CCQM-P151 Final Report
Pilot Study CCQM P151
Halocarbons in Dry Whole Air

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Field

Amount of substance

Subject

Halocarbons in Dry Whole Air

Participants

KRISS, NIST, NOAA, SIO, Empa

Organizing body

CCQM-GAWG

INDEX

Abstract

The growing awareness of climate change/global warming and continuing concerns regarding stratospheric ozone depletion will require future measurements and standards for many compounds, in particular halocarbons that are linked to these issues. In order to track and control the emissions of these species globally in the atmosphere, it is necessary to demonstrate measurement equivalence at the highest levels of accuracy for assigned values of standards. This report describes the results of a pilot study between National Metrology Institutes and atmospheric research laboratories for several of the more important halocarbons at atmospheric concentration levels. The comparison includes 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 key comparison is to compare the measurement capabilities of the participants for these halocarbons at trace atmospheric levels.

1. Introduction

The growing concern of climate change/global warming and continuing concerns regarding stratospheric ozone depletion will require future measurements and standards for many compounds, in particular halocarbons that are linked to these issues. In order to track and the emissions of these species globally in the atmosphere and relate data from many laboratories, it is necessary to demonstrate measurement equivalence at the lowest levels of uncertainty. This becomes reliant on very reproducible measurements and precision for assigned values of these analytes in a whole air sample or real time measurement. These are of particular importance to the atmospheric monitoring and measurement communities such as the World Metrological Organization (WMO) and Advanced Global Atmospheric Gases Experiment (AGAGE), which NOAA, SIO and Empa participate. Their main objectives are to: 1) maintain adequate stability of their laboratories' internal calibration scales and thereby insure that the atmospheric records they produce are internally consistent in describing trends, and 2) maintain close links with other WMO and AGAGE laboratories so that atmospheric data may be reliably merged across multiple laboratories and methods.

National Metrology Institutes (NMIs), through the 1999 CIPM Mutual Recognition Agreement (MRA), have agreed to a establish a quality system, in which through a process of documentation, review, and assessment, each NMI needs to establish credentials related to their individual standard's needs.   Through this process they demonstrate equivalence among standards in order to support global commerce and point source emissions, and therefore are concerned about accuracy of standards. Degrees of equivalence are calculated for key comparisons in order to support NMI Calibration and Measurement Capabilities (CMCs). The CCQM defines that a KCRV can only be determined using data from CCQM member participants in a key comparison. Therefore a parallel CCQM-K83 comparison for halocarbons in real air was undertaken with CCQM-NMI members KRISS and NIST participating.

There have been very few opportunities between the two communities to compare standards and scales. This pilot study evaluates and compares the reported results of all the participants to CCQM-K83 key comparison reference value (KCRV).   This report describes the results of a pilot study for several of the more important halocarbons at atmospheric concentration levels to include: chlorofluorocarbon (CFC): dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and 1,1,2-trichlorotrifluoroethane (CFC-113), hydrochlorofluorocarbon (HCFC): chlorodifluoromethane (HCFC-22) and 1-chloro-1,1-difluoroethane (HCFC-142b), and hydrofluorocarbon (HFC): 1,1,1,2-tetrafluoroethane (HFC-134a) in a real, dry, air sample. Since the non-member participants NOAA, SIO and Empa have no requirements for CMCs, degrees of equivalence are not calculated for this pilot study. Rather, it is viewed as an assessment of the how each participant compares to each other.

2. Quantities and Units

In this protocol the measurands were the mole fraction of each of six halocarbons in dried whole air with measurement results expressed in pmol/mol.

3. Participants

A total of two CCQM member National Metrology Institutes (NMIs) and three non-member laboratories took part in this pilot study and are listed in Table 1.

Table 1. List of participating laboratories.

Acronym	Country	Institute
KRISS (CCQM)	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NIST (CCQM)	US	National Institute of Standards and Technology, Gaithersburg, MD, USA
NOAA	US	National Oceanographic and Atmospheric Administration, Boulder, CO United States of America
SIO	US	Scripps Institution of Oceanography, La Jolla, CA, USA
Empa	CH	Swiss Federal Laboratories Materials Science and Technology, Dubendorf, Switzerland

4. Schedule

The revised schedule for this pilot study was as follows:

November 2011	Preparation of mixture and analysis by NOAA
February 2011	Analysis of mixture by NIST
March 2011	Analysis of mixture by SIO
February 2012	Analysis of mixture by Empa
August 2012	Analysis of mixture by KRISS
October – November 2012	2nd Analysis of mixture by NIST
February 2013	2nd Analysis of mixture by NOAA
March 2013	Reports of the participants due
April 2013	Distribution of Draft A report

5. Measurement Sample

The single gas mixture circulated as the pilot study sample was prepared by the Global Monitoring Division, Earth Systems Research Laboratory, NOAA, in Boulder, Colorado, US. The cylinder mixture, AAL073358, was also the sample used in CCQM-K83. Whole air was sampled, dried and pumped at Niwot Ridge, Colorado, into a new, nominal 30 L, aluminum cylinder that had been treated with a process called Aculife (Air Liquide America Gases, Plumsteadville, Pennsylvania, US) to passivate the cylinder walls. The cylinder was pressurized to nominal 12.5 Mpa. This Niwot Ridge facility is used by NOAA to prepare cylinder mixtures of dried whole air for various uses including supplying certified mixtures for greenhouse gases used by researchers making atmospheric measurements.

NIST analyzed the measurement standard 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 data for those analyses are given in Table 2. Note that for the

NIST data the CFC-12, CFC-111, CFC-113 and HCFC-142b uncertainties are larger for the December 2012 data compared to February 2012. The precision of consecutive injection for a single standard and comparison sample were larger for the December 2012 measurements than what was obtained during February 2012.

Table 2. Stability study data for P-151 sample.

Halocarbon	NOAA October 2010 Measurement		NOAA January 2011 Measurement		NIST February 2012[a] Measurement		NIST December 2012[b] Measurement		NOAA February 2013 Measurement	
	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	1.6	530.5	1.6	529.6	3.4	530.0	4.4	529.9	1.0
Trichlorofluoromethane (CFC-11)	241.0	1.6	241.0	1.4	240.7	0.8	240.6	2.4	241.7	1.6
1,1,2-Trichlorotrifluoroehtane (CFC-113)	76.6[d]	0.4	76.6[d]	0.2	77.68	0..38	77.4	1.6	76.3[d]	0.4
1,1,1,2-Tetrafluoroethane (HFC-134a)			65.3	0.4	63.4	2.2	65.7	3.6	65.0	0.4
Chlorodifluoromethane (HCFC-22)			224.7	0.4	221.5	3.0	221.9	3.0	223.4	0.3
1-Chloro-1,1-difluoroethane (HCFC-142b)			22.07	0.10	21.67	0.54	22.37	1.00	21.99	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.
[d]NOAA value was determined by GC/ECD. NOAA's official P151 value for CFC-113 was determined by GC/MS.

The stability data in Table 2 are displayed graphically in Figures 1-6. In Figure 1, the dichlorodifluoromethane (CFC-12) stability data statistically indicate, as all error bars overlap, that there has been no drift over time for each laboratories individual set of data points.

