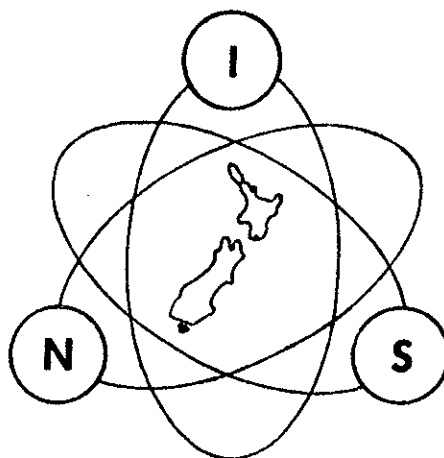


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A Review of CO₂ in Air
Calibration Gas Mixtures used at
Baring Head, New Zealand

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ABSTRACT

Comparative measurements of CO₂ concentrations in calibration gases are made regularly as part of our standard procedures for operating the atmospheric CO₂ monitoring station at Baring Head, New Zealand. In the period from May 1983 to March 1985, 15 CO₂-in-air gas mixtures, obtained from three different sources, were analysed at various times. We were particularly concerned to assess the consistency of air based mixtures, prior to using these rather than Nitrogen based mixtures for routine calibrating of our gas analyser.

Our data imply an inconsistency in the concentrations assigned by the calibrating organizations. This takes the form of an inconsistency within the calibrations supplied by the WMO Central Calibrating Laboratory (CCL) and an apparent difference between the 1985 WMO scale determined by the CCL and separate calibrations provided by the US National Bureau of Standards (NBS). This inconsistency in the definition of the CO₂ concentration scale is a major limiting factor in the precision that can be achieved by atmospheric CO₂ monitoring stations at present.

In the analysis presented here special care has been taken to allow for minor variations in the apparent concentration determined by our gas analyser, due to small variations in the local analyser scale which is derived from different sets of calibration gases at different times. We present a conceptually simple but powerful statistical technique based on generalized least squares analysis, for treating this problem. The technique provides a good identification of instrumental drift and drift in individual calibration gas mixtures, and could have application in other areas where instruments are subject to drifting calibration scales.

KEYWORDS

Atmospheric Composition
Baring Head
Calibrating
Carbon dioxide
Gas analysis
Least Squares Analysis
Infra-red analysis

1. INTRODUCTION

To explain the motivation for some of the analysis and assessments made in this report it is necessary to background the present status of calibrating high precision atmospheric CO₂ measurements.

In order to obtain measurements of atmospheric CO₂ concentrations with a precision of 0.3 ppmv or better using non-dispersive infra red gas (NDIR) analysers, it is necessary to have gas mixtures for calibration purposes which have assigned concentrations with even better precision. In addition it is necessary to make frequent (e.g. hourly) use of such gases to track the calibration of the NDIR analyser, as this is known to drift.

Recognizing the problem of intercomparing results from the different organizations monitoring atmospheric CO₂ concentration around the world, the World Meteorological Organization (WMO) has co-ordinated a mutually agreed policy of using a central calibrating laboratory (CCL) to provide a consistent set of concentrations for calibration gases. Since the inception of this scheme the CCL has been the Scripps Institution of Oceanography, University of California, San Diego (SIO). The CCL has provided a high degree of absolute accuracy in their measurements through use of manometric measurements of CO₂ concentrations. However it is important to realize that the primary benefit to the CO₂ monitoring community has been the maintenance of a set of primary gas standards with assigned concentrations of high relative consistency, and hence internal precision. These primary standards are the basis for assigning concentrations to calibrating gases used by the monitoring sites.

Recently the issue of improving the absolute accuracy has received more prominence. Several groups have reported an ability to produce gravimetrically prepared CO₂ gas mixtures to an accuracy approaching that of NDIR measurements. At a meeting of experts convened by the WMO at Lake Arrowhead, California, in November 1985, it was agreed that there was a need to clearly separate the roles of providing a precise calibration scale for the monitoring network, and of determining the absolute accuracy of values on this scale. The latter role, at least in the USA, is to be performed by the US National Bureau of Standards (NBS).

The agreement to separate CO₂ concentration calibration scales on these lines was demonstrated by the meeting's agreement to report results in a 1985 WMO scale determined by the CCL, even though there was preliminary evidence that this was slightly different from the best absolute scale that could be determined from manometric measurements.

