Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-air Standards: Revision of 1999

Addendum: Alternate Formulation of 1985-1999 Calibrations after Re-calibration of 4 cc Chamber Volume of Mercury Manometer

by

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February, 2002

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1. Introduction and Background

Here we discuss an alternative formulation of our primary reference gas calibrations for atmospheric CO_2 measurements which takes into account additional, recently acquired data indicating that the effective volume of the 4 cc chamber of our constant-volume mercury manometer (CMM) has not varied over time. Using this formulation, we establish what we call the "X99B" calibrating scale. This scale is tentative, pending further calibrations and retrospective interpretation of past data. Meanwhile the X99A calibration scale of the main report on the calibration of primary references gases (SIO Reference Series, 01-11) is our preferred scale. The X99A scale assumes that the mole fractions of CO_2 in our primary standards on average have not changed over time.

In the main report, we attributed an apparent upward drift in the manometrically measured mole fractions of CO_2 of our primary reference gases from 1985 to 1999, to a slowly decreasing effective volume of the 4 cc chamber of the CMM. If, in contrast, we assume an invariant effective volume of the chamber, the measured mole fractions of CO_2 in our primary reference gases are calculated to increase approximately in proportion to mole fraction, as documented in the main report in Tables 9.2a and 9.2b (pp. 45-46) and in Figure 3 (p. 25), this proportional increase suggestive of a shifting performance of the manometer. Direct volume calibrations of the 4 cc chamber of the CMM performed during the 1990’s using plenums (Table 5.1, p. 18, and Figure 2, p. 24), however, do not provide clear evidence to corroborate such a proposed change in effective volume of the 4 cc chamber. Also, we have not identified a possible cause for a decreasing volume, which is opposite to the inferred volume drift in the early 1980’s, that we attributed to the mercury becoming contaminated with an oxide coating, an effect directly observed [Keeling et al., 1986].

In 2000, we checked, independently and retrospectively, for possible erratic behavior of the effective volume of the 4 cc chamber of the CMM, taking advantage of archived samples of CO_2 extracted from sea water that had been measured precisely on the CMM. During the 1990's, the Carbon Dioxide Research Group (CDRG) performed analyses of seawater reference materials (CRM's) prepared by the laboratory of A. Dickson of SIO in order to certify their concentrations of dissolved inorganic carbon. An established laboratory vacuum extraction procedure was carried out on weighed aliquots of the CRM's, and the evolved pure CO_2 gas was measured in the 4 cc chamber of the CMM. After measurement, the gas samples were sealed into glass ampules ("flame-off tubes"). By 2000 we had accumulated about 500 of these samples. When precisely measured by another instrument, an electronic constant-volume manometer (ECM), they provide us with a history of the behavior of the 4 cc chamber of the CMM in the 1990's.

In the ECM procedure, each archived CO_2 gas sample is cryogenically transferred into a constant volume chamber of the ECM; a chamber partly made of glass, but also partly a compartment of a metallic differential pressure gauge manufactured by Ruska Instrument Corporation. The gas pressure exerted on a second compartment of the pressure gauge, separated from the first compartment by a diaphragm, is made equal to the sample pressure by supplying pressure from a Ruska DDR6000 quartz spiral manometer, configured as a pressure delivery source. This quartz spiral is mechanically immobile, held in place by an opposing electromagnetic field from which the pressure is accurately calculated. The position of the diaphragm in the differential pressure transducer is additionally detected electrically to very high precision.

The ECM has performed well. From its first use in 1991, its volume calibration has been linked to the CMM calibration by frequent measurements of the same samples in both instruments. The CO_2 gas pressure was sometimes erratic in the constant volume chamber of the ECM, attributed to the presence of stainless steel. However, when operated by Guy Emanuele of our staff in a consistent way, the stability of the instrument is now generally satisfactory. In March, 2000 after the CMM had become inoperative in April, 1999 he calibrated the effective volume of the ECM with respect to the measured volumes of five of seven plenums used previously to calibrate the 4 cc chamber of the CMM. He then analyzed a series of archived CO_2 samples, as discussed in Section 4, below.