Figure 1. Stability data for dichlorodifluoromethane (CFC-12).
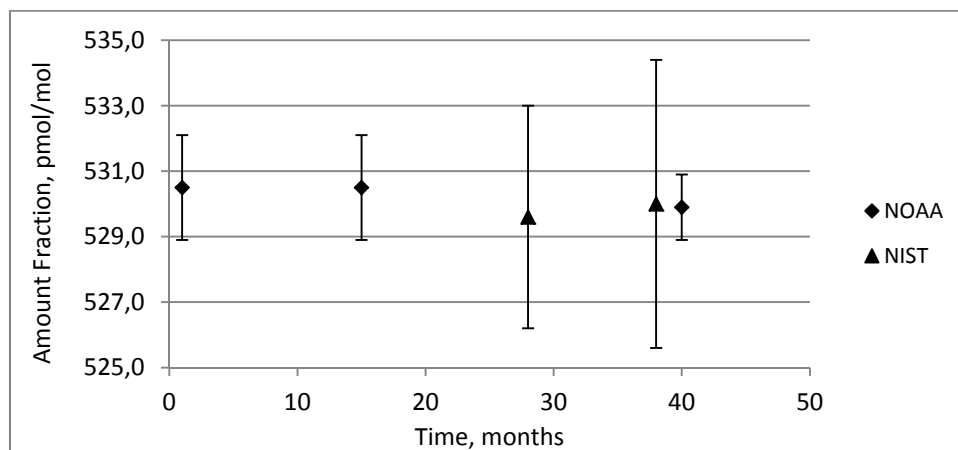
The trichlorofluoromethane (CFC-11) stability data in Figure 2 statistically indicate, as all error bars overlap, that there has been no drift over time for each laboratories individual set of data points.

Figure 2. Stability data for trichlorofluoromethane (CFC-11).

Figure 3 shows the stability data for 1,1,2-trichlorotrifluoroethane (CFC-113). While the NIST and NOAA data indicate a small bias in reported values, the individual sets of data show stability, as all error bars overlap for each data set. Of note is that the NOAA uncertainties, *k=2*, are only based on their measurement precision. Therefore no drift over time for each laboratory individual set of data points.

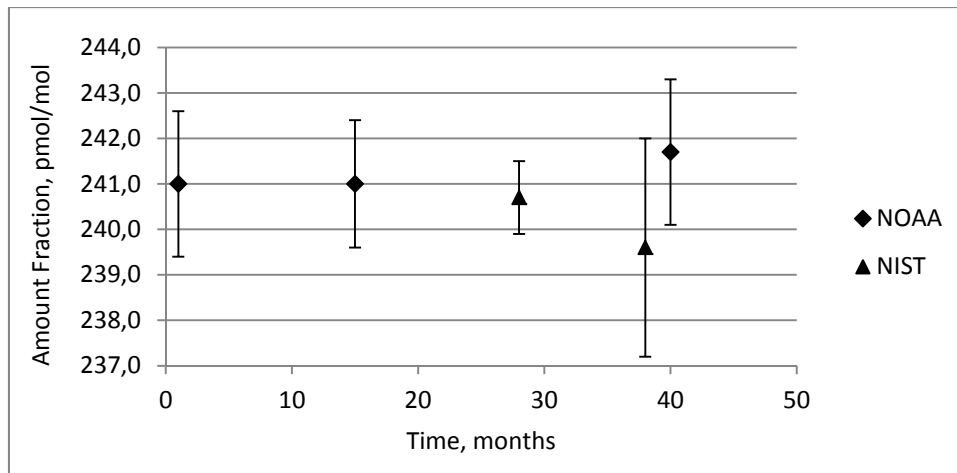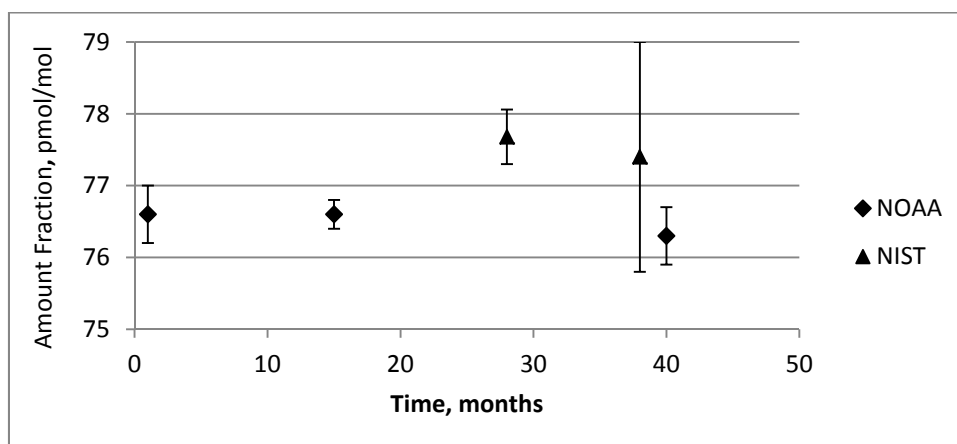Figure 3. Stability data for 1,1,2-trichlorotrifluoroethane (CFC-113).

The 1,1,1,2-tetrafluoroethane (HFC-134a) stability data are shown in Figure 4. The $k = 2$ error bars do overlap for the NIST data points, suggesting that the HFC-134a has remained stable. However, the difference between the two data points is 2.3 pmol/mol, suggesting it has increased in the cylinder; since the cylinder was not pretreated with the target component, desorption from the cylinder wall is not likely and chemical reaction is also an unlikely scenario. However, both NOAA data points agree within the $k=2$ error bars, and the 2nd NIST data point is in agreement, thus suggesting stability. An explanation for the larger difference between the 1st and 2nd NIST data points is most likely instrumental. The 1st data point was analyzed by GC/FID/preconcentration of the sample. The HCF-134a peak eluted on the tail of a rather large unknown peak in the K-83 sample, making the peak area determination difficult. The 2nd NIST measurement was taken using a GC/MSD system which was not previously available for the 1st analysis; the data taken and reported as the NIST P151 reported values (see Appendices). While the standard uncertainty, 1.8 pmol/mol, is much larger for the measurement by GC/MSD, the column used for this measurement nicely separated the HFC-134a from the other halocarbons. The 2nd NIST stability data point is most likely a more accurate representation of the mole fraction of the HFC-134a in the pilot study sample.