At the international conference on atmospheric CO₂ in Kandersteg, Switzerland, in September 1985, the authors (Manning and Pohl, 1985) presented some data on the consistency of CO₂-in-air gas mixtures used at the Baring Head station, and showed an apparent separation between gas concentrations assigned by CCL and by NBS. These remarks were further amplified in a verbal presentation at the Lake Arrowhead meeting referred to above. In this report we have updated our results to reflect the latest data available on the calibrating gases and have used concentrations assigned by the CCL in the 1985 WMO manometric scale. This revision has reduced but not eliminated the apparent discrepancy between the NBS and CCL assignments.

2. CALIBRATION AND DATA ANALYSIS PROCEDURES

Our data presented in this report were obtained using a URAS-2T non dispersive infra-red (NDIR) gas analyser which was in continuous use at Baring Head, New Zealand. Details of the instrumental system have changed slightly since results from this station were reported by Lowe et al (1979), however the overall philosophy is very similar. Information on the changes that have been made will be covered by a separate report.

Throughout the period concerned the base calibration for the analyser was obtained using a suite of CO₂-in-Nitrogen gas mixtures. However, as the analyser response to CO₂ concentration depends on the carrier gas, CO₂-in-air gas mixtures with known concentrations were analysed at regular intervals. The results for these air gases provide a carrier gas correction which is used to determine atmospheric CO₂ concentrations.

Major analyser calibration "run"s are performed at approximately monthly intervals. In a typical run we repeatedly analyse about 6 CO₂ in Nitrogen gases and about 5 CO₂ in air gases over a 4 to 5 hour period. The Nitrogen gases are used to determine a base calibration scale obtained by a quadratic fit of differences in analyser response to differences in concentrations assigned by the CCL for these gases. Then concentrations on this base scale are assigned to the air gases from the analyser data. The deviations between the values assigned on the base scale for the air gases and their concentrations assigned either by the CCL or NBS are used to determine the carrier gas correction for the analyser.

Theoretical considerations of the carrier gas effect (Griffith et al, 1982) suggest that the carrier gas correction is approximately proportional to CO₂ concentration. Thus if a regression line,

$$E_i = A + B X_i \quad (1)$$

is fit to the deviations E_i for air gases i with concentrations X_i . Then \bar{A} should be near to zero and the data E_i should be distributed about the line with a spread determined by the precision of our analyser measurements. In fact as will be seen below we find that the spread of the data about the line is significantly larger than the analyser precision alone would imply.

The data obtained in these regular calibration runs are also analysed to detect changes over months or years in the concentration of individual gas mixtures, and in the response of the analyser itself. In particular we carefully monitor the carrier gas correction term and the quadratic coefficient for the base scale. It is not practical to run all gas mixtures in each calibration run, and over a long period of time calibration gases are used up and replaced. Such considerations make it necessary to apply analysis techniques over the long term that take into account:

- a. small errors in the assigned concentration for a calibration gas

- b. variations in the analyser response over time, particularly in the carrier gas correction
- c. small variations in the analyser's base scale as determined by different sets of calibration gases at different times
- d. rejection of any implicit weighting of the concentration assigned to a particular gas arising from the frequency of use of that gas.

Before considering the analysis technique further it may be useful for the reader to look ahead at Table 2 which gives the particular set of data to be considered later. This is typical in terms of the frequency of the data and the extent of overlapping of results for different gas mixtures.

In order to separate effects in the data along the lines mentioned above, we separate out a time-dependent factor C and a gas mixture dependent factor D in the data according to:

$$E_{t,i} = C_t + D_i + e_{t,i} \quad (2)$$

where the time-dependence of the deviations E is now written explicitly and e denotes a residual error term. The factors C and D are determined by a least squares approach minimizing the residuals according to

$$\delta \sum_i \{e_{t,i}\}^2 = \delta \sum_i \{E_{t,i} - C_t - D_i\}^2 = 0. \quad (3)$$

In this minimization we vary the C components for each date and the D components for each gas mixture independently, but subject to the constraint

$$\sum_i D_i = 0 \quad (4)$$

which ensures that the gas mixture dependent factor does not produce any net shift in the assigned concentrations as a whole. The D_i will be referred to as the gas mixture offsets from now on.

