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Further studies of the comparability of baseline atmospheric carbon dioxide measurements

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ABSTRACT

The paper describes an international intercomparison of the major baseline atmospheric carbon dioxide monitoring stations. Six compressed gas tanks, three containing CO_2/N_2 mixtures and three CO_2/air mixtures, were used to check the precision of the intercalibration system and determine the magnitude of the carrier gas error at each station.

For each of the CO_2/N_2 mixtures, the mean concentration for all stations differed by less than 0.3 ppmv from that measured at any one station. In most cases the agreement was better than 0.1 ppmv.

Stations using NDIR analysers with parallel detector cells indicated CO_2 concentrations in the CO_2/air mixtures 3 to 4 ppmv below the average for all stations, while those using series type detector instruments indicated $1\frac{1}{2}$ to 4 ppmv above average. Significant differences between stations using the same detector configurations are suggested to be due to differences in analyser model, length of sample cell and ambient pressure. However, where carrier gas effects for analysers had been measured, they did not fully explain the differences in indicated concentration observed during this study.

Problems of non-linearity in the calibration scale and in the analysers are also shown as possible causes of error up to 0.3 ppmv. Consequently, reported mean atmospheric CO_2 concentration differences between stations of up to 1 or 2 ppmv cannot be interpreted as evidence for large-scale horizontal gradients in the atmosphere.

Methods for improving the comparability of data are discussed with reference to recommendations given by the WMO meeting of "experts on CO_2 monitoring" held at La Jolla in March 1975.

Introduction

High quality measurements of atmospheric carbon dioxide (CO_2) have been made at several monitoring locations around the world during the past 17 years. With the anticipated expansion of the WMO baseline station network, it is likely that the number of stations measuring CO_2 will increase.

It is probably true that the monitoring of secular trends in CO_2 concentration could be accomplished using observations from only one or two suitably located stations. The justification for the expansion in the observation network is the need for more detailed information on the space and time distribution of CO_2 in the atmosphere, leading to a better understanding of large-scale CO_2 transfer in the atmosphere and between the atmosphere and ocean. Interpretation of the data in this way requires high precision inter-station calibration techniques to ensure a high degree of comparability between stations. This particular problem is the main subject of this paper.

At each of the existing stations measurements are made using non-dispersive infrared (NDIR) gas analysers. The precision of these measurements relative to standard reference gases is generally about ±0.2 ppmv (parts per million by volume). The standard reference gases used at all stations, with one exception, are CO_2/N_2 (nitrogen) mixtures calibrated by the Scripps Institution of Oceanography. The exception is the station operated by The University of Stockholm, which uses CO_2/air mixtures as standards, which are also calibrated by the Scripps Institution.

However, it has become increasingly obvious in the last 1–2 years that inter-station systems comparability is lacking in precision, a conclusion reached by a WMO meeting of "experts on CO_2 monitoring" held at La Jolla, California, in March 1975.

Preceding this meeting the author performed a series of gas tank comparisons at several monitoring laboratories during October–November 1974. Non-linearity errors arising in the calibration systems and NDIR analysers were also investigiated. The paper discusses the main results, particularly in the context of the recommendations of the WMO meeting.

An international baseline CO_2 systems intercomparison

Recently the operators of baseline atmospheric CO_2 monitoring programmes have become aware of the so-called carrier gas error that influences the accuracy of their measurements (see Bischof, 1975; Pearman & Garratt, 1975). NDIR CO_2 analysers indicate erroneous results when the carrier gas composition in the calibrating gases differs from that in the air to be measured. Measurements recorded in the above publications, together with further unpublished work in several laboratories, indicate that both the sign and magnitude of the carrier gas error depend on the make and model of analyser used and the ambient pressure at which measurements are made.

Insufficient data are available on the performance of the various types of analysers in use. The author therefore undertook to visit each station during October and November 1974. The purpose was to obtain comparative measurements on gas mixtures containing CO_2 + air and $CO_2 + N_2$, and thus ascertain the precision of the existing system of calibration and the magnitude of the carrier gas effect at each station. (The stations visited, together with some relevant information, are listed in Table 1).

1. General procedure

Six tanks of compressed gas (each containing 1 m^3 of gas at s.t.p., but pressurized to approximately 140 atm) were obtained from the Commonwealth Industrial Gases (CIG) Company in Melbourne. Three of the tanks (coded MM, GG, HH) contained CO_2/N_2 mixtures with CO_2 concentrations covering a small range about the ambient atmospheric value, while the remainder (DA10, DA8, DA3) contained air with a similar range of CO_2 concentrations.

A single CIG pressure-reducing gas regulator was used to extract gas mixtures from the tanks during each analysis.

At each laboratory a standard calibration of the resident NDIR analyser was first performed which involved ten comparisons between each of three Scripps tanks[1] (designated high-H, medium-M and low-L). Only two tanks were used to calibrate the analysers at the Mauna Loa Observatory. For all the analyses CO_2 concentrations were expressed in the Scripps Index Scale (see below).