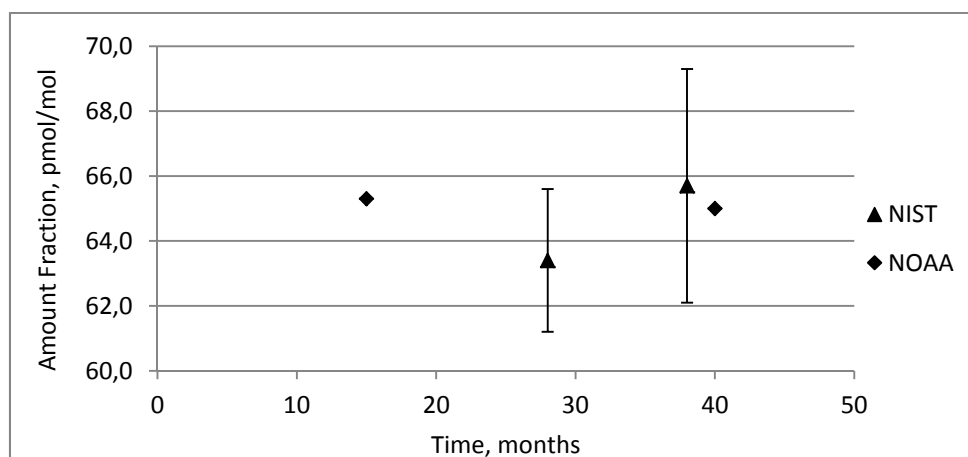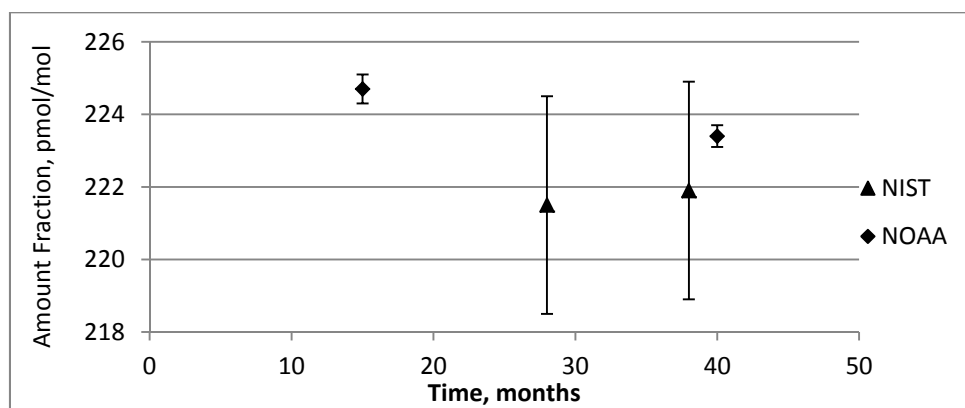Figure 4. Stability data for 1,1,1,2-tetrafluoroethane (HFC-134a).

Figure 5 shows the stability data for chlorodifluoromethane (HCFC-22). The NIST and NOAA data agree within the $k=2$ error bars and therefore suggests stability of this halocarbon in the pilot study sample.

Figure 5. Stability data for chlorodifluoromethane (HCFC-22).

The 1-chloro-1,1,-difluoroethane (HCFC-142b) stability data are shown in Figure 6. This data is very similar to that for the HFC-134a in that the 1st NIST data point was measured by GC/FID/preconcentration, and the 2nd data point was analyzed using GC/MSD. In both cases the HCFC-142b peak was a baseline-to-baseline separation with no interferences. Even though the 2nd NIST data point is 0.7 pmol/mol (3.2 % relative) higher than the 2nd, it is not a likely scenario that the HCFC-142b is increasing. The cylinder was not pretreated with the target component and therefore desorption of adsorb HCFC-142b from the cylinder wall is not likely and chemical reaction is also an unlikely scenario.. Peaks for the first NIST data points for both the HFC-134a and HCFC-142b were very small, making peak area determinations a challenge. The two NOAA data points are in agreement, suggesting stability.

Figure 6. Stability data for 1-chloro-1,1-difluoroethane (HCFC-142b).
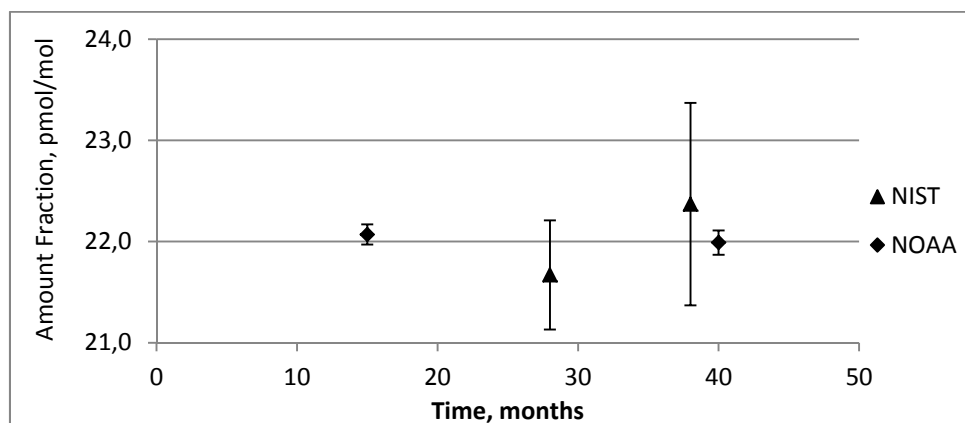
6. Measurement Protocol

The measurement protocol requested participants to provide the value and uncertainty of each halocarbon mole fraction measured for at least 3 individual determinations. An uncertainty budget, description of their analysis procedure, and their calibration methods were also requested. Methods used for their gas analysis were solely at laboratory discretion, and are reported individually in the Appendices – Measurement reports of participants.

7. Measurement Methods

The measurement methods and calibration methods used by the participating laboratories in this comparison are listed in Table 3.

Table 3. Measurement and calibration methods used by participating laboratories.

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

8. Results

The CCQM-P151 report forms as submitted are found in the Appendices. All final mole fractions were given with $k=2$ expanded uncertainties. Table 4 lists the laboratories reported mole fractions (x_i) and expanded uncertainties ($U(x_i)$), $k=2$, for each halocarbon as reported. It should be noted that while NOAA used GC/ECD for the CFC-113 stability data as listed in Table 2, the value as reported as their measurement value for this intercomparison was determined by GC/MS. NOAA sees a 1 pmol/mol bias between GC/MS and GC/ECD related to choice of standards. They are working to reconcile this bias, but at this time are being consistent with prior data reported and use their GC/MS value.

Table 4. Laboratory measurement results for halocarbons.

CCQM-P151 Measurements, pmol/mol

Halocarbon	KRISS		NIST		NOAA		SIO		Empa	
	x_i	$U(x_i)$[a]	x_i	$U(x_i)$[a]	x_i	$U(x_i)$[a]	x_i	$U(x_i)$[a]	x_i	$U(x_i)$[a]
CFC-12	529.44	2.65	529.6	3.4	530.5	3.7	533.2	5.6	530.25	10.7
CFC-11	239.09	1.91	240.7	0.8	241.0	2.7	239.8	2.6	238.93	5.2
CFC-113	75.10	0.90	77.68	0.38	75.4[b]	1.7	75.17	1.12	74.24	7.3
HFC-134a	68.90	6.89	63.4	2.2	65.3	0.7	64.88	1.02	64.37	2.0
HCFC-22	222.29	17.78	221.5	3.0	224.7	2.9	223.7	2.5	221.7	4.6
HCFC-142b	21.73	2.17	21.67	0.54	22.07	0.29	22.47	0.51	22.51	0.95

[a] $k=2$ expanded uncertainty
[b] The NOAA value reported here is based on GC/MS and is consistent with other NOAA reported data.

