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Calculations of carrier gas effects in non-dispersive infrared analyzers. II. Comparisons with experiment

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ABSTRACT

A numerical model for calculating carrier gas effects in non-dispersive infrared gas analyzers was presented in the preceding paper. This model is applied here to sets of data from several analyzers used in measuring atmospheric CO_2 concentrations at a world-wide network of baseline stations. The agreement between the model and the experimental results is generally satisfactory, and the model can be used to better understand the behaviour of non-dispersive analyzers.

1. Introduction

When non-dispersive infrared (NDIR) gas analyzers are used to measure atmospheric CO_2 concentrations, carrier gas corrections arise because at most measuring stations analyzers are calibrated with gas mixtures of CO_2-in-nitrogen whereas the sampled air contains oxygen, argon, and other minor constituents. The resulting corrections, of the order of 1%, cannot be neglected if the measurements are to achieve the precision required in atmospheric CO_2 studies at baseline stations (Bischof, 1975; Pearman and Garratt, 1975; Keeling et al., 1976; Pearman, 1977).

In the preceding paper, a numerical infrared spectral model was described for calculating the changes in instrument response which arise in NDIR analyzers when the composition of the diluent, or 'carrier', gas in the sample cell is changed. In brief, the model assumes that the analyzer's response is proportional to the radiative energy absorbed in the detector. This assumption has been shown by Hill and Powell (1968) to be a good approximation for NDIR condenser microphone detectors of the kind used at these measuring stations. In the model the absorbed energy is calculated from the known CO_2 spectrum, analyzer cell lengths, and other related parameters using a digital computer. Changes in carrier gas are simulated by varying the line-broadening factors for the gases in the analyzer's sample cell. The method was shown to give negligible numerical errors and reasonably precise predictions.

In this paper we present sets of data on the carrier gas effect from two laboratories and four different analyzers, and we compare these data with calculations using the spectral model. The generally good agreement between prediction and observations gives us sufficient confidence in the model that we are able to establish several practical points related to routine calibrations of NDIR analyzers in current use.

2. APC analyzers[2]

The longest running and most extensive atmospheric CO_2 measurement program has been that of

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[2] Applied Physics Corporation, Pasadena, California, U.S.A. These NDIR analyzers (model no. 70) are no longer in production, but have been used since the inception of the Scripps CO_2 measurement program. The analyzer discussed here was manufactured in 1956.

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the Scripps Institution of Oceanography (SIO), La Jolla, California which began in 1957. In 1974 this laboratory established accurate CO_2 reference gas standards on which the 1974 CO_2 mole fraction scale of the World Meteorological Organization and most other atmospheric CO_2 measurements are based (Keeling et al., 1976; WMO, 1977). The mole fraction of CO_2 in these gas mixtures was determined using a precise constant volume manometer. The mixtures were then compared with each other and additional gas standards using APC analyzer, serial no. 55 (referred to below as analyzer 55).

Investigations of carrier gas effects were also carried out using the manometer and analyzer 55. The results of these studies, based on data obtained mainly in 1974, are presented here for comparison with predictions of the spectral model. Additional studies in which CO_2 mole fractions were volumetrically determined are also discussed.

Concentrations of CO_2-in-air from SIO have been routinely reported on an "adjusted index scale" (Keeling et al., 1976), which we will denote by the symbol, J, and refer to as the "APC index". This scale is by definition linearly related to the response of analyzer 55 to CO_2-in-N_2 gas mixtures and by choice has values (called here "index units") similar to true concentrations expressed as mole fractions in parts per million of dry air (p.p.m.) near the CO_2 concentration of normal air. To obtain CO_2 concentrations in air based on the 1974 WMO scale the APC index, J, must firstly be corrected for the change in carrier gas. For CO_2-in-air gas mixtures analyzed with analyzer 55, this has been done (Guenther and Keeling, 1981) in practice by multiplying J by a factor:

$$G(P) = 1.01201(1.003157 - 2.237 \times 10^{-6} \cdot P - 2.522 \times 10^{-9} \cdot P^2) \quad (1)$$

where P is the total gas pressure in mm Hg within the instrument sample cell. The resulting product

$$J_c = G \cdot J \quad (2)$$

is converted to the WMO scale, denoted by X, using the cubic expression

$$X = 76.582 + 0.584910\ J_c + 3.1151 \times 10^{-4} \cdot J_c^2 + 7.3225 \times 10^{-7} \cdot J_c^3 \quad (3)$$

The already published coefficients in eqs. (1) and (3) were obtained from the experimental fits of the manometric data obtained in 1974. Eq. (3) is applicable for CO_2-in-N_2 mixtures by setting $G = 1$. The term "derived manometric APC index", symbol $J_m(X)$, will be used to refer to calculated values of J_c obtained from inversion of (3) when the mole fraction X is known from manometric data.