After the initial calibration, ten comparisons (called Run 1) were made between each of the CIG tanks and one of the Scripp's tanks and then followed by a second standard calibration. Finally comparison Run 2 was performed and then followed by a third standard calibration.

Following inspection of the calibration data a decision was made as to whether the recorder scale factor (sensitivity) could be considered constant or variable with time. In the latter case linear interpolation was used to decide on the best scale factor to use. Some instruments were stable with little or no apparent change in sensitivity, while others were extremely variable (see Table 2).

Using the recorder scale factors determined in this way the concentration of each CIG tank was estimated together with standard deviations for the ten comparisons. These data make up the bulk of Table 2.

2. Stability of the comparison tanks

The CIG tanks were prepared during the five months prior to the experiment. It was planned that throughout this period and following the intercomparisons, calibration would be performed on many occasions against Scripps tanks (Secondary Standards) and our own CO_2/N_2 tertiary standards. Difficulties with leaking valves and concentration instability meant that calibration was performed on only four to nine separate occasions (see Table 3), depending on which tank is considered.

These calibrations show:

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[1] Scripps tanks refer to Secondary Standards provided by the Scripps Institution of Oceanography, being CO_2/N_2 mixtures in 0.05 m^3 steel tanks at initial pressures of about 150 atm. These tanks are calibrated by NDIR comparison with similar tanks, Primary Standards, the CO_2 concentration in the latter having been determined manometrically.

Table 1. *Major baseline atmospheric carbon dioxide monitoring stations*

Each laboratory involved in operating these was visited by the author during the CO_2 systems intercomparison, October–November, 1974

Monitoring station	Agency	Altitude	Type of measurement	Type of analyser
South Pole	(a) Scripps[1]	2.8 km (analysis at sea level)	Flask (1957+) Continuous (1960–63)	A.P.C.[8] A.P.C.
(Antarctica)	(b) NOAA[2]	2.8 km	Continuous (1957+)	URAS 2T[9]
Australia	CSIRO[3]	3.5–12 km (analysis at sea level)	Flask (1972+)	UNOR 2[10] URAS 2
Barrow (Alaska)	(a) Univ.[4] Alaska	26 m	Continuous (1962)	LIRA 200[11]
	(b) NOAA	26 m	Continuous (1973)	UNOR 2
Baring Head (New Zealand)	DSIR[5]	Sea level	Continuous (1972+)	URAS 1[9]
Mauna Loa	(a) Scripps	3.4 km	Continuous (1957+)	A.P.C.
(Hawaii)	(b) NOAA	3.4 km	Continuous (1974+)	URAS 2
North Atlantic	Univ. Stockholm[6]	~10–12 km	Flask (1961+)	UNOR 2 UNOR 5B[10]
Ocean weather ship "P"	(a) Envir.[7] Canada	Sea level	Flask (1974+)	URAS 2T[9], URAS 2
	(b) Scripps	Sea level	Flask (1972+)	A.P.C.
Samoa	NOAA	Sea level	Flask (1973+) Continuous (1975+)	UNOR 2 or URAS 2

[1] Scripps Institution of Oceanography, La Jolla, California, Dr C. D. Keeling.

[2] National Oceanic and Atmospheric Administration, Environmental Research Laboratory, Boulder, Colorado, Mr W. D. Komhyr.

[3] Commonwealth Scientific and Industrial Research Organization, Division of Atmospheric Physics, Aspendale, Australia, Dr G. I. Pearman.

[4] University of Alaska, Department of Meteorology, Fairbanks, Alaska. Not participating now. Dr J. Kelley.

[5] Department of Scientific and Industrial Research, Nuclear Sciences Institute, Wellington, New Zealand, Dr C. D. Keeling and Mr D. C. Lowe.

[6] University of Stockholm, Institute of Meteorology, Stockholm, Mr W. Bischof.

[7] Ocean Chemistry, Environment Canada, Victoria, British Columbia, Dr C. S. Wong.

[8] Applied Physics Company, California. No longer in production.

[9] Hartman and Braun, A.G. Frankfurt/Main.

[10] H. Maihak, A.G. 2000 Hamburg 39.

[11] Mine Safety Appliances, U.S.A.

(1) During the pre-comparison period the measurements on each tank had a standard deviation of <0.21 ppmv. This amount of variance is similar to that commonly experienced from day to day with NDIR analysers.

(2) All tanks except DA8 showed a similar degree of stability during the post-comparison period.

(3) All tanks showed an increase in concentration between the pre- and post-comparison calibrations which, excepting for DA8, was only marginally greater than the ~ 0.2 ppmv precision mentioned above. DA8 showed an increase of 2 ppmv and although the data collected using this tank are included for comparison, they will not be considered further in the discussion.