9. Comparison of Participants Results to CCQM-K83 Reference Value

The same measurement sample was used for CCQM-K83. The key comparison reference value
(KCRV) determined for each of the halocarbons from that K-83 comparison is given in Table 5.

Table 5. CCQM-K83 KCRVs for halocarbons in comparison mixture.

derSimonian-Laird Estimates

Halocarbon	x_{KCRV}	$U(x_{KCRV})$[a]	
	pmol/mol	pmol/mol	Relative
CFC-12	529.5	2.2	0.42%
CFC-11	240.2	1.5	0.62%
CFC-113	76.4	2.6	3.4 %
HFC-134a	65.5	5.3	8.1%
HCFC-22	221.5	3	1.4%
HCFC-142b	21.67	0.52	2.4%

The participants reported data in Table 4 are graphically displayed in Figures 7-12 in
relationship to the K-83 KCRV; the black line in each figure with corresponding expanded
uncertainties shown as the red lines. Participants in black on the *x-axis* are NMIs (CCQM
members) while non-members are in red. The error bars of each participants data point
represent the expanded uncertainty ($U(x_i)$), *k=2*, of the respective laboratory results. In all cases

the participant data points are within the KCRV expanded uncertainty limits, or the data point error bars intersect those uncertainty limits. These results demonstrate good agreement between all participants.

Figure 7. Dichlorodifluoromethane (CFC-12) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, $k=2$, reported by participants.
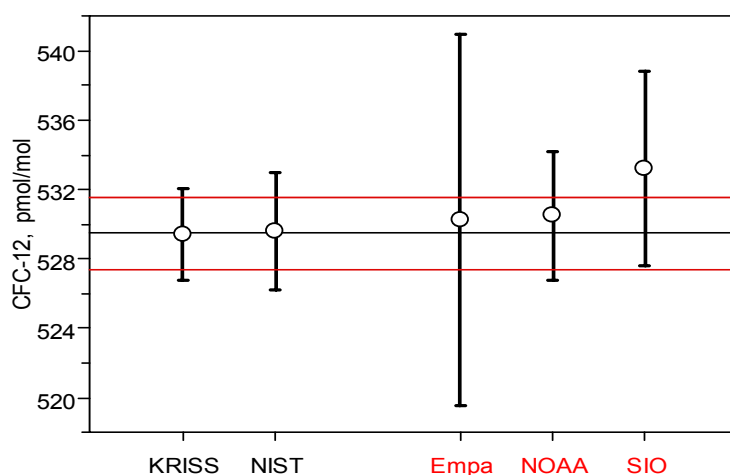
Figure 8. Trichlorofluoromethane (CFC-11) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, $k=2$, reported by participants.
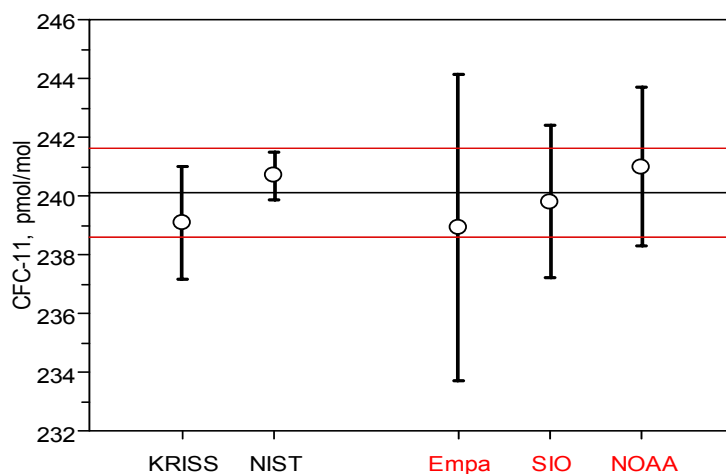
Figure 9. 1,1,2-Trichlorotrifluoromethane (CFC-113) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, *k=2*, reported by participants.
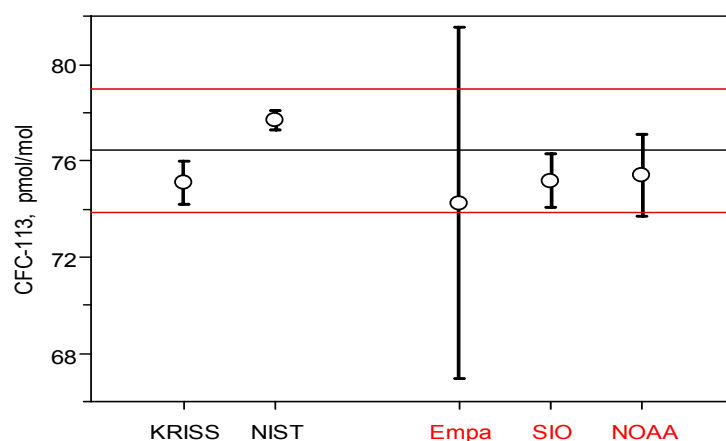
Figure 10. 1,1,1,2-Tetrafluoroethane (HFC-134a) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, *k=2*, reported by participants.

Figure 11. Chlorodifluoromethane (HCFC-22) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, *k=2*, reported by participants.
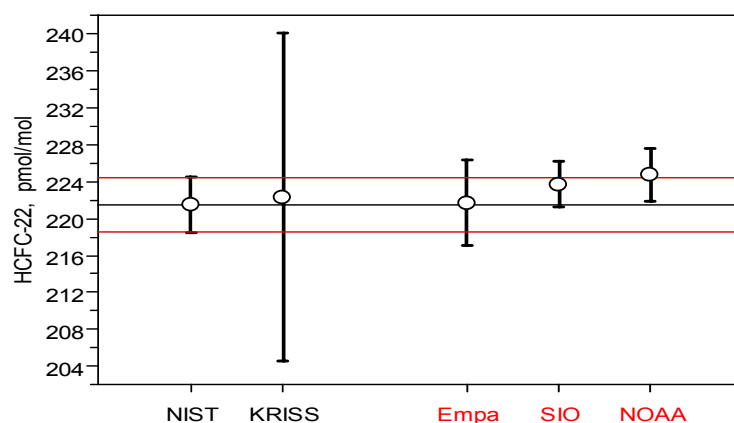
Figure 12. 1-Chloro-1,1-difluoroethane (HCFC-142b) mole fractions as reported by participating laboratories in relationship to the CCQM-K83 KCRV. The error bar represents the expanded uncertainty, *k=2*, reported by participants.
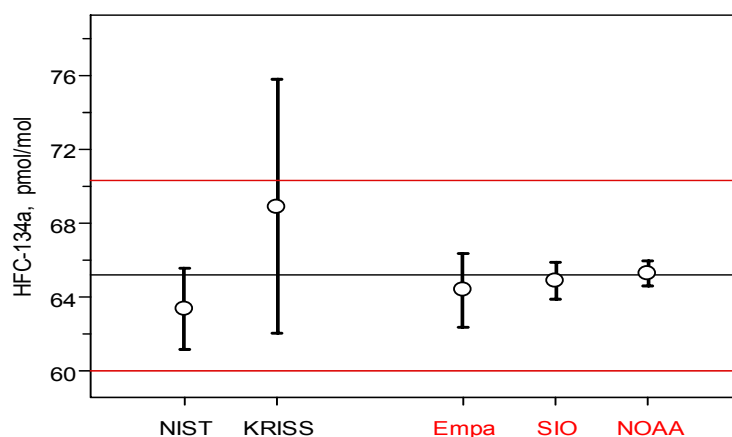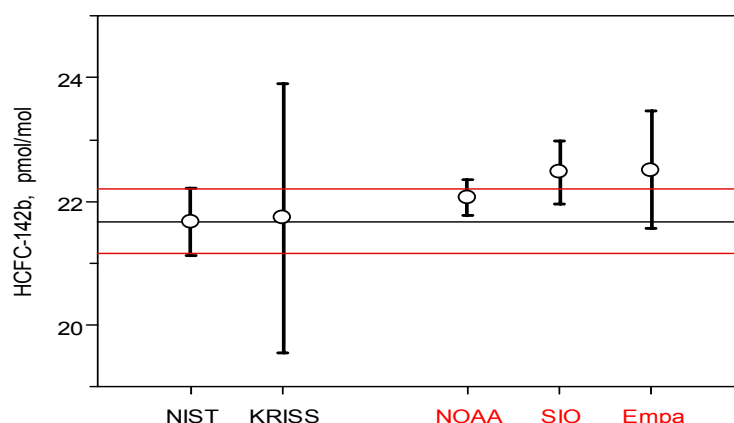