2. Recalibration of Plenum Volumes

In 1974, Alexander Adams calibrated the volumes of the seven plenums, mentioned above, by weighing them filled with mercury [Keeling et al., 1986]. Since then, balance technology has improved, making it possible to weigh them filled with water, while maintaining satisfactory precision. In July, 1999 Guy Emanuele made volume calibrations of all seven plenums, by weighing them evacuated and then filled with pure, degassed water. His results are listed in Table A1, along with the original calibrations using mercury. The percent differences in the measured volumes, with reference to the 1974 volumes, indicate systematic bias between the two sets of calibrations. As discussed in the main report (section 5), the volumes of plenums 4 and 5 appear to have decreased significantly, in comparison to the volumes of the other plenums, between 1974 and 1985. The measured volumes of plenums 1,2,3,6, and 7 are found to be slightly lower in 1999 than in 1974, on average by 0.0320% (0.0006 cc). The reason for these decreases has not been determined. Additional volume measurements need to be made, including recalibration of the plenums using mercury, to prove any shifts to higher precision. Tbl A1

Table A1. Calibrated Plenum Volumes

Plenum No.	1974 (Mercury) No. of Detns.	Vol. (cc)	s_i (cc)	1999 (Water) No. of Detns.	Vol. (cc)	s_i (cc)	% Difference (1999–1974)
1	5	1.2978	0.00019	2	1.2974	0.00009	–0.0308
2	5	1.4619	0.00004	2	1.4617	0.00013	–0.0137
3	5	1.6360	0.00015	4	1.6354	0.00021	–0.0367
4	5	1.7457	0.00013	4	1.7431	0.00014	–0.1489
5	5	1.8359	0.00015	4	1.8339	0.00031	–0.1089
6	5	2.0367	0.00011	4	2.0359	0.00025	–0.0393
7	5	2.2733	0.00009	4	2.2724	0.00015	–0.0396
					Average	(1,2,3,6,7)	–0.0320%
						s_i	0.0108%

3. Calibration of Chamber Volume of the Electronic Manometer

The plenums were filled with pure CO_2 gas to a pressure of approximately 737 torr, determined precisely by a gas lubricated piston pressure gauge (Ruska Instrument Corporation, model 2465-754, with low range piston (0.2-25.0 psi)). Plenums 1 and 2 were not used because of their small size. The temperature was assumed to be that measured in a water bath into which the plenums were immersed. Using a virial equation of state (equation (1) of main report, p. 9) and recording the temperature, pressure, and calibrated volume of each plenum, as measured in 1999 and listed in Table A1, the moles of CO_2 contained in each plenum were calculated. The CO_2 gas sample in each plenum was transferred promptly into a flame-off tube to await measurement on the ECM.

On each of three days, April 4, 6, and 10, 2000, samples of CO_2 from the plenums were transferred into the constant volume chamber of the ECM and the pressure and temperature of the device measured. Using the equation of state referred to in the previous paragraph, and with the number of moles of CO_2 calculated for the plenum fillings, the volume of the ECM chamber was calculated, as summarized in Table A2. Tbl A2

Table A2. ECM Volume Calibrations

Date	Plenum Nos.	Avg. ECM Volume (cc)	s_i (cc)
4 Apr 00	3,4,5,6,7	8.7365	0.0015
6 Apr 00	4,6,7*	8.7380	0.0024
10 Apr 00	3,4,5,6,7	8.7383	0.0009
Avg. (of 13 determinations)		8.7375	0.0016

* Plenums 3,5 had fill problems on this day - runs rejected.

4. Measurements of Archived CO_2 Samples to Infer the Volume of the 4 cc Chamber of the CMM

On each of the same three days, cited in Table A2 above, 20 archived CO_2 samples, extractions from CRM's, were also analyzed on the ECM. On each of these days 20 samples were selected such that the dates of their original measurements on the CMM were evenly distributed from 1990 to 1999. Data and results are listed in Table A3. Using the average volume of the ECM chamber, 8.7375 cc, as listed in Table A2, the number of moles of CO_2 in each sample was calculated using the virial equation of state cited above. Tbl A3

The number of moles of CO_2 in each sample of sea water, calculated from original measurements made with the CMM, assumed that the 4 cc chamber of the CMM had an invariant volume of 3.7955 cc, as established by measurements in 1985 and 1986 using plenums calibrated with mercury (see Table 9.4a of the main report, p. 63). Estimates of the chamber volume consistent with these retrospective ECM measurements, listed in the last column of Table A3, were made by multiplying 3.7955 cc by the calculated number of moles of CO_2 of each archived sample based on ECM measurements, divided by the corresponding moles based on CMM measurements.