(4) The small instabilities in the CO_2 concentration in the tanks probably relate to their relatively small size and the fact that they were commercial tanks with no special precautions being taken prior to filling. No attempt was made to ascertain the cause of the drifts in concentration. All tanks contained more than 35 atm pressure at the completion of the experiment.

Table 2. *Results of the international CO_2 systems intercomparison with some additional relevant data*

Institute			*INS, DSIR*	*Scripps*	*NOAA*	*Scripps*	*NOAA*	*NOAA*	*NOAA*	*OC, EC**	*Univ. Stockholm*†	*DAP, CSIRO*
Location			Baring Head	Mauna Loa	Mauna Loa	La Jolla	Boulder	Boulder	Barrow	Victoria	Stockholm	Melbourne
Date			15–16 Oct.	22–23 Oct.	22–23 Oct.	25–27 Oct.	3–4 Nov.	4 Nov.	9–10 Nov.	12–13 Nov.	26–27 Nov.	20 Feb.
Time			0913–0510	1051–0249	1534–0444	1135–1706	0855–0445	0949–1944	1200–1143	1455–1158		0905–1723
Calibration gases:		H	2418 (330.74)	10077 (341.79)	45958 (327.80)	4285 (343.01)	39327 (340.27)	30357 (333.10)	39444 (342.08)	75086 (331.22)	444234 (332.07)	43349 (327.28)
(Tank code and		M	35224 (323.45)	3760 (322.87)	39348 (320.39)	6071 (317.16)	39415 (326.05)	39461 (324.33)	39349 (325.64)	75091 (324.26)	443213 (321.44)	43345 (322.39)
index value)		L	18208 (317.84)			4295 (311.97)	47269 (314.13)	30416 (313.58)	39376 (314.10)	75087 (318.73)	443929 (305.40)	43297 (314.91)
Analyser			URAS 1	APC	URAS 2	APC	UNOR 2	LIRA	UNOR 2	URAS 2	UNOR 5B	UNOR 2
CO_2/N_2 tanks	MM	Run 1	323.48 (.08)	323.56 (.08)	323.56 (.05)	323.85 (.04)	323.75 (.03)	323.69 (.19)	323.83 (.05)	323.83 (.49)	317.07 (.03)	323.65 (.03)
		Run 2	323.54 (.09)	323.57 (.08)	323.74 (.03)	323.72 (.07)	323.66 (.02)	323.78 (.17)	323.75 (.04)		317.14 (.05)	
		Mean	323.51	323.56	323.65	323.79	323.70	323.73	323.79	323.83	317.11	323.65
	GG	Run 1	329.36 (.12)	328.99 (.31)	329.32 (.05)	329.60 (.05)	329.35 (.03)	329.60 (.17)	329.34 (.03)	329.71 (.32)	322.34 (.03)	329.22 (.03)
		Run 2	329.26 (.14)	329.37 (.28)		329.39 (.08)	329.30 (.03)	329.01 (.53)	329.44 (.03)		322.47 (.06)	
		Mean	329.32	329.18	329.32	329.50	329.33	329.31	329.39	329.71	322.41	329.22
	HH	Run 1	334.16 (.05)	333.94 (.18)	333.97 (.07)	334.48 (.03)	334.13 (.04)	335.25 (.24)	334.19 (.04)	333.59 (.31)	327.45 (.05)	334.32 (.06)
		Run 2	334.28 (.07)	334.11 (.13)	334.28 (.06)	334.44 (.08)	334.12 (.02)	334.55 (.19)	334.27 (.03)		327.36 (.03)	
		Mean	334.22	334.02	334.13	334.46	334.13	334.90	334.23	333.59	327.41	334.32
CO_2/air tanks	DA10	Run 1	315.93 (.08)	315.99 (.18)	316.01 (.07)	316.63 (.05)	321.50 (.03)	316.42 (.08)	322.55 (.04)	313.38 (1.62)	316.58 (.08)	323.34 (.02)
		Run 2	316.00 (.05)	316.19 (.13)		316.59 (.05)	321.48 (.03)	316.86 (.20)	322.60 (.05)		316.72 (.07)	
		Mean	315.96	316.09	316.01	316.61	321.49	316.64	322.57	313.38	316.65	323.34
	DA8	Run 1	325.32 (.08)	325.32 (.27)	325.42 (.04)	326.25 (.08)	331.10 (.02)	326.77 (.10)	332.07 (.03)	326.74 (.32)	326.18 (.13)	334.91 (.04)
		Run 2	325.37 (.08)	325.13 (.54)	325.49 (.06)	326.12 (.04)	331.09 (.02)	326.30 (.14)	332.25 (.10)		326.24 (.04)	
		Mean	325.34	325.22	325.46	326.19	331.10	326.54	332.16	326.74	326.21	334.91
	DA3	Run 1	326.51 (.11)	326.91 (.27)	326.62 (.06)	327.16 (.05)	332.11 (0.3)	327.55 (.17)	332.95 (.02)	327.63 (.14)	326.91 (.06)	334.11 (.01)
		Run 2	326.67 (.10)	326.85 (.18)	326.81 (.02)	327.10 (.06)	332.07 (.02)	327.30 (.13)	333.05 (.04)		327.00 (.05)	
		Mean	326.59	326.88	326.72	327.13	332.09	327.43	333.00	327.63	326.96	334.11
Local personnel			D. Lowe	J. Chin	J. Chin	C. Keeling P. Guenther A. Adams	W. Komhyr T. Harris	W. Komhyr T. Harris	L. Westerman C. McIsaacs	C. Wong P. Munro K. Rennie	W. Bischof	D. Beardsmore
Range of recorder scale factors			0.71–0.77 (ppmv div⁻¹)	1.08–1.16 (ppmv div⁻¹)	0.394–0.404 (ppmv div⁻¹)	0.806–0.818 (ppmv div⁻¹)	0.477–0.485 (ppmv div⁻¹)	0.855–0.908 (ppmv div⁻¹)	0.484–0.522 (ppmv div⁻¹)	0.519–1.023 (ppmv div⁻¹)		0.328–0.331 (ppmv div⁻¹)