10. Conclusion

This pilot study has served to bring two communities who are involved in some manner to support those who need standards for measurements of components present in the atmosphere, responsible for an impact on climate change. Each of the communities has a different need and approach.   The atmospheric community needs a stable scale, not necessarily accurate, based on precise measurements and continuity in order to establish trends of these gases in the atmosphere, and to relate many measurements sets. The CCQM, whose members are 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 pilot study serves only as a measure of how the standards and scales for trace level halocarbons from these two communities compare, and not as a benchmark to assess accuracy.

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 standards of some of these halocarbons at trace levels, but not the level of experience measuring whole air samples. Considering these factors, the results of this pilot study/comparison indicate good agreement between the participants. All reported values or associated uncertainties, *k=2,* lie within the CCQM-K83 KCRV *k=2* uncertainty

limits. This demonstrates that the different methods and techniques used to prepare standards/scales, and the measurement systems and techniques used to value assign halocarbons in a dry whole air sample are consistent within the uncertainties reported.   The only participant that does not make their own standards is Empa; they use the SIO scales. There values are in very good agreement with the SIO data, demonstrating that the analytical systems are in good control.

Appendix A Measurement Report: KRISS

CCQM-K83 Measurement report: Halocarbons in Dry Whole Air

Laboratory: Korea Research Institute of Standards and Science (KRISS)
Laboratory code : KRISS

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)	Std. dev. (%, relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	Sep. 18	529.538	0.1	4
Trichlorofluoromethane (CFC-11)	Sep. 18	238.923	0.2	4
1,1,2-Trichlorotrifluoroethane (CFC-113)	Sep. 18	75.094	0.2	4

Measurement No. 2	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	Sep. 19	529.295	0.1	2
Trichlorofluoromethane (CFC-11)	Sep. 19	238.983	0.1	2
1,1,2-Trichlorotrifluoroethane (CFC-113)	Sep. 19	75.094	0.2	2

Measurement No. 2	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	Sep. 20	529.563	0.1	2
Trichlorofluoromethane (CFC-11)	Sep. 20	239.213	0.1	2
1,1,2-Trichlorotrifluoroethane (CFC-113)	Sep. 20	75.103	0.2	2

Gas Mixture Component	Result (assigned value) pmol/mol	Coverage factor	Assigned expanded Uncertainty [%]
Dichlorodifluoromethane (CFC-12)	529.44	2	0.5
Trichlorofluoromethane (CFC-11)	239.09	2	0.8
1,1,2-Trichlorotrifluoroethane (CFC-113)	75.10	2	1.2

Measurement No. 1	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		70.21	1.06	
Chlorodifluoromethane (HCFC-22)	Sep. 17	221.81	0.56	1
1,1-Difluoro-1-chloroethane (HCFC-142b)		20.23	0.45	

Measurement No. 2	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		65.67	0.60	
Chlorodifluoromethane (HCFC-22)	Sep. 18	210.64	0.65	1
1,1-Difluoro-1-chloroethane (HCFC-142b)		22.88	0.51	

Measurement No. 3	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		72.08	3.4	
Chlorodifluoromethane (HCFC-22)	Sep. 19	228.43	6.6	2
1,1-Difluoro-1-chloroethane (HCFC-142b)		22.55	0.1	

Measurement No. 4	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		64.44	2.75	
Chlorodifluoromethane (HCFC-22)	Sep. 20	216.84	1.81	1
1,1-Difluoro-1-chloroethane (HCFC-142b)		21.96	3.07	

Measurement No. 5	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		68.39	10.89	
Chlorodifluoromethane (HCFC-22)	Sep. 21	231.47	7.58	1
1,1-Difluoro-1-chloroethane (HCFC-142b)		21.29	0.63	

Measurement No. 6	Date	Result (pmol/mol)	Std. dev. (%, relative)	# of sub-measurements
1,1,1,2-Tetrafluoroethane (HFC-134a)		69.41	1.87	
Chlorodifluoromethane (HCFC-22)	Sep. 24	218.42	1.33	1
1,1-Difluoro-1-chloroethane (HCFC-142b)		20.64	0.48	

Gas Mixture Component	Result (assigned value) pmol/mol	Coverage factor	Assigned expanded Uncertainty [%]
1,1,1,2-Tetrafluoroethane (HFC-134a)	68.90	2	10
Chlorodifluoromethane (HCFC-22)	222.29	2	8
1,1-Difluoro-1-chloroethane (HCFC-142b)	21.73	2	10

Reference Method:

CFCs Analysis: The CFCs were analyzed using a GC/ECD (HP 7890). Prior to any connection of a sample to the analyzer, each analysis begins with purging the sample line and regulator of each cylinder several (5 or 6) times. In figure 1, a schematic diagram of analyzing system and analytical condition are shown. The measurement took 22 minutes to take a chromatogram. During the analysis, single control cylinder among various standard cylinders was used for drift control and ratio determination. Repeatability of 3 individual measurements was very good and a drift between cylinders was cons iderable compared to their repeatability uncertainty. The measurement was performed for a week.

