

Manometric Analyses of NOAA Primary
CO₂ Reference Gas Standards at SIO

Technical Report by
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Introduction

In March and April of 1999, the Carbon Dioxide Research Group at Scripps Institution of Oceanography (SIO) made analyses on its constant-volume mercury-column manometer (CMM) of the CO₂ content in 8 primary natural air reference standards of the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration. These 8 gas mixtures are a subset of 15 primary reference gas standards whose CO₂ contents have been determined on the CMDL manometer. The CMDL became the Central CO₂ Calibrating Laboratory (CCL) of the World Meteorological Organization in 1995. The set of 15 reference gases constitutes the calibration standard for international measurements of atmospheric CO₂. The intercomparison exercise was designed to compare closely the manometric calibration of CMDL with that of SIO, the designated CCL prior to 1995.

The Data: Table 1

The results of each measurement, in mole fraction (X) of CO₂, are listed in Table 1. (For a detailed description of the methods of measurement and calculation of the results from the original manometric data, see Guenther and Keeling [1981]). Calculation of the mole fraction of CO₂ has until now been based provisionally on a manometric volume ratio (VR), V_{5000cc}/V_{4cc} , determined in 1974 to be 1320.61. "Individual Determinations," in Table 1, represent replicate measurements (usually two) of the CO₂ gas fraction in the small volume chamber (nominally 4 cc) of the manometer combined with a single measurement of the total gas fraction in the large volume chamber (nominally 5000 cc) of the manometer. The column in Table 1 labeled "Run Difference" lists the difference between two independent measurements of each reference gas, determined for two separate aliquots of total gas drawn from the reference gas cylinder. In cases where there are

more than two runs, the differences between successive runs are listed. The column labeled "Overall Average" lists the average of all measurements, usually four, for a particular reference gas. In 1998 the primary reference gas standards of SIO were measured on the CMM [Keeling et al, 2000]. Based upon a hypothesis that the mole fractions of CO₂ of the SIO primary reference gases have, on average, not drifted, a provisional 1998 VR of 1322.30 was assigned. The column in Table 1 labeled "Volume Adjusted" shows the CMDL gas results calculated using the VR assigned in 1998.

The natural air reference gases of both CMDL and SIO contain approximately the normal atmospheric abundance of N₂O, i.e. approximately 1 part in 1000 of the CO₂ abundance. This N₂O gas is included in the manometric measurement of the extracted CO₂ gas. The mole fraction of N₂O in each reference gas, determined by gas chromatography in the laboratory of R.F. Weiss at SIO, is listed on Table 1 in the column labeled "N₂O." The last column in Table 1, labeled "1999" value, lists the CO₂ mole fraction with the N₂O fraction subtracted.

Imprecision of the Data

The data in Table 1 include two sets of replicate measurements. The first replicate is of individual determinations of the CO₂ gas fraction on the small manometer combined with a single total gas fraction measurement, all shown on one line. The second replicate is of completely independent calibrations (termed "Runs" in Table 1), shown on succeeding lines. Estimates of the imprecision of the data set have been made from both kinds of replicate data. The sample standard deviation, s_r , of an individual 4 cc volume measurement, as calculated from the 41 individual determinations of 20 runs, is 0.087 ppm, a dispersion slightly higher than the previous performance (repeatability) of the CMM, arising mostly

from errors in the 4 cc volume measurements.

A similar calculation of the s_i from the replicate run data estimates the imprecision of an entire calibration of a specific gas mixture including the gas transfer and extraction of the CO_2 fraction. The resultant s_i from the data on 18 selected "good" runs of the set of 8 reference gases is 0.192 ppm. This s_i is approximately three times greater than previous performance of the CMM. For comparison, the s_i calculated from the 50 runs of SIO primary reference gases in 1998 was 0.056 ppm. The high dispersion was primarily caused by the analyses of Reference Gases 103 and 105. In both cases, a run had to be rejected due to a blunder that resulted in incomplete extraction of CO_2 from the aliquot. In both cases a total of three "good" runs were eventually made, but with the result that no two of the runs were in satisfactory agreement. The s_i for a run improves to 0.139 ppm if the results for gas 103 are rejected.

Discussion: Table 2

The CMDL and SIO manometric calibration data are compared in Table 2. The result for Reference Gas 103 is about two times the standard deviation away from the average. Because of the difficulties in reproducibility discussed above, it seems justifiable to reject the results for Reference Gas 103. The SIO results on average are then lower than the CMDL calibration data by 0.17 ppm ($s_i=0.14$ ppm) for the remaining 7 gases.