These estimates of the 4 cc chamber volume are plotted versus the dates of the original CMM measurements in Figure A1. A bold horizontal line on the plot indicates their average (3.7961 cc). Two additional thin horizontal lines indicate ±2 times the Fig A1

Table A3. Volumes of 4 cc Chamber of CMM Inferred from Measurements of Archived Samples on ECM

Analysis Date ECM (year, month day)	Analysis Date CMM	CRM No.	ECM Temp. (C)	ECM Pressure (Torr)	Calculated Moles CO_2 ECM (10^5)	Calculated Moles CO_2 CMM (10^5)	Factor ECM/CMM	Inferred CMM Volume[a] (cc)
000404	960724	SG265	39.8500	185.781	8.32471	8.32287	1.00022	3.7963
	990108	SS583	39.8500	187.870	8.41843	8.41563	1.00033	3.7968
	940308	PU127	39.8200	190.120	8.52019	8.51870	1.00017	3.7962
	990308	SU135	39.8180	181.105	8.11580	8.11407	1.00021	3.7963
	960306	SG354	39.8060	191.288	8.57296	8.57460	0.99981	3.7948
	971023	SN581	39.8600	186.856	8.37269	8.37146	1.00015	3.7961
	930623	PN149	39.8720	192.212	8.61260	8.61551	0.99966	3.7942
	970717	SL422	39.8580	191.280	8.57118	8.56996	1.00014	3.7960
	940811	PT526	39.8600	186.909	8.37506	8.37338	1.00020	3.7963
	980702	SR71	39.8700	195.058	8.74031	8.74238	0.99976	3.7946
	980204	SP71	39.8620	182.835	8.19227	8.18844	1.00047	3.7973
	981029	SS473	39.8340	187.887	8.41960	8.41563	1.00047	3.7973
	950721	SD192	39.8560	179.025	8.02154	8.02036	1.00015	3.7961
	950216	PZ29	39.8680	187.502	8.40143	8.40330	0.99978	3.7947
	940630	PW321	39.8660	190.357	8.52955	8.53112	0.99982	3.7948
	930120	PO452	39.8580	182.528	8.17859	8.17913	0.99993	3.7953
	901102	SB282	39.8420	187.052	8.38197	8.38550	0.99958	3.7939
	961211	SD9	39.8820	185.719	8.32107	8.31952	1.00019	3.7962
	920123	PG82	39.8800	182.414	8.17289	8.16960	1.00040	3.7970
	970213	SJ285	39.8740	196.732	8.81529	8.81319	1.00024	3.7964
000406	950106	PZ139	39.8700	188.070	8.42687	8.42847	0.99981	3.7948
	941104	PT473	39.8760	187.160	8.38588	8.38487	1.00012	3.7960
	951208	PY32	39.8860	198.640	8.90053	8.89290	1.00086	3.7988
	990401	SU374	39.8660	187.440	8.39872	8.39444	1.00051	3.7974
	980521	SQ94	39.8700	179.414	8.03862	8.03287	1.00072	3.7982
	920701	PG317	39.8700	179.431	8.03939	8.03736	1.00025	3.7965
	940427	PT214	39.8800	184.271	8.25620	8.25279	1.00041	3.7971
	970831	SL335B	39.8660	191.424	8.57741	8.57630	1.00013	3.7960
	981119	SS195	39.8700	187.957	8.42181	8.42267	0.99990	3.7951
	970423	SD127	39.8860	183.705	8.23065	8.22997	1.00008	3.7958
	930422	PP54	39.8860	194.369	8.70897	8.71145	0.99971	3.7944
	960904	SH106	39.9040	196.597	8.80841	8.81066	0.99975	3.7945

[a] Factor listed in previous column multiplied by 3.7955 cc.

Table A3 (cont.)