<< **Analytical condition** >>
Detector : μECD
Detector temp. : 375 ℃
Oven temp. : 40 ℃ 7 min, 25 ℃/min
80 ℃ 8.5min, 30 ℃/min 145 ℃ 5min
Column : Restek CP9999 max
240 ℃ AL-F1 80/100 24ft
Sample loop : μL
Sample flow : 200 mL/min
Carrier gas : CH4/N2(P-5)
Carrier gas flow : 55.1 psi
Valve box temp. : 100 ℃
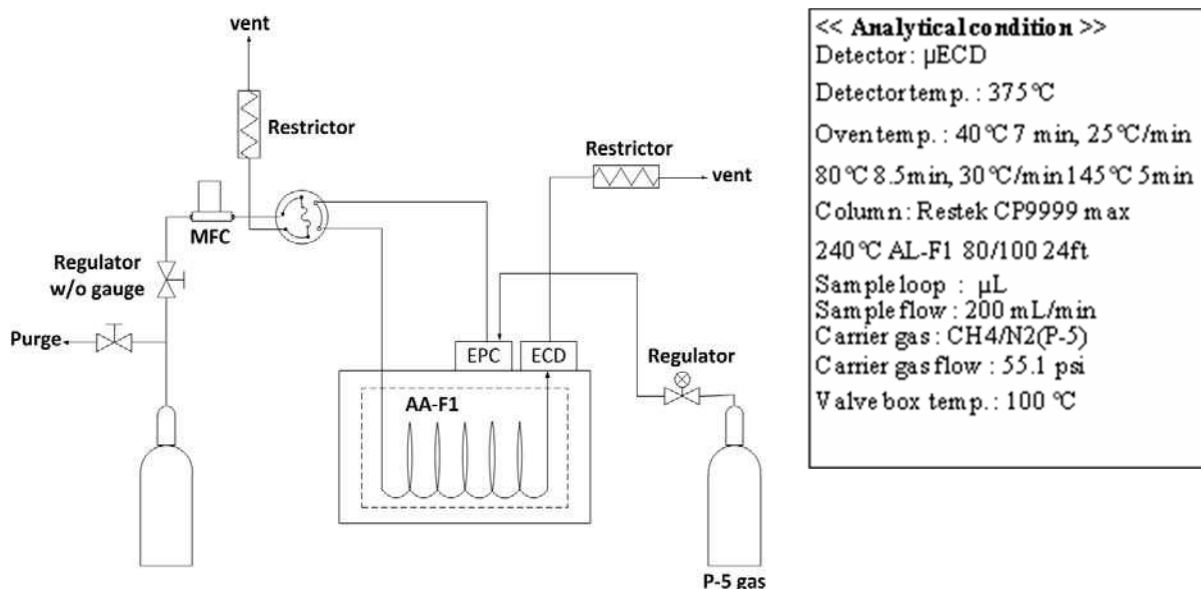
Fig 1. Schematic diagram of analyzing system and its analytical conditions of CFCs

HFCs Analysis: The HFCs were analyzed using a GC/MSD analyzer (HP 7890) with pre-concentrator (Gerstel co.). Before analysis, sample lines and regulators were purged 5 or 6 times. In figure 2, a schematic diagram of analyzing system and analytical condition are shown. It took to get a chromatogram about 60 minutes. Most of the measurement time was spent to concentrate target substances in ~ 17 L of gas mixture. During the analysis, one standard cylinder of which concentration s are the closest to the AAL073358 cylinder was used to quantify an amount of HFCs in air. Measurement was conducted for a week.
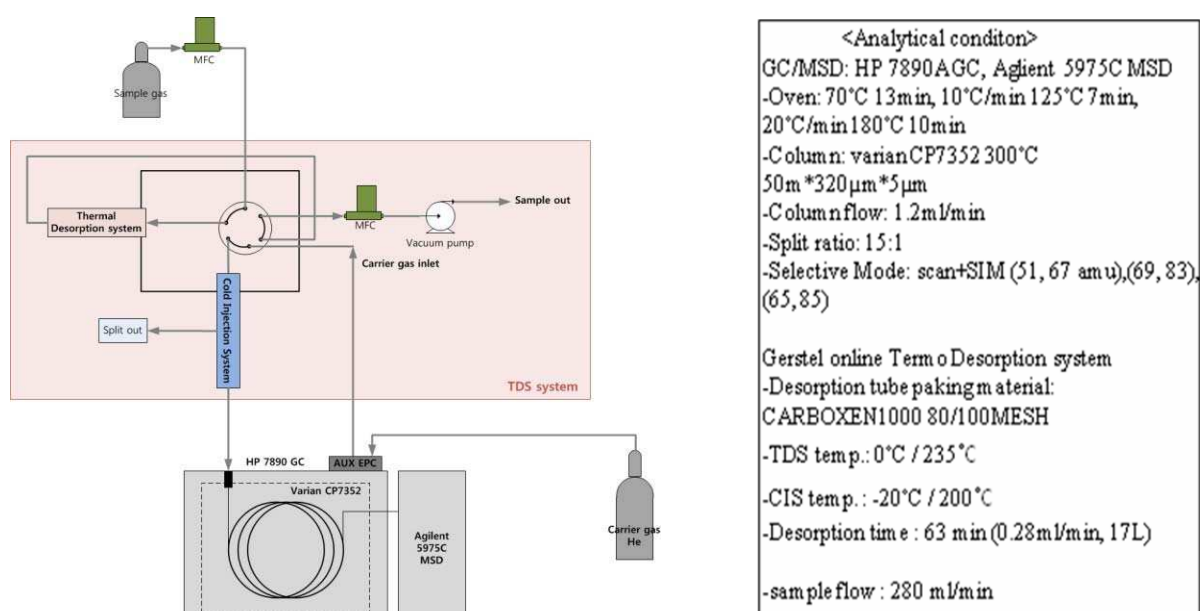
Fig 2. Schematic diagram of analyzing system and its analytical conditions of HFCs

Calibration Standards:

- CFCs standards:
Total eight (six (CFCs, N2, O2) and two (CFCs, N2, O2, and Ar)) KRISS primary standard mixtures were gravimetrically prepared to have various concentrations around ambient level according to ISO 6142:2001 "Gas analysis – Preparation of calibration gas mixtures - Gravimetric method". Impurities of pure gases such as N2, O2, Ar and CFCs were analyzed. Significant amount of CFC impurities was not detected in the balance gases. D727508 cylinder was set t o a control cylinder. The PSMs used for this comparison are listed below:

Cylinder number	CFC12	CFC11 [pmol/mol]	CFC113	O2 (%)	N2 (%)	Ar (%)
D014953	521.69	235.30	72.55	20.694	79.306	
rel. Unc. (%, $k = 2$)	0.2	0.4	0.4			
D985590	527.99	231.49	71.72	21.775	78.225	
rel. Unc. (%, $k = 2$)	0.2	0.4	0.4			
D014942	530.90	243.67	75.07	20.588	79.412	
rel. Unc. (%, $k = 2$)	0.2	0.4	0.4			
D727508	526.30	241.47	75.10	20.924	78.035	1.040
rel. Unc. (%, $k = 2$)	0.2	0.4	0.4			
D985691	525.54	239.31	75.08	20.616	79.383	
rel. Unc. (%, $k = 2$)	0.2	0.4	0.4			

- HFCs standards:
Six (HFCs, N2, O2) KRISS primary standard mixtures were gravimetrically prepared to have various concentrations around ambient level, according to ISO 6142:2001 "Gas analysis -Preparation of calibration gas mixtures - Gravimetric method". Impurities of pure gases such as N2, O2 and each HFCs were analyzed. Significant amount of HFC impurities was not detected in the balance gases. Basically, GC FID with pre cooling device was used for the measurement of HFCs. However, for the comparison with the cylinder (#AAL073358) HFCs mixtures were concentrated for 50 minutes in our pre cooling system to be introduced to GC MSD. Because of the necessity of long time and large sample volume, a

measurement was performed in a way of sequence, such as A-B-C-D-A. Two cylinders whose response are the nearest to the AAL073358 cylinder were used for this comparison:

Cylinder number	HFC134a	HFC22 [pmol/mol]	HFC142b	O2 (%)	N2 (%)	Ar (%)
D014989	63.970	222.54	22.192	20.68207	79.31793	
rel. Unc. (%, $k = 2$)	2	2	2			
D985689	67.265	217.63	22.495	21.00723	78.99277	
rel. Unc. (%, $k = 2$)	2	2	2			

Instrument Calibration:

CFCs calibration: KRISS PSMs are used for the calibration of instrument. Because ECD detector nonlinearly responds to the amount of analytes, the nearest 2 points in concentration were selected for the calibration of signal responses. During measurements, laboratory temperature were set to 26 ± 2 ℃. Inner pressure of gas lines was kept steady by using restrictors at the end.