* During this comparison, the NDIR analyser displayed a large change in sensitivity and zero position. Hence the data are not reliable. Following the measurements, the analyser failed completely (C. S. Wong, personal communication).

† Calibration gases at this laboratory are CO_2/air mixtures.

Table 3. *Measurements made at Aspendale on the six gas tanks used in the international CO_2 systems intercomparison, before and after the experiment*

			1	2	3	4
		Dates	6 June–4 Oct.	14 January	3–4 February	20 February
		Comparison tanks	Secondaries and tertiaries	Tertiaries	Tertiaries	Secondaries
CO_2/N_2 tanks	MM	Mean and S.D.	323.45(.13)	323.79(.03)	323.76(.04)	323.65(.03)
		Days of calibration	4	1	1	1
		No. of comparisons	25	10	8	10
	GG	Mean and S.D.	329.08(.14)	329.45(.03)	329.23(.06)	329.22(.03)
		Days of calibration	9	1	1	1
		No. of comparisons	38	10	6	10
	HH	Mean and S.D.	333.93(.12)	334.14(.03)	334.14(.06)	334.32(.06)
		Days of calibration	8	1	1	1
		No. of comparisons	43	10	7	10
CO_2/air tanks	DA10	Mean and S.D.	322.85(.10)	323.23(.02)	323.35(.06)	323.34(.02)
		Days of calibration	4	1	1	1
		No. of comparisons	29	10	8	10
	DA8	Mean and S.D.	332.02(.21)	333.93(.02)	334.30(.06)	334.91(.04)
		Days of calibration	5	1	1	1
		No. of comparisons	30	10	8	10
	DA3	Mean and S.D.	333.54(.08)	333.85(.03)	333.87(.06)	334.11(.01)
		Days of calibration	4	1	1	1
		No. of comparisons	23	10	7	10

3. Results of the comparison

The following conclusions can be drawn from the data:

(a) The standard deviation about the mean of ten consecutive measurements was, for most of the NDIR analyers investigated, < 0.1 ppmv (see Table 2). Notable exceptions were the APC instruments at Mauna Loa and the URAS 2 at Victoria. For the former, a relatively low sensitivity and drift in analyser output were responsible while in the latter a rapidly changing analyser output and sensitivity occurred which culminated in a complete breakdown of the instrument following the comparison (C. S. Wong, personal communication).

(b) The difference between mean concentrations determined on a given analyser during two separate sets of ten comparisons is generally < 0.2 ppmv.

(c) Large differences between measurements made at Victoria and the mean for all stations are known to be due to malfunction of the Victoria instrument.

(d) With the exception of Stockholm (see later), all stations were shown to be able to measure concentrations for each of the CO_2/N_2 tanks which were within 0.3 ppmv of the mean for all stations. In most cases the agreement was better than 0.1 ppmv. Such agreement is excellent considering the reproducibility of NDIR analysers and the errors which can arise due to non-linearities (see later discussion).