Analysis Date ECM (year, month, day)	Analysis Date CMM	CRM No.	ECM Temp. (C)	ECM Pressure (Torr)	Calculated Moles CO_2 ECM (10^5)	Calculated Moles CO_2 CMM (10^5)	Factor ECM/CMM	Inferred CMM Volume[a] (cc)
000406	910517	PE5	39.9040	188.801	8.45875	8.45693	1.00021	3.7963
	930304	PO326	39.8920	192.506	8.62522	8.62737	0.99975	3.7946
	921215	PP267	39.8840	183.989	8.24346	8.23863	1.00059	3.7977
	971219	SO391	39.8900	188.191	8.43173	8.43446	0.99968	3.7943
	940518	PW18	39.8800	185.222	8.29884	8.30481	0.99928	3.7928
	950822	SD309	39.8800	189.117	8.47355	8.46476	1.00104	3.7994
	950427	SB235	39.8960	189.775	8.50262	8.49971	1.00034	3.7968
	910118	PB264	39.8920	187.237	8.38891	8.38707	1.00022	3.7963
000410	941014	PW42	39.840	189.204	8.47855	8.46979	1.00103	3.7994
	940211	PT132	39.850	188.240	8.43502	8.42588	1.00108	3.7996
	960509	SG133	39.820	191.356	8.57561	8.57432	1.00015	3.7961
	960418	SF231	39.780	184.633	8.27507	8.27111	1.00048	3.7973
	990204	ST348	39.788	182.122	8.16222	8.15917	1.00037	3.7969
	970206	SJ162	39.838	187.337	8.39486	8.39284	1.00024	3.7964
	970611	SK472	39.860	194.717	8.72530	8.72605	0.99991	3.7952
	950511	SB265	39.854	179.523	8.04393	8.04450	0.99993	3.7952
	971120	SN352	39.886	191.393	8.57547	8.57431	1.00013	3.7960
	930211	PO114	39.860	189.324	8.48337	8.48145	1.00023	3.7964
	930813	PN112	39.888	199.460	8.93727	8.93977	0.99972	3.7944
	980416	SO18	39.840	188.252	8.43584	8.42953	1.00075	3.7983
	930902	PP143	39.844	194.244	8.70455	8.69803	1.00075	3.7983
	961017	SE348	39.868	180.958	8.10791	8.10923	0.99984	3.7949
	940712	PU168	39.828	185.221	8.30017	8.29892	1.00015	3.7961
	951102	SF28	39.832	190.551	8.53918	8.53950	0.99996	3.7954
	980925	SS604	39.864	185.243	8.30021	8.29620	1.00048	3.7973
	920318	PL583	39.854	189.615	8.49662	8.49532	1.00015	3.7961
	930720	PN276	39.862	209.108	9.37088	9.37404	0.99966	3.7942
	941214	PX346	39.866	187.403	8.39705	8.39884	0.99979	3.7947

[a] Factor listed in previous column multiplied by 3.7955 cc.

Volume of the 4 cc Chamber of the CMM from 1990 to 2000 Inferred from Retrospective Measurements using the ECM.