HFCs calibration: Most of procedure was same with the case of CFCs calibration. Two PSMs were used instead. One point calibration was performed using the nearest.

Sample Handling:

Cylinders had stayed at the laboratory more than 2 weeks before the measurements. Cylinder was equipped with the regulator without the gauge that was purged several times between measurements. MFC then controlled the constant flow of sample.

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.

a)   Uncertainty table: (for example, CFC12)

Uncertainty source X_I	Estimate x_I	Assumed distribution	relative Standard uncertainty $u(x_i)$ [%]
Cylinder #1 gravimetrically prepared	525.635	normal	0.1
Cylinder #2 Gravimetrically prepared	521.688	normal	0.1
Reproducibility	529.39	-	0.1
Drift		-	0.2
Expanded uncertainty, $k = 2$ (relative, %)			0.5

(for example, CFC11)

Uncertainty source X_I	Estimate x_I	Assumed distribution	relative Standard uncertainty $u(x_i)$ [%]
Cylinder #1 gravimetrically prepared	239.31	normal	0.2
Cylinder #2 Gravimetrically prepared	243.67	normal	0.2
Reproducibility	529.39		0.1
Drift			0.3
Expanded uncertainty, $k = 2$ (relative, %)			0.8

(for example, CFC113)

Uncertainty source X_I	Estimate x_I	Assumed distribution	relative Standard uncertainty $u(x_i)$ [%]
Cylinder #1 Gravimetrically prepared	75.08	normal	0.2
Cylinder #2 Gravimetrically prepared	75.07	normal	0.2
Reproducibility	529.39	-	0.2
Drift		-	0.5
Expanded uncertainty, $k = 2$ (relative, %)			1.2

Appendix B Measurement Report: NIST

CCQM-K83 Measurement report: Halocarbons in Dry Whole Air

Laboratory : National Institute of Standards and Technology (NIST)
Laboratory code : NIST

Cylinder number : AAL073358

NOMINAL COMPOSITION: Various from 20×10^{-12} to 550×10^{-12} (pmol/mol; ppt)

Measurement No. 1	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	06-Feb-12	530.9	1.4	3
Trichlorofluoromethane (CFC-11)	31-Oct-11	240.21	0.80	3
1,1,2-Trichlorotrifluoroethane (CFC-113)	13-Dec-11	77.63	0.19	3
1,1,1,2-Tetrafluoroethane (HFC-134a)	01-Feb-12	64.45	1.08	3
Chlorodifluoromethane (HCFC-22)	01-Feb-12	219.54	1.42	3
1,1-Difluoro-1-chloroethane (HCFC-142b)	01-Feb-12	21.78	0.27	3

Measurement No. 2	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	07-Feb-12	528.92	0.56	3
Trichlorofluoromethane (CFC-11)	01-Nov-11	241.94	0.37	3
1,1,2-Trichlorotrifluoroethane (CFC-113)	13-Dec-11	77.69	0.19	3
1,1,1,2-Tetrafluoroethane (HFC-134a)	02-Feb-12	63.03	1.12	3
Chlorodifluoromethane (HCFC-22)	02-Feb-12	221.95	1.44	3
1,1-Difluoro-1-chloroethane (HCFC-142b)	02-Feb-12	21.80	0.27	3

Measurement No. 3	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	09-Feb-12	528.87	0.92	3
Trichlorofluoromethane (CFC-11)	03-Nov-11	240.06	0.30	3
1,1,2-Trichlorotrifluoroethane (CFC-113)	14-Dec-11	77.68	0.19	3
1,1,1,2-Tetrafluoroethane (HFC-134a)	06-Feb-12	62.66	1.11	3
Chlorodifluoromethane (HCFC-22)	06-Feb-12	222.42	1.44	3
1,1-Difluoro-1-chloroethane (HCFC-142b)	06-Feb-12	21.72	0.27	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)	529.6	2	3.4
Trichlorofluoromethane (CFC-11)	240.7	2	0.8
1,1,2-Trichlorotrifluoroethane (CFC-113)	77.68	2	0.38
1,1,1,2-Tetrafluoroethane (HFC-134a)	63.4	2	2.2
Chlorodifluoromethane (HCFC-22)	221.5	2	3.0
1,1-Difluoro-1-chloroethane (HCFC-142b)	21.77	2	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 K83 sample, AAL073358, are given below:

PSM Cylinder #	Year	CFC-12	CFC-11	CFC-113	HCFC-22	HCFC-142b	HFC-134a
		-------------------------Gravimetric Concentration, pmol/mol (ppt)[a]----------------					
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					

[a]Relative combined uncertainty, in ( ), with the coverage factor $k=1$ (68 % confidence interval).

The K83 sample was used as a control; it was analyzed first followed by two primary gravimetric standards, followed by the K83 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 K83 sample, before moving to the next sample. A ratio was calculated for each gravimetric standard to the K83 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 K83 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 K83 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.

    a)   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

    b)   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

    c)   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

    d)   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

e) Uncertainty table**: HCFC-22**

Uncertainty component	Estimate (ppt) $u(k=1)$	Assumed distribution	Contribution to standard uncertainty, u_i(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

f) Uncertainty table**: HCFC-142b**

Uncertainty component	Estimate (ppt) $u(k=1)$	Assumed distribution	Contribution to standard uncertainty, u_i(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

Appendix C Measurement Report: NOAA

CCQM-K83 Measurement report: Halocarbons in Dry Whole Air

Laboratory   : **NOAA**
Laboratory code   :

Cylinder number   : AAL073358

NOMINAL COMPOSITION: Various from 20×10^{-12} to 550×10^{-12} (pmol/mol; ppt)

Summary Results:

Gas Mixture Component	Result (assigned value) pmol/mol (ppt)	Coverage factor	Assigned expanded Uncertainty pmol/mol (ppt)
Dichlorodifluoromethane (CFC-12)	530.5	k=2 (all)	3.7
Trichlorofluoromethane (CFC-11)	241.0		2.7
1,1,2-Trichlorotrifluoroethane (CFC-113)	75.4		1.7
1,1,1,2-Tetrafluoroethane (HFC-134a)	65.3		0.7
Chlorodifluoromethane (HCFC-22)	224.7		2.9
1,1-Difluoro-1-chloroethane (HCFC-142b)	22.07		0.29