(e) The excellent agreement between stations for measurements on CO_2/N_2 tanks was not found for the CO_2/air tank data. On the basis of the measurements made using the CO_2/air tanks (DA8 excluded), the various stations can be divided into two distinct groups. Those using UNOR analysers (which have series type detectors) indicate CO_2 concentrations higher than the average for all stations, whilst those using APC, LIRA and URAS analysers (having parallel type detectors) indicate CO_2 concentrations that are lower than average. This is consistent with the results of laboratory experiments on the carrier gas effect (Bischof,

Table 4. *Shows the mean and standard deviation of all station estimates for each tank*
Data for Victoria and Stockholm excluded because of instrument malfunction and the use of air reference gases at these stations respectively. The deviation of the station means from the overall mean are shown in the body of the table

	CO_2/N_2 tanks				CO_2/air tanks			
	MM	GG	HH	Mean difference for three CO_2/N_2 tanks	DA10	DA8	DA3	Mean difference for DA10 and DA3 CO_2/air tanks
Mean and standard deviation for all station means	323.67 (0.12)	329.30 (0.12)	334.24 (0.26)		319.83 (3.46)	329.74 (3.99)	330.47 (3.42)	
Deviation of individual station means from mean								
Melbourne (1)	−0.22	−0.22	−0.31	−0.25	+3.02	+2.28	+3.07	+3.05
Baring Head	−0.16	+0.01	−0.02	−0.06	−3.87	−4.40	−3.88	−3.88
MLO–Scripps	−0.11	−0.12	−0.22	−0.15	−3.74	−4.52	−3.59	−3.67
MLO–NOAA	−0.02	+0.02	−0.11	−0.04	−3.82	−4.28	−3.75	−3.79
La Jolla	+0.12	+0.20	+0.22	+0.18	−3.22	−4.55	−3.33	−3.28
Boulder (1)	−0.03	+0.03	−0.11	−0.02	+1.66	+1.36	+1.62	+1.64
Boulder (2)	+0.06	+0.01	+0.66*	+0.24(+0.04)*	−3.19	−3.20	−3.04	−3.12
Barrow	+0.12	+0.09	−0.01	+0.07	+2.74	+2.42	+2.53	+2.64
Victoria	+0.16	+0.41	−0.65	−0.03	−6.45	−3.00	−2.84	−4.65
Stockholm	−6.60	−6.96	−6.79	−6.78	−3.18	−3.53	−3.51	−3.35
Melbourne (2)	+0.08	+0.15	−0.10	+0.04	+3.40	+4.19	+3.38	+3.39
Melbourne (3)	+0.09	−0.07	−0.10	−0.03	+3.52	+4.56	+3.40	+3.46
Melbourne (4)	−0.02	−0.08	+0.08	−0.01	+3.51	+5.17	+3.64	+3.58

* Large difference without obvious explanation. Difference in parentheses excludes this value.

1975; Pearman & Garratt, 1975). Closer scrutiny, however, does reveal a number of potentially important discrepancies between the present measurements and the previously determined carrier gas effects.

(f) A comparison of the measurements made on the CO_2/N_2 tanks at different stations shows that a large discrepancy exists between the mean values determined at Stockholm and the mean for all other stations (see Table 4). The Stockholm station uses CO_2/air reference gases calibrated by the Scripps Institution so that carrier gas errors occur during the initial calibration of the Stockholm tanks and again during the measurement of the CO_2/N_2 CIG tanks. At the WMO meeting of experts, Keeling (personal communication) indicated that the carrier gas error for the APC analyser used for calibration at Scripps is −3.9 ppmv. That is, when the instrument is calibrated with CO_2/N_2 mixtures and used to measure CO_2/air it reads low by this amount. Bischof (1975) indicates a carrier gas error for his UNOR 5B of +3.8 ppmv. Thus one would expect the discrepancy between measurements made at Stockholm and La Jolla on CO_2/N_2 mixtures to be about 7.7 ppmv. The average of the observed discrepancy for the three CO_2/N_2 tanks was 7.0 ppmv (from Table 4). Thus the observed difference is some 0.7 ppmv smaller than the expected difference.

Similarly, at ambient CO_2 concentrations, the carrier gas effect for the Melbourne UNOR 2 used in the comparison has been measured by methods described by Pearman & Garratt (1975), to be +4.6 ppmv (+4.3 due to 21% O_2, see Fig. 1, and 0.3 due to 1% argon, see Fig. 2), giving an expected difference between the indicated CO_2 concentration in the CO_2/air tanks at Melbourne and at La Jolla of 8.5 ppmv. The observed differences (in Table 4) for tanks DA10 and DA3 were 6.7 and 7.0 ppmv respectively.