As discussed in more detail in the preceding paper, the CO_2 spectrum for the model calculations is obtained from the AFGL listing of line parameters (McLatchey et al., 1973; Rothman, 1978), and from relative line broadening factors for N_2, O_2, Ar, and CO_2 as given by Burch et al. (1962, 1969). For analyzer 55 the sample cell length is 40.6 cm, the detector path length is 4.7 cm, assuming 90% reflection from the polished stainless steel rear wall, the detector is nominally filled with a 1.3% CO_2-in-air mixture, and the instrument is thermostatted to 50°C. Infrared windows are of silver chloride and sapphire.

A comparison of the experimentally obtained APC index, J, with the instrument response, R, computed by the spectral model provides an initial test of the model's predictability. Table 1 lists experimental values of X and J, and calculated values of R, for the ten CO_2-in-N_2 mixtures used at Scripps in order to determine the relationship of X to J for analyzer 55 (eq. (3)) (Guenther and Keeling, 1981). The model calculations to determine R for prescribed values of X were performed as outlined in the preceding paper. R is in arbitrary units but would be linearly related to J if the calculations were exact, so for comparison of R with J, values of calculated index, J_R, have been determined from R by a linear-least-squares fit of R to J. The values of J_R, and of the residuals $J_R - J$, are listed in Table 1 and the residuals are plotted against X in Fig. 1. As can be seen, $J_R - J$ does not exceed 1.8 index units in the range 200–470 p.p.m., and thus the model-predicted response agrees quite well with observations. This good agreement gives us confidence that the response of analyzer 55 is closely proportional to the radiative energy absorbed in the detector as assumed by the model, and that the model calculates this absorbed energy well although not within the dispersion of measurements (root mean square departure from eq. (3) of 0.09 p.p.m.).

Exhaustive attempts to reduce the non-linearity between the model and experimental data by varying physically reasonable model assumptions

Table 1. *Experimental and calculated responses of an APC analyzer for CO_2-in-N_2 mixtures*

CO_2 mol. frac.* X (p.p.m.)	APC index† J (index units)	Calc. response R (arb. units)	Calc. index J_R (index units)	Residual $J_R - J$ (index units)
196.90	180.83	40.3447	179.07	−1.76
246.02	241.32	38.4859	241.34	0.02
276.80	275.55	37.4421	276.31	0.76
310.82	311.17	36.3775	311.98	0.81
324.05	324.23	35.9857	325.10	0.87
332.78	332.82	35.7334	333.55	0.73
355.60	354.47	35.0959	354.91	0.44
380.56	377.02	34.4321	377.15	0.13
415.06	406.55	33.5663	406.16	−0.39
472.97	452.55	32.2297	450.94	−1.61

* Determined manometrically.

† Determined with APC analyzer, serial no. 55, at the Scripps Institution of Oceanography.

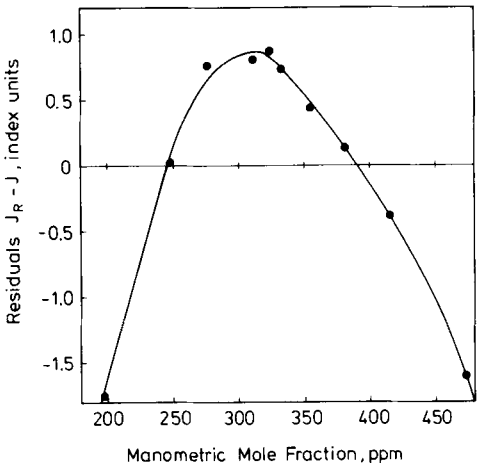

Fig. 1. Residuals $J_R - J$ from calculated and observed responses of APC analyzer 55 to CO_2-in-N_2 mixtures.

were unsuccessful. The small residual-linearity may be due either to errors in the model assumptions or to non-linearity in the amplifier electronics. The latter, however, should be small since the electronics are of null-balance type.

Data from SIO on measured carrier gas shifts

$$\Delta_{obs} = J - J_m(X) \tag{4}$$

fall into three groups which are now treated separately.

2.1. *Volumetric data*

In 1974 a series of experiments was performed in which mixtures of CO_2 in pure N_2, O_2 and Ar were prepared. CO_2 mole fractions lying between 240 and 440 p.p.m were determined by volumetric methods independent of the precision manometer in which CO_2 in calibrated 1.3 to 2.3 ml pyrex glass plenums at ambient pressure was mixed with pure O_2, N_2, and Ar in calibrated 5 l glass flasks also at ambient pressure. The APC indices of these gas mixtures were obtained with analyzer 55. The data for CO_2-in-N_2 were used to derive a best-fit cubic relationship analogous to eq. (3) between the volumetrically-determined mole-fraction, X, in p.p.m., and the APC index, J. This relationship:

$$X = 39.706 + 0.93795 \cdot J_c - 8.0035 \times 10^{-4} \cdot J_c^2 + 1.8923 \times 10^{-6} \cdot J_c^3 \tag{5}$$

is slightly different (less than 0.1% in the range of interest) from the manometric calibration eq. (3), presumably for reasons of an unidentified systematic error. The term "derived volumetric APC index", symbol $J_v(X)$, will be used to refer to values of J_c obtained from inversion of eq. (5) when the mole fraction X is known from volumetric data. The carrier gas effects for pure O_2 and pure Ar against N_2 are determined from corresponding J and $J_v(X)$ values, analogous to eq. (4).

