3.7% (± 2.0%; ± 3.4%)[c]**	**3.3% (± 2.2%; ± 3.4%)[c]**	
HCFC-142b (this work)	-1.8% (± 2.5%; ± 1.3%)	1.8% (± 2.2%; ± 1.3%)	2.0% (± 2.4%; ± 1.3%)	-1.5% (± 10%; ± 1.3%)

[a] First uncertainties in parentheses are either NIST, SIO, Empa or KRISS, followed by the second uncertainty for NOAA for the reported value in the comparison; expanded uncertainties at the approximate 95% confidence interval.

[b] The uncertainties reported in parenthesis for the IHALACE comparison (undiluted samples) are standard deviations and not expanded. In addition, the CFC-113 is a comparison of MS results from IHALACE.

[c] Differences in bold type indicate that the uncertainty bounds of the submitted values do not cover the % difference of the reported values and may be significant.

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