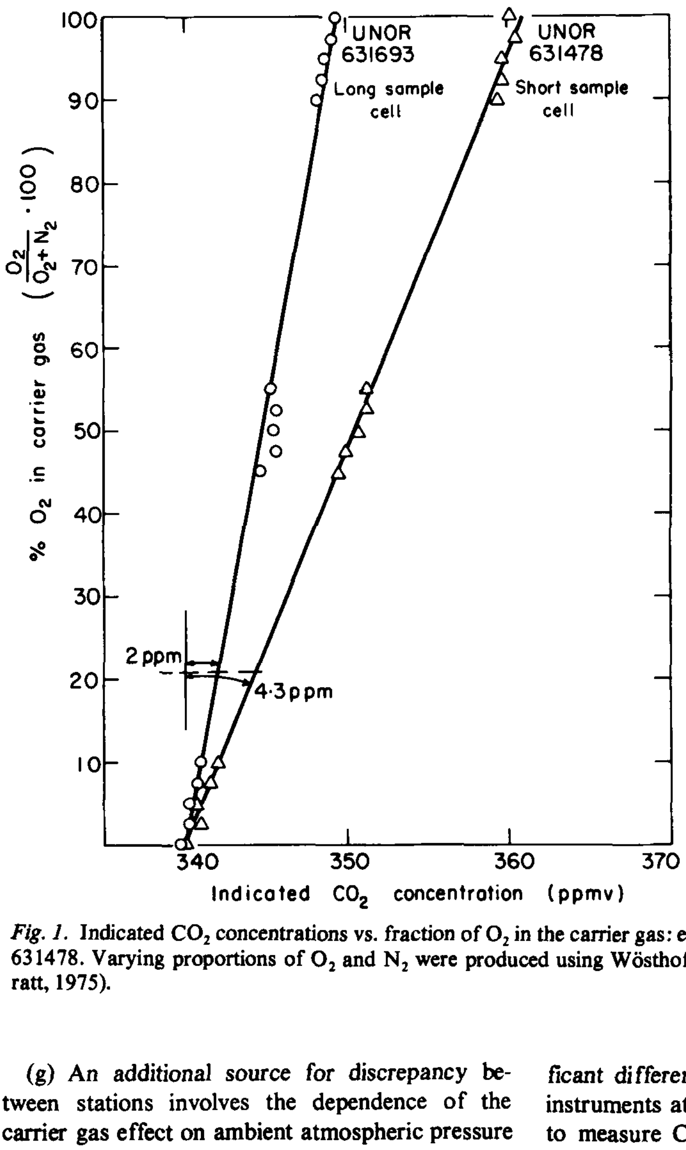

Fig. 1. Indicated CO_2 concentrations vs. fraction of O_2 in the carrier gas: experimental data for UNOR 2 631693 and 631478. Varying proportions of O_2 and N_2 were produced using Wösthoff gas mixing pumps (see Pearman & Garratt, 1975).

(g) An additional source for discrepancy between stations involves the dependence of the carrier gas effect on ambient atmospheric pressure and hence station altitude (see Pearman & Garratt, 1975). It should be noted however, that the La Jolla, Melbourne and Stockholm measurements discussed in (f) above were made at sea level and therefore at nearly equal ambient pressures.

In contrast, a comparison of the two UNOR 2's used by NOAA at Boulder and Barrow (Table 2) shows that the Boulder instrument read CO_2/air mixtures lower than the Barrow instrument by ~1 ppmv, consistent with the altitude pressure difference between the stations of ~ 1.6 km, (see Pearman & Garratt, 1975). On the other hand, no significant difference was observed between the APC instruments at Mauna Loa and La Jolla when used to measure CO_2/air mixtures, despite an altitude difference of ~3 km. This is surprising as a similar altitude difference was shown by Pearman & Garratt (1975) to cause a difference in carrier gas effect of ~0.6 ppmv when measurements were made with a URAS 2. Similarly there appears to be no significant difference between the indicated CO_2 concentration in the CO_2/air tanks when measured at Baring Head (URAS 1) and Mauna Loa (URAS 2 and APC). Bischof (1975) ascribes a carrier gas effect of −4.9 ppmv to his URAS 1 while Keeling (personal communication) gives a value of −3.9 ppmv for the La Jolla APC. If we assume that the

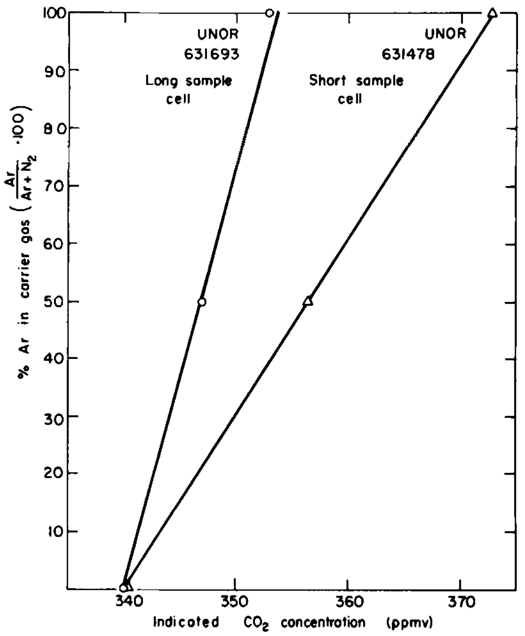

Fig. 2. Indicated CO_2 concentration vs. fraction of argon in the carrier gas.