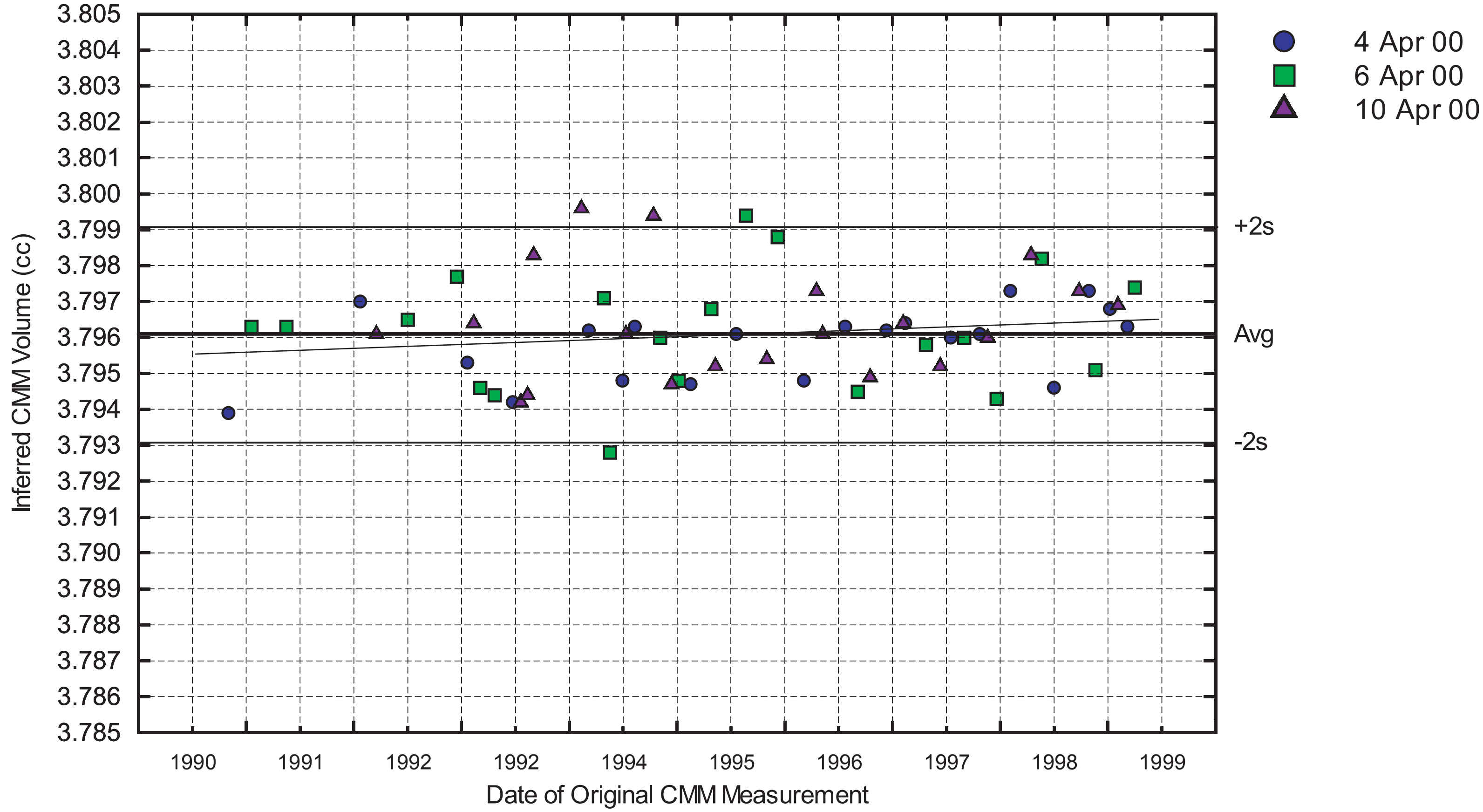

Figure A1. Volume of the 4 cc chamber of constant-volume mercury-column manometer (CMM), as inferred from reruns of archived samples on our electronic constant-volume manometer (ECM). The volume inferred from each ECM measurement is plotted versus the date of the original measurement on the CMM. Solid circles denote ECM measurements on 4 Apr 2000, solid squares, on 6 Apr 00, and solid triangles, on 10 Apr 00. The bold horizontal line indicates the average of all 60 measurements (3.7961 cc) and the thin horizontal lines indicate the level of two times the individual standard deviation (s = 0.00144 cc). The upward sloping line is a linear fit to the 60 measurements. The slope of the line is 0.000103 cc/year (standard error of slope = 0.000082 cc/year).

standard deviation (0.00144 cc) from this average. A third upward sloping thin line represents a linear fit to all 60 measurements versus time. The slope of the line is 0.000103 cc/year, having a standard error of 0.000082 cc/year, and is not significantly different than zero at the 90% level of confidence. The slope, being positive, clearly does not support a decrease in volume, as assumed by the X99A scale. The standard deviation of the set of 60 measurements (relatively, 1 part in 2600 of a measurement) is consistent with that observed historically for the difference between measurements of CO_2 gas samples, extracted from sea water collected at sea and measured at nearly the same time on both manometers (1 part in 2900). Averages of each of the daily set of 20 measurements do not differ significantly (3.7958 cc, 3.7961 cc, and 3.7964 cc for 4, 6, and 10 April, 2000, respectively).

5. Comparison of Inferred Volumes of the 4 cc Chamber of the CMM

Figure A2 compares three ways of determining the volume of the 4 cc chamber of the CMM: (1) as inferred from the ECM measurements made in 2000 on archived samples (small solid circles); (2) by direct measurements made from 1985 to 1999 using plenums calibrated with mercury (large solid triangles) and (3) consistent with assuming that our set of primary reference gases have not drifted on average, as assumed in the main report (large solid diamonds). The average of all 60 data points of Table A3, inferred from ECM measurements (3.7961 cc) by Method (1), is plotted as a bold horizontal line as in Figure A1. The direct measurements of the 4 cc chamber volume of the CMM by Method (2) were made in 1985-1986, 1988, 1990, 1993-1994, and 1998-1999. Fig A2