The deviations $E_{t,i}$ reported here are values of the concentration assigned by the CCL or NBS minus the concentration determined from the base CO₂-in-Nitrogen scale for our analyser. Because of the carrier gas effect, this is positive for CO₂-in-air mixtures and of the order of 3 ppmv. The time dependent factor C_t is effectively the mean carrier gas correction over the range of all CO₂ concentrations considered, for the date t. Variations in this value arise from real variations in the carrier gas correction of the analyser and from small fluctuations in the CO₂-in-Nitrogen scale derived from different sets of calibrating gases at different times.

In the period prior to 1983 our URAS-2T analyser exhibited considerable changes in its carrier gas effect, however for the period discussed below the variation was not significant.

The D_i values represent our best estimate, pooling all measurements, of the difference between the gas mixture concentration assigned by the CCL or NBS and that which we would infer based on fitting all such assigned values to a quadratic curve. Note that positive values imply that the concentration assigned to the gas mixture is higher than implied by our measurements. We will refer to the D_i values as gas mixture offsets. In order to estimate the variation of carrier gas correction with concentration we fit a regression line to the D_i values as

$$D_i = A + B X_i \quad (5)$$

rather than using (1) above.

The separation into factors in (2) above is a form of generalized least squares analysis in statistics but special care is needed in the algorithm used, to allow for the sparsity of the data matrix E. We use a FORTRAN program to analyse our data on a regular basis, and this has been checked by an independent analysis (Rhoades, 1984) using the GENSTAT statistical package.

A similar analysis for the deviations of the CO₂-in-Nitrogen gas mixtures is performed routinely. In this case there is some circularity as all the Nitrogen gases are used to determine the base scale from which the deviation is measured. However the analysis has proved very useful and enables us to detect drift in an individual gas mixture through variation in the $e_{t,i}$ values with time, rather more easily than by examining the original $E_{t,i}$ values.

In general we find that the C_i term for Nitrogen gases is small. It fluctuates about zero and for the period discussed here has a root mean squared value of 0.035ppm. This gives a measure of the variation in the base scale due to varying sets of Nitrogen calibration gases. Although small, the C_i terms do not appear to be entirely random, for example the number of sign changes is significantly smaller than expected from a random sample. Thus we have evidence for small variations in the base scale due to changing sets of calibration gases.

3. RESULTS FOR AIR GASES (1983 - 1985)

The 15 air gases discussed here are summarized in table 1. The 3 NBS gases were obtained in 1983 as NBS Standard Reference Materials 1670, 1671 and 1672, and are supplied in small Aluminium cylinders.

The 4 gases denoted ACO were obtained as CO₂ in synthetic air mixtures prepared by Airco Industrial Gases, New Jersey, to our specifications. As there is no apparent separation of the ACO gases from the others in our data, we will not detail the specifications for the synthetic air or Airco's level of adherence to those. These gases are contained in Aluminium cylinders with a proprietary SpectraSeal coating.

The 8 gases denoted SIO/A or SIO/B are derived from natural air pumped at the Scripps pier in San Diego by SIO. The SIO/A gases are contained in carefully prepared steel cylinders, whereas the SIO/B ones are in Aluminium SpectraSeal cylinders obtained from Airco with original fillings of Nitrogen only.

TABLE 1

Details of CO₂ in Air Gas Mixtures Used

Cylinder No	Source	First Calibration			Second Calibration		
		Concentration (ppmv)	Date	Pressure (psi)	Concentration (ppmv)	Date	Pressure (psi)
9555	ACO	323.83	May 1981	1920	323.71	May 1983	1770
3241	ACO	332.64	May 1981	1930	332.50	May 1983	1750
1205	SIO/B	333.08	Jan 1984	1950			
2425	SIO/A	333.62	Jul 1982	2100	333.50	Nov 1984	2100
18003	NBS	335.6	May 1983				
4231	SIO/B	338.79	Jan 1984	2000			
75902	SIO/A	339.49	Jul 1982	2100	339.54	Nov 1984	2050
619	SIO/B	341.37	Feb 1984	2050			
16995	NBS	342.5	May 1983				
15246	ACO	343.05	May 1981	1930	342.96	May 1983	1750
10068	SIO/A	343.97	Jul 1982	2130	343.96	Nov 1984	2090
18020	NBS	350.9	May 1983				
4515	SIO/B	351.65	Mar 1984	2050			
3758	SIO/A	353.90	Jul 1982	1830	353.96	Nov 1984	1830
14779	ACO	355.11	May 1981	1910	355.09	May 1983	1660

For the NBS gases the concentrations quoted in table 1 are those on the NBS Certificate of Analysis. For all the other gases the concentrations are those given by the CCL in the 1985 WMO manometric scale in a complete revision of all their calibration measurements made in November 1985. Note that the ACO gases were calibrated by the CCL quite independently of the analysis and preparation by Airco Industrial Gases.