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.

a) 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

b) 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

   c)   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

   d)   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

   e)   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

    f)   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

CCQM-K83 Measurement report: Halocarbons in Dry Whole Air

Laboratory   : Scripps Institution of Oceanography, R.F. Weiss, C.M. Harth, J. Mühle
Laboratory code   :

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 (%	# 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
Chlorodifluoromethane (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

Measurement No. 2	Date	Result (pmol/mol)	stand. deviation (%	# 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
Chlorodifluoromethane (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

Measurement No. 3	Date	Result (pmol/mol)	stand. deviation	# 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
Chlorodifluoromethane (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

Summary Results:

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Gas Mixture Component	Result (assigned value) pmol/mol (ppt)	Coverage factor	Assigned Expanded Uncertainty pmol/mol (ppt)	
			Precision	Accuracy
Dichlorodifluoromethane (CFC-12)	53	1	1.3	5.
Trichlorofluoromethane (CFC-11)	3.	1	0.7	5
1,1,2-Trichlorotrifluoroethane (CFC-113)	2	1	0.2	2.
1,1,1,2-Tetrafluoroethane (HFC-134a)	23	1	0.2	5
Chlorodifluoromethane (HCFC-22)	9.	1	0.7	1.
1,1-Difluoro-1-chloroethane (HCFC-142b)	8	1	0.1	1
	75			1.

Reference Method:

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).

Calibration Standards:

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 CO_2 and N_2O. See cited Prinn et al. (2000) and Miller et al. (2008) for discussion and details.

	Primary Scale	Number of Primary Standards in	Relative Standard Deviation of Scale (Internal Agreement)	Quoted Reagent Purity
CFC-12	SIO-05	2	0.25 %	≥ 99.97%
CFC-11	SIO-05	7	0.29 %	≥ 99.9%
CFC-113	SIO-05	2	0.21 %	≥ 99.9%
HFC-134a	SIO-05	3	0.28	≥ 99.9%
HCFC-22	SIO-05	1		≥ 99.9%
HCFC-142b	SIO-05	7		≥ 99.4%
		1		

Instrument Calibration:

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.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to t h e 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).

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.

a) Uncertainty table:

Uncertainty source X_i	Gas Mixture Component	Estimate x_i	Assumed distribution	Standard uncertaint y $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Primary Standard Preparation (Internal Agreement)**	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	0.25% 0.29% 0.21% 0.28% 0.27% 0.21%	Normal			
Propagation from Primaries to Final Analysis	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	0.03% 0.08% 0.08% 0.15% 0.19% 0.44%	Normal			
Estimated Analytical Interference Uncertainty (including reagent impurity)	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	1% 1% 1.5% 1.5% 1% 2%	Normal (except reagent impurity component)			

Coverage factor: 1
Expanded uncertainty (see below):

Final Analysis Precision Relative to Calibration Scale	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	0.25% 0.30% 0.22% 0.32% 0.33% 0.49%	Normal			
Absolute Accuracy	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	1% 1% 1.5% 1.5% 1% 2%	Normal (except reagent impurity component)			

** Note that gravimetric weighing accuracies and precisions are not included in this table, since, at less than one part in 5000 (<0.02%) in all cases, they are an order of magnitude lower than the 0.2% to 0.3% standard preparation reproducibility determined by direct measurement.

Appendix E Measurement Report: EMPA

CCQM-K83 Measurement report: Halocarbons in Dry Whole Air

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

Cylinder number   : AAL073358

NOMINAL COMPOSITION: Various from 20×10^{-12} to 550×10^{-12} (pmol/mol; ppt)

Measurement No. 1 **vs J-127**	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	22 June 2012	530.25	0.08	7
Trichlorofluoromethane (CFC-11)		238.93	0.31	7
1,1,2-Trichlorotrifluoroethane (CFC-113)		74.24	3.4	7
1,1,1,2-Tetrafluoroethane (HFC-134a)		64.371	0.23	7
Chlorodifluoromethane (HCFC-22)		221.70	0.20	7
1,1-Difluoro-1-chloroethane (HCFC-142b)		22.510	0.47	7

Measurement No. 2 **vs EG-003**	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	23 June 2012	530.25	0.12	6
Trichlorofluoromethane (CFC-11)		239.57	0.19	6
1,1,2-Trichlorotrifluoroethane (CFC-113)		74.57	2.2	6
1,1,1,2-Tetrafluoroethane (HFC-134a)		64.598	0.15	6
Chlorodifluoromethane (HCFC-22)		221.77	0.25	6
1,1-Difluoro-1-chloroethane (HCFC-142b)		22.427	0.56	6

Measurement No. 3 **vs E-071B**	Date	Result (pmol/mol)	stand. deviation (% relative)	# of sub-measurements
Dichlorodifluoromethane (CFC-12)	23 June 2012	530.81	0.08	7
Trichlorofluoromethane (CFC-11)		239.53	0.20	7
1,1,2-Trichlorotrifluoroethane (CFC-113)		75.72	2.5	7
1,1,1,2-Tetrafluoroethane (HFC-134a)		64.719	0.29	7
Chlorodifluoromethane (HCFC-22)		222.45	0.16	7
1,1-Difluoro-1-chloroethane (HCFC-142b)		22.526	0.13	7

Gas Mixture Component	Result	Coverage	Assigned expanded

	(assigned value) pmol/mol (ppt)	factor	Uncertainty pmol/mol (ppt)
Dichlorodifluoromethane (CFC-12)	530.25		10.7
Trichlorofluoromethane (CFC-11)	238.93		5.2
1,1,2-Trichlorotrifluoroethane (CFC-113)	74.24		7.3
1,1,1,2-Tetrafluoroethane (HFC-134a)	64.371		2.0
Chlorodifluoromethane (HCFC-22)	221.70		4.6
1,1-Difluoro-1-chloroethane (HCFC-142b)	22.510		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 earlier 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: This is approximated by the Estimated Analytical Interference Uncertainty (incl. reagent impurities). This information was given to us by SIO, it is the uncertainty related to the preparation of the primary standards. 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-K83. Nevertheless for the sake of simplicity we assume it to be equal the measurement uncertainty.

3) Measurement uncertainty: Is the uncertainty (1-std) given in the results tables above

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.

g) Uncertainty table:

Uncertainty source X_I	Compound	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
1) Estimated Analytical Interference Uncertainty (including reagent impurity). We requested this information from SIO	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	1 % 1 % 1.5 % 1.5 % 1 % 2 %				
2) Propagation uncertainty (from primary scale to Empa instrument working standards)	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	0.08 % 0.31 % 3.4 % 0.23 % 0.20 % 0.47 %				
3) Measurement uncertainty	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	0.08 % 0.31 % 3.4 % 0.23 % 0.20 % 0.47 %				
Overall expanded uncertainty 2 x SQRT of sum of 1)-3)	CFC-12 CFC-11 CFC-113 HFC-134a HCFC-22 HCFC-142b	2.02 % 2.18 % 9.9 % 3.07 % 2.08 % 4.2 %				