It is evident that the new ECM measurements reported here (Method (1)) do not support a conclusion that the effective volume of the 4 cc chamber in the CMM has drifted downward after 1990. Furthermore, the direct volume calibrations (Method (2) are inconclusive: those made in 1993-1994 support the drifting volume hypothesis,

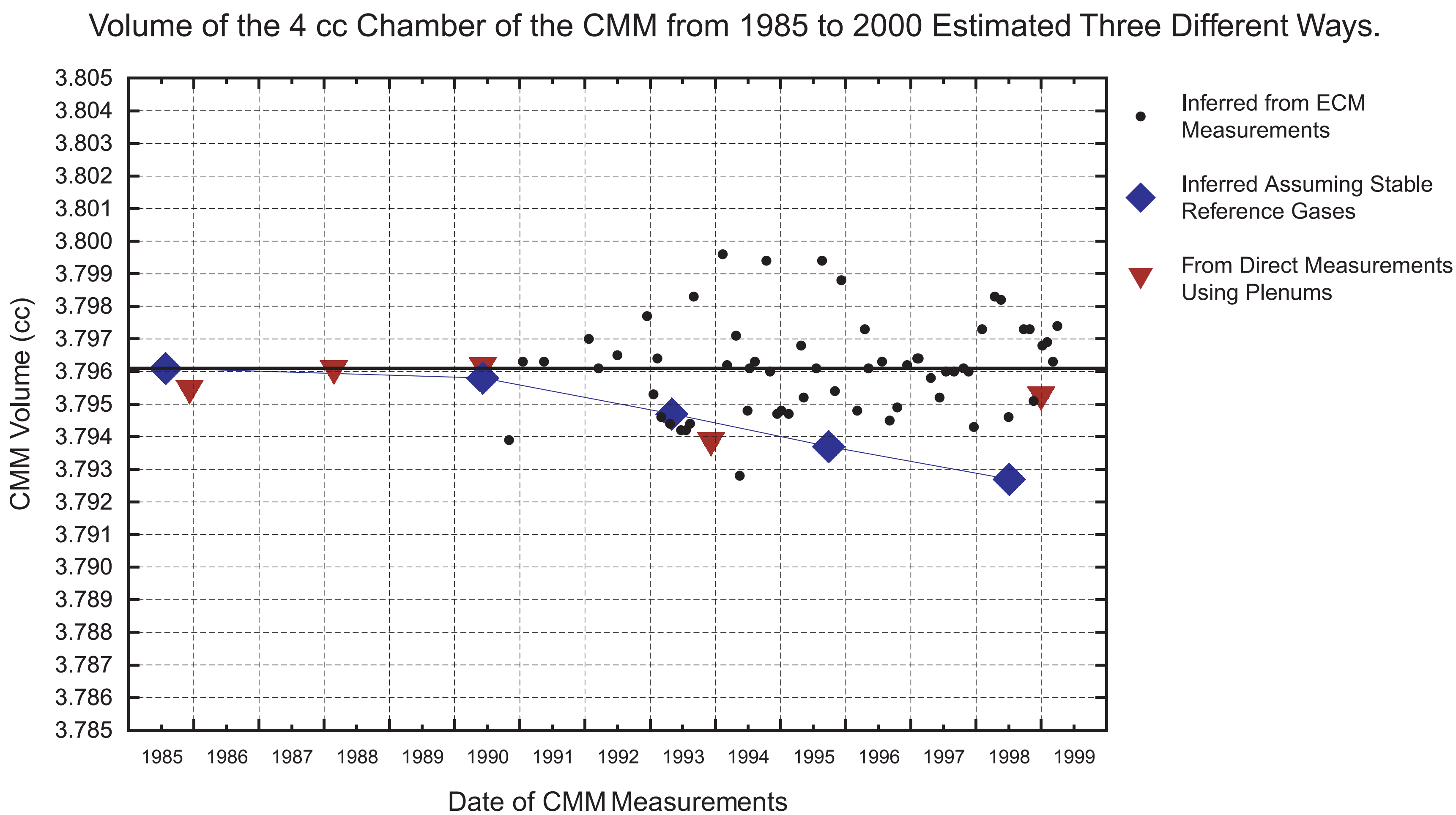

Figure A2. Comparison of the inferred volume of 4 cc chamber of constant-volume mercury-column manometer (CMM) from measurements of archived samples by the ECM (Method (1)) with direct volume measurements using the CMM (Method (2)) and with volumes inferred assuming that our primary reference gas measurements have not drifted (Method (3)). Inferred volumes from ECM measurements are plotted versus dates of original measurement on CMM. All 60 data points from Figure A1 are plotted as solid circles. Their average is shown by a bold horizontal line. Direct volume measurements (Table 6.3 of main report column labeled "Measured Volume") are plotted as large solid triangles. Volumes inferred from measurements of primary reference gases, assumed to be stable on average (Table 6.3 of main report, column labeled "Assigned volume for X99A scale"), are plotted as large solid diamonds, connected by thin line segments.

those in 1998-1999 do not at a significant level.