This average difference between the CMDL and SIO manometric calibration data may be due to an incorrectly assigned 4 cc chamber volume in the SIO manometer. Based on the hypothesis that the SIO primary reference gases have not drifted, the volume of the 4 cc chamber for 1998 was determined to be 3.7927 cc. This assignment disagrees with a direct calibration, using 5 calibrated plenums, made in December 1998 and January 1999 yielding 3.7953 cc [Keeling et al,

2000]. Perhaps the effective volume of the SIO small manometer changed between mid-1998, when the SIO primary reference gases were measured manometrically, and the spring of 1999, when the CMDL reference gases were measured. If we use the CMDL manometric values for the seven gases (rejecting Reference Gas 103) to determine the effective VR of the SIO manometer, we find 1321.70 ($s_f=0.44$). Using the same 5000 cc chamber volume (5015.09 cc), this VR implies a 4 cc chamber volume of 3.7944 cc.

If the 1998-1999 volume of 3.7953 cc derived from plenums is used to calculate the CMDL reference gases, the average difference between SIO and CMDL for the seven gases becomes 0.08 ppm, the SIO values higher.

The results reported here should be considered provisional pending further measurements. We have approximately 500 CO₂ samples stored in breakoff tubes that have been measured on the mercury manometer between 1990 and its shut-down in April 1999. This period of time encompasses the period during which measurements of the SIO primary reference gases imply that the effective volume of the 4 cc chamber was shifting to lower values. We plan to run a subset of the saved samples on our Ruska electronic manometer to determine whether the shifting 4 cc chamber hypothesis is supported. There is also a small possibility that the mercury manometer itself may be placed back into operation sometime in the future, and that further calibrations may provide evidence bearing on its performance in 1998 and 1999.

References

Guenther, P. R. and C. D. Keeling, Manometer Report III: Manometric Calibrations of Primary CO₂ Reference Gases During 1974, *SIO Reference Series No. 81-19*, Scripps Institution of Oceanography, La Jolla, CA, 71 pp., 1981.

Keeling, C. D., P. R. Guenther, G. Emanuele, A. Bollenbacher, and D. J. Moss, Scripps Reference Gas Calibration System for Carbon Dioxide-in-air Standards: Revision of 1999, in preparation, *SIO Reference Series*, Scripps Institution of Oceanography, La Jolla, CA, 2000.

Table 1. Manometric analyses of NOAA CO₂-in-air standards during 1999 (ppm mole fraction CO₂)

Cylinder	Run No.	Date of Analysis	Individual Determinations	Run Average	Run Difference	Overall [†] Average	Volume* Adjusted	N ₂ O	1999 [†] Value
110	1	03Mar99	247.13	247.07	247.10				
	2	04Mar99	247.07	247.03	247.05	-0.05	247.075	0.29	246.469
	1	04Mar99	324.59	324.53	324.56				
103	2	05Mar99	324.59	324.53	324.56	0.00	324.560	0.29	323.855
	1	10Mar99	349.08††	349.02††	349.05††				
139	2	10Mar99	353.48	353.54	353.51				
	3	17Mar99	353.10	353.19	353.14	-0.37			
	4	30Mar99	353.80	353.80	353.80	0.66	353.485	0.31	352.723
	1	11Mar99	361.56	361.55	361.56				
105	2	11Mar99	361.37	361.41	361.39	-0.17	361.472	0.31	360.700
	1	25Mar99	369.80	369.94	369.87				
	2	26Mar99	370.30	370.30	370.30	0.43			
136	3	31Mar99	363.73††	363.99††					
		31Mar99	364.10††		363.94††				
	4	13Apr99	370.28	369.97	370.12	-0.18	370.098	0.31	369.315
	1	24Mar99	382.08	382.20	382.14				
101	2	25Mar99	382.09	382.02	382.06	-0.08	382.098	0.31	381.300
	1	18Mar99	396.61	396.69	396.65				
107	2	18Mar99	396.85	396.85	396.85	0.20	396.750	0.31	395.933
	1	16Mar99	453.71	453.78	453.74				
	2	17Mar99	453.96	453.95	453.96	0.22	453.850	0.31	452.960

[†] Using V_{4cc} = 3.7974cc (V_{5000cc}/V_{4cc} = 1320.61) and final meniscus corrections.

* Overall average times 1320.61/1322.30 [using 1998 V_{4cc} = 3.7927cc]

[†] Volume adjusted value minus N₂O

†† Rejected (extraction blunder)

Table 2. NOAA and SIO Manometric Analyses of
NOAA Primary Reference Gas Standards

Cylinder No.	X(NOAA) (ppm)	X(SIO) (ppm)	$\Delta X(\text{SIO-NOAA})$ (ppm)
110	246.59	246.47	-0.12
111	323.96	323.86	-0.10
103	353.37	352.72	-0.65*
139	360.92	360.70	-0.22
105	369.35	369.32	-0.03
136	381.33	381.30	-0.03
101	396.34	395.93	-0.41
107	453.22	452.96	-0.26
		Av. of 8	-0.23
		s_j	0.21
		Av. of 7*	-0.17
		s_j	0.14

* Rejected