TABLE 2

Cylinder Deviations in units of 0.01 ppmv

	Cylinder														
	9555	3241	1205	2425	18003	4231	75902	619	16995	15246	10068	18020	4515	3758	14779
ite															
May83	327	306
May83	323	310
Jun83	325	316
Aug83	328	323	332	375	..
Sep83	327	288	..	320	..	302	..	324	323	..	361	..
Oct83	..	309	..	336	289	..	318	..	300	310	319	314	..	356	329
Nov83	..	305	..	320	284	..	317	..	292	308	316	313	..	350	325
Jan84	..	302	..	327	310	306	315
Feb84	289	296	..	309	311	308	324	323
Apr84	297	309	..	332	296	..	324	..	309	323	334	311	..	349	317
May84	316	306
Jun84	..	300	311	327	281	305	317	309	287	307	317	307	..	357	327
Jun84	326	308	309	..	294	347	..
Oct84	312	..	300
Nov84	315	310
Dec84	..	290	309	318	..	314	301	..	337
Feb85	269	309	284	300	289
Mar85	306	327

There is now evidence that NDIR analysers, operated carefully, can achieve precisions of significantly better than 0.1 ppmv (Tanaka et al, 1983). However if we are to rely on CO₂-in-air calibration gas mixtures as currently available it would appear that this precision will not be achievable between different stations, or for the results of a single station across changes in the sets of calibration gases.

There has been considerable interest recently in determining the level of agreement between concentrations measured by the CCL and by NBS for reasons outlined in the introduction. Our data suggest that there is a small separation which can be quantified as follows. We have taken the distance of the point for each gas mixture from the robust regression line (which was determined without reference to the origin of the mixtures) and calculated means and standard deviations grouped by origin of the mixture as follows:

Table 4

Mean and Standard Deviation of Gas Mixture Offsets
Grouped by Origin

	ACO	SIO	NBS
Mean	-0.01	0.08	-0.15
Standard deviation	0.04	0.15	0.07

This shows that while much of the total scatter in the data comes from the SIO group, it is the NBS group that consistently deviates from the others. We are lead to infer from these results that the NBS calibrations yield concentrations about 0.15 ppmv lower than calibrations of the CCL.

A recent report of the CCL by Guenther et al (1986), detailing results initially presented at the Lake Arrowhead meeting mentioned above, strongly suggests that the WMO 1985 calibration scale should be revised upwards by a factor of 1.000356. This correction is related to changes in the effective volume of the manometer used at the CCL for absolute measurements.

In the concentration range considered here, this will increase the concentrations for the SIO and ACO gas mixtures calibrated by the CCL, by between 0.11 and 0.13 ppmv. The gas mixtures from NBS are unaffected and the apparent difference in calibration scales will become 0.25 ppmv. While both NBS and the CCL quote an uncertainty of 0.20 ppmv in the analyses of individual gas mixtures, the corresponding uncertainty in a comparison of 3 mixtures from one organization with 12 from another could be expected to be 0.13 ppmv. Thus the difference in scales is in our view significant.

In fact our data on the difference in these scales is very close to that reported by Guenther et al (1986). They show (their table 16) a mean difference between NBS and CCL measurements of 0.213 ppmv, in the same direction as shown here, for 6 NBS cylinders whose

contents were aliquots of the gas mixtures used to prepare the standard reference materials we have used. It should be noted that comparisons of other gas mixtures by the two calibrating organizations have produced closer results.

It can be seen from table 4 and from inspection of figure 1 that the ACO group of gas mixtures, based on synthetic air, produce the most consistent results. This suggests that synthetic air based calibration gas mixtures may be more suitable for calibration purposes within the CO₂ monitoring network than the so called natural air used by the CCL and NBS. In fact the air used in those cases is derived from purportedly clean atmospheric conditions but without quantitative assessment of this cleanliness, and subjected to unspecified chemical cleaning processes. We would suggest that such a preparation methodology is not adequate for future international calibration standards.

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