6. An Alternative Formulation of Cubic Calibration Equations: X99B Scale

As Figure A2 indicates, all three methods of determining the volume of the 4 cc chamber of the CMM agree well from 1985 to 1990, a time when calibrating activities were especially frequent. Taking this agreement into account, as well as the evidence already cited, we propose here an alternative calibration scale, the X99B scale, which assumes an invariant volume for the 4 cc chamber. We use, as a datum, the average of the 51 direct volume calibrations of the 4 cc chamber that were made in 1985-86, 1988, and 1990 (see Tables 5.1 and section 6 of the main report, pp. 18 and 21, respectively). This average volume, 3.79593 cc, based on plenums calibrated with mercury, when combined with the well determined volume of the large ("5000 cc") chamber of the CMM, measured in 1974 (5015.09 cc, see section 5, main report), results in a 5000 cc chamber to 4 cc chamber volume ratio of 1321.176 for the CMM. This ratio is adopted as a datum in the main report to which an inferred variable 4 cc chamber over time after 1985 is anchored (main report, section 6). Application of this invariant manometric volume ratio to the 1985 to 1999 period as the X99B scale, results in differences in manometrically determined mole fractions from those listed in Table 9.5 of the main report and hence the cubic calibration equations used to calibrate other gas mixtures. The cubic coefficients for the X99B scale for the period 1985-1999 as modifications of the coefficients for the X99A scale, listed in Table 7.1 of the main report, have been calculated by multiplying each coefficient by the ratio of the applicable manometric volume ratio listed in Table 6.4 of the main report to the time-invariant volume ratio, 1321.176. Table A4 lists the coefficients of the cubic calibration equations that define the X99B scale, for both CO_2-in-N_2 and CO_2-in-air primary reference gases, for the period from 1985 to 1999. Tbl A4

Table A4. Coefficients of Infrared Analyzer Calibration Equations (Invariant 4 cc Volume Case): X99B Scale

Year	Central Date	C_0	C_1	C_2 $\times 10^4$	C_3 $\times 10^7$
1985 N_2	29 Jul 85	87.5092	0.532420	4.01667E-04	6.71973E-07
1985 Air	29 Jul 85	87.4152	0.540804	4.04841E-04	6.97208E-07
1987 N_2	6 Dec 87	89.3540	0.516378	4.44785E-04	6.41282E-07
1987 Air	6 Dec 87	88.4989	0.532239	4.25385E-04	6.87526E-07
1989 N_2	3 Mar 89	86.3058	0.547567	3.41814E-04	7.52792E-07
1989 Air	3 Mar 89	85.5459	0.562650	3.26690E-04	7.90742E-07
1990 N_2	22 May 90	87.1404	0.533727	3.87620E-04	7.17593E-07
1990 Air	22 May 90	86.8175	0.544578	3.85630E-04	7.42200E-07
1993 N_2	20 May 93	81.7216	0.566042	3.08876E-04	8.16473E-07
1993 Air	20 May 93	78.3455	0.606515	2.15485E-04	9.33726E-07
1995 N_2	9 Jul 95	86.0792	0.539942	3.57975E-04	7.92101E-07
1995 Air	9 Jul 95	83.4300	0.576017	2.71783E-04	9.08357E-07
1997 N_2	19 Aug 97	89.2240	0.519612	4.10200E-04	7.44683E-07
1997 Air	19 Aug 97	90.0638	0.519871	4.37675E-04	7.45508E-07
1999 N_2	1 Jan 99	87.3060	0.538140	3.43424E-04	8.27709E-07
1999 Air	1 Jan 99	87.1627	0.548643	3.38266E-04	8.60887E-07

Note: Calibration equations are cubic polynomials, of the form:
$X = C_0 + C_1\,J + C_2\,J^2 + C_3\,J^3$