Mauna Loa APC instrument has a similar carrier gas effect to the La Jolla instrument then it is difficult to explain why the difference between these carrier gas effects, i.e. 1.0 ppmv (plus an amount due to the decrease in carrier gas effect at the altitude of Mauna Loa), was not observed during the intercomparison. Indeed (f) and (g) above indicate that our present knowledge of the carrier gas effect cannot adequately explain the differences in measurements at these stations to better than 1 to 2 ppmv.

(h) Yet another source for discrepancy relates to variations in cell length between analysers of the same model. Laboratory data from Aspendale (Figs. 1 and 2) show that a short-celled UNOR 2 has a carrier gas effect of 4.6 ppmv at ambient CO_2 concentration, whilst a long-celled instrument has a smaller effect of about 2.1 ppmv. Bischof (1975) showed effects of 3.8 ppmv and 1.3 ppmv for short- and long-celled UNOR's respectively. Table 2 shows that the Melbourne UNOR 2 (short cell) indicates CO_2 concentrations in CO_2/air mixtures which are higher than those for the UNOR 2 (long cell) at Barrow by ~1 ppmv, consistent with the above.

4. Non-linearities as a source of error

The Scripps Secondary Standard tanks which serve as the basis of the global calibration system are ascribed "index" concentrations which relate linearly to the recorder scale differences observed during the comparisons of tanks using an APC instrument. The "index" concentration relates back to approximate concentrations ascribed to two primary tanks established in 1958. In 1959 Dr C. D. Keeling used manometrically determined concentrations to relate the "index" concentrations to actual concentrations. The relationship was found to be:

$$J = (I - 311.51)1.2186 + 311.51 \qquad (1)$$

where J is the actual CO_2 concentration according to the 1959 manometric calibration and I is the "index" value. Because this relationship is linear it has been accepted practice to calibrate analysers using "index" values, linearly interpolate to determine "index" concentrations of air, and then convert these concentrations to actual concentration using eq. (1).

Recently, further manometric measurements by Dr C. D. Keeling and Mr P. R. Guenther (personal communication) have indicated that the relationship between actual CO_2 concentration (x)[1] and the "index" scale is not linear and that the 1974 scale deviates significantly from the 1959 manometric scale. Dr Keeling has proposed the use of the following relationship to obtain actual concentrations from data quoted in the 1959 manometric scale:

$$X = 76.58 + 5.84910 \times 10^{-1}J + 3.1151 \times 10^{-4}J^2 + 7.3225 \times 10^{-7}J^3 \qquad (2)$$

Errors can arise whenever linear interpolation is used and either the instrument or the calibration scale is not linear. The APC NDIR CO_2 gas analyser by definition responds linearly with respect to the "index" concentration scale. That is it is nonlinear with respect to actual concentration. In this case it is therefore legitimate to use linear interpolations between the "index" values of two calibration tanks to ascribe an "index" value to an un-

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[1] At the WMO sponsored Expert Meeting on Carbon Dioxide Monitoring held at La Jolla, March 1975, it was recommended that this new scale be referred to as the WMO 1974 CO_2 Calibration Scale.

known. The latter can be then converted to actual concentration using eqs. (1) and (2).

An alternative instrument, for example the short-celled UNOR 2 used in Melbourne, is very near to linear with respect to actual concentration. In this case it is legitimate to make linear interpolation using the WMO 1974 scale, but not the "index" scale.

Consider the reference gases actually used in the intercomparison at La Jolla and Melbourne (see Table 5). In each case the measured index value is given after interpolation using the "index" scale and the WMO 1974 scale. The table demonstrates that under the conditions of the example, errors of up to 0.3 ppmv can result depending on what linearity assumptions are made.

Throughout this paper I have assumed, as is normal practice at baseline stations, that all analysers are linear with respect to the "index" scale. We know that our short-celled analyser is linear with respect to actual concentration while the longer-celled UNOR is non-linear. At present we do not know the linearity characteristics of all the analysers used, but it should be clear from the above example that differences between station measurements of a few tenths of a ppmv might result in this way.

5. Conclusions

The ability of this intercomparison to define the inter-station precision of the CO_2 monitoring network was limited by the reproducibility of the NDIR analysers and the drifts of concentration of the gases which were circulated. Excluding tank DA8, the tanks appeared to increase in concentration by slightly more than 0.2 ppmv which is the day-to-day variation expected for NDIR analysers.

Thus differences of greater than about 0.5 ppmv were considered to be indicative of real errors. Such differences were not obtained during the CO_2/N_2 cylinder comparison, thus confirming the high degree of precision of the Scripps Secondary Standard tanks.

In the case of the CO_2/air measurements however, aside from the major difference of about 5 to 8 ppmv between parallel and series detector instruments, there were differences between instruments of the same detector configuration which exceeded 0.5 ppmv.