For the period prior to 1985, the volume adjustment presented in the main report (Equation 7 of main report, p. 30) is already referenced to the 3.79593 cc datum discussed above. Therefore the calibration of the pre-1985 data for the X99B scale is the same as for the X99A scale. (See section 7 of the main report for details on the use of the equations to convert APC analyzer index values to mole fractions.) In Table A5, the X99B scale, for natural-air reference gases, is compared for the period from 1984 to 1999 with the X99A calibration scale, as reported in the main report. Tbl A5

7. Conclusion

We have presented evidence here that the effective volume of the 4 cc chamber of the CMM has remained constant from 1985 to 1999. A revised series of cubic calibration equations for the APC non-dispersive infrared gas analyzer, creating an alternative X99B calibration of our primary reference gases, assuming an invariant 4 cc

Table A5. Difference in Mole Fractions of CO_2-in-Air Computed with the 1999 Alternative (X99B) Calibration Scale and with the X99A Scale (X99B – X99A), from 1984 to 1999 (in hundredths of a ppm)

YEAR	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
J																
170	0	-1	-1	-1	-1	0	1	2	4	5	8	10	12	15	16	16
180	0	-1	-1	-1	-1	0	1	2	4	6	8	10	13	15	17	17
190	0	-1	-1	-1	-1	0	1	2	4	6	8	11	13	16	18	18
200	0	-1	-1	-1	-1	0	1	2	4	6	8	11	14	17	18	18
210	0	-1	-1	-1	-1	0	1	2	4	6	9	12	14	17	19	19
220	0	-1	-1	-1	-1	0	1	2	4	6	9	12	15	18	20	20
230	0	-1	-1	-1	-1	0	1	2	4	7	9	12	15	18	20	20
240	0	-1	-1	-1	-1	0	1	2	5	7	10	13	16	19	21	21
250	0	-1	-1	-1	-1	0	1	2	5	7	10	13	17	20	22	22
260	0	-1	-1	-1	-1	0	1	2	5	7	10	14	17	20	23	23
270	0	-1	-1	-1	-1	0	1	2	5	8	11	14	18	21	23	23
280	0	-1	-2	-2	-1	0	1	2	5	8	11	15	18	22	24	24
290	0	-1	-2	-2	-1	0	1	3	5	8	12	15	19	23	25	25
300	0	-1	-2	-2	-1	0	1	3	6	9	12	16	20	23	26	26
310	0	-1	-2	-2	-2	0	1	3	6	9	12	16	20	24	27	27
320	0	-1	-2	-2	-2	1	1	3	6	9	13	17	21	25	27	27
330	0	-1	-2	-2	-2	1	1	3	6	9	13	17	21	26	28	28
340	0	-1	-2	-2	-2	1	1	3	6	10	14	18	22	26	29	29
350	0	-1	-2	-2	-2	1	1	3	7	10	14	18	23	27	30	30
360	0	-1	-2	-2	-2	1	1	3	7	10	14	19	24	28	31	31
370	0	-1	-2	-2	-2	1	1	3	7	11	15	20	24	29	32	32
380	0	-1	-2	-2	-2	1	1	3	7	11	15	20	25	30	33	33
390	0	-1	-2	-2	-2	1	1	3	7	11	16	21	26	31	34	34
400	0	-2	-2	-2	-2	1	1	4	8	12	16	21	27	32	35	35
410	0	-2	-2	-2	-2	1	1	4	8	12	17	22	27	33	36	36
420	0	-2	-2	-2	-2	1	1	4	8	12	17	23	28	34	37	37
430	0	-2	-2	-2	-2	1	1	4	8	13	18	23	29	35	38	38
440	0	-2	-2	-2	-2	1	1	4	8	13	18	24	30	36	39	39
450	0	-2	-3	-3	-2	1	1	4	9	13	19	25	31	37	41	41

chamber volume, is formulated and compared with a previous X99A formulation where it is assumed that the manometrically measured concentrations of CO_2-in-air and CO_2-in-N_2 primary reference gases on average remained constant. Adoption of the invariant-volume formulation implies that, on average, the primary reference gas mixtures, both with natural-air and N_2 as the carrier gas, drifted upward in CO_2 concentration by approximately 0.3 ppm between 1985 and 1999 (see Figure 1 of the main report, p. 22). At present we have no explanation for why a drift could have occurred in all of the cylinders of primary reference gas, more or less proportional to CO_2 mole fraction.