We have evidence that some of these differences are due to sample cell size, ambient pressure and instrument model. However, in those cases where laboratories had determined the carrier gas effect for their own instruments, the measured errors did not equal those observed during the intercomparison. As this discrepancy is about 1 to 2 ppmv, this would appear to be the relative precision of the global network at present. Since published differences in mean annual concentration between network stations are also of this order, we cannot at this stage use these differences as evidence for global scale concentration gradients of CO_2.

Table 5. *Shows the discrepancies in concentrations ascribed to CO_2/N_2 tanks when linear interpolation is made using the non-linear "index" concentration scale or the linear WMO 1974 concentration scale*

	Reference tank code	Ascribed index concentration (ppmv)	Equivalent WMO 1974 concentration (ppmv)	Interpolation using index scale		Interpolation using WMO 1974 scale	
				Index (ppmv)	WMO 1974 (ppmv)	Index (ppmv)	WMO 1974 (ppmv)
At La Jolla	4285	343.01	350.74	—	—	—	—
	4295	311.97	311.71	—	—	—	—
	MM	—	—	323.79	326.22	324.07	326.57
	HH	—	—	334.46	339.69	334.69	339.99
At Melbourne	43349	327.28	330.59	—	—	—	—
	43345	322.39	324.48	—	—	—	—
	MM	—	—	323.65	326.05	323.65	326.05
	HH	—	—	334.32	339.51	334.22	339.39

Accepting that these carrier gas effects exist and need to be corrected for, the WMO "meeting of experts" recommended that the following remedial action be taken:

(i) CO_2/N_2 reference gases should continue to be used for calibrations. An investigation of the long-term stability of CO_2/air mixtures should begin with the objective of eventually replacing N_2 with air as the carrier gas if it can be demonstrated that the latter behaves identically to the former.

(ii) A continuing programme of CO_2 analyser system checks be implemented around the world using the following methods:

(a) Periodic shipment from the WMO Central CO_2 Laboratory (at the Scripps Institution) to field stations of calibrated CO_2/air reference gases.

(b) Weekly, parallel CO_2 flask and analyser sampling at field stations, with subsequent analysis of the flask samples at central facilities, augmented by periodic exchanges and analyses of selected samples of atmospheric CO_2 by the central facilities and the WMO Central CO_2 Laboratory.

(c) In addition it would be desirable to compare field station analysers with a portable CO_2 analyser using reference gases traceable to the WMO Primary Reference Gases.

In addition to these recommendations, each station or group of stations (e.g. national group) should make every attempt to ascertain by experiment the carrier gas error of their own analysers and the dependence of this error on pressure.

The WMO "meeting of experts" considered that each baseline station should acquire a minimum of four secondary reference gases from the WMO Central CO_2 Laboratory. In this way each station would be able to satisfactorily establish the linearity of its analyser(s) with respect to the WMO 1974 CO_2 Calibration Scale.

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ДАЛЬНЕЙШЕЕ ИЗУЧЕНИЕ СРАВНИМОСТИ БАЗОВЫХ ИЗМЕРЕНИЙ ДВУОКИСИ УГЛЕРОДА

В статье описываются результаты международного сравнения датчиков базовых станций, следящих за концентрацией углекислого газа в атмосфере. Для проверки точности системы взаимной калибровки и определения величины ошибки, связанной с несущим газом для каждой станции, использовались шесть баллонов со сжатым газом, три со смесью CO_2–$И_2$ и три со смесью CO_2–воздух. Для каждой из смесей CO_2–$И_2$ средняя концентрация для всех станций отличалась меньше, чем на 0,3 ppmv от измеренной на любой из станций. В большинстве случаев согласие было лучше, чем в 0,1 ppmv. Станции, использующие анализаторы NDIR с параллельными детектирующими ячейками указывали концентрации CO_2 в смеси CO_2-воздух от 3 до 4 ppmv ниже среднего для всех станций, в то время как станции, использующие приборы с детекторами серийного типа, показывали от 1,5 до 4 ppmv выше среднего. Предполагается, что значительные различия между станциями, использующими одинаковые детекторы, возникают из-за различий в моделях анализатора, в длине заборной ячейки, в величине давления окружающего воздуха. Однако, когда были измерены эффекты несущего газа на анализатор, то это не объяснило полностью различия в покузаниях концентрации, наблюдавшиеся во время этого сравнения.

В качестве возможных источников ошибок до 0,3 ppmv указываются нелинейности в калибровчной шкале и в анализаторах. Следовательно, сообщавшиеся разницы в концентрациях атмосферного CO_2 между станциями, достигавшие от 1 до 2 ppmv не могут интерпретироваться как указание на существование крупномасштабных горизонтальных градиентов в атмосфере.

Обсуждаются методы улучшения сопоставимости данных измерений со ссылкой на рекомендации, данные конференцией экспертов по мониторингу CO_2, созванной ВМО в Ла-Хойе в марте 1975 г.