To compare experimental and model-calculated carrier gas shifts for O_2 versus N_2, calculations were performed as follows: firstly the calculation of the response, R, for CO_2-in-N_2 was repeated at closely spaced values of X in the range from 200 to 450 p.p.m. This was followed by calculations of R at the experimental values of X for CO-in-O_2 by replacing the line-broadening factor $F(N_2)$ by $F(O_2)$, leaving all the other model parameters the same. CO_2 mole fractions in N_2 and O_2 corresponding to the same R value were then determined by interpolation of R versus X for CO_2-in-N_2. These values of X, denoted X_{N_2} and X_{O_2}, were converted to derived volumetric APC indices $J_v(X_{N_2})$ and $J_v(X_{O_2})$ by inversion of eq. (5) and the carrier gas shift

$$\Delta_{calc} = J_v(X_{N_2}) - J_v(X_{O_2}) \quad (6)$$

was then calculated. Values of Δ_{calc} were consistently 6 index units higher than those given by experiment when the value from Burch et al. (1962) of $F(O_2) = 0.81$ was used in the calculation. However, increasing $F(O_2)$ to 0.853, a value within the uncertainty stated by Burch et al. (1962), gave optimal agreement with the data. The observed and calculated carrier gas shifts are shown in Table 2a and Fig. 2a. The results for analogous treatment of the CO_2-in-Ar data are shown in Table 2b and Fig. 2b. The larger scatter is due to poorer concordance of the experimental results. (The root mean square departure from cubic best fit was 0.20 p.p.m. for CO_2-in-O_2, 0.62 p.p.m. for CO_2-in-Ar.) The F(Ar) value of 0.783 which gives the optimal fit agrees well with previous literature values of 0.78 (Boulet et al., 1972, 1974) and 0.76 (Burch et al., 1962), as described in the preceding paper.

2.2. *Manometric data*

We next describe calculations to compare with manometric experiments carried out with analyzer 55 on CO_2 in carrier gas mixtures containing approximately 20, 40, 60 and 80% O_2-in-N_2, as well as pure O_2 and air. Some of these measurements were carried out in 1980 as a supplement to the measurements of 1974. Oxygen percentages were measured to ±0.1% by mass spectrometry. The data are tabulated in Table 3 along with matching calculations of the carrier gas shifts defined analogously to eq. (6). Line broadening factors for air are calculated from

$$F(\text{air}) = 0.781\,F(N_2) + 0.210\,F(O_2) + 0.009\,F(\text{Ar}) \quad (7)$$

Table 2. *Experimental and calculated carrier gas shifts for CO_2-in-O_2 and CO_2-in-Ar mixtures for an APC analyzer*

	CO_2 mol. frac.* X (p.p.m.)	APC index† J (index units)	Carrier gas shifts: observed Δ_{obs} (index units)	Carrier gas shifts: calculated Δ_{calc} (index units)
(a)	CO_2-in-O_2 mixtures			
	242.39	224.21	−12.97	−12.33
	275.01	258.93	−14.49	−14.55
	309.08	292.94	−16.20	−16.55
	330.59	312.77	−17.73	−17.66
	347.98	328.89	−18.21	−18.46
	391.74	366.37	−19.98	−20.18
	438.34	403.42	−21.04	−21.61
(b)	CO_2-in-Ar mixtures			
	241.63	215.90	−20.41	−19.38
	274.51	249.90	−22.98	−22.84
	307.96	282.70	−25.30	−25.90
	329.15	301.65	−27.45	−27.58
	346.73	317.42	−28.51	−28.83
	390.23	354.84	−30.21	−31.48
	437.02	389.63	−33.80	−33.71

* Determined volumetrically.
† Determined with APC analyzer 55 at SIO.

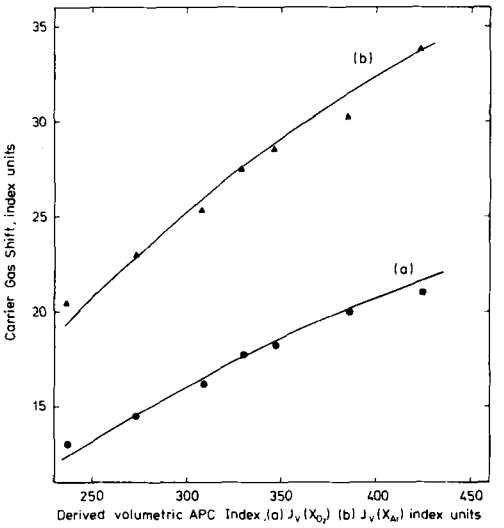

Fig. 2. Calculated and observed carrier gas shift versus CO_2 adjusted index for (a) CO_2-in-O_2 and (b) CO_2-in-Ar mixtures. The points are observed shifts, the lines are calculated with $F(O_2) = 0.853$ and $F(\text{Ar}) = 0.783$.

Table 3. *Experimental and calculated carrier gas shifts for CO_2-in-air and CO_2-in-N_2, O_2 mixtures for an APC analyzer*

	CO_2 mol. frac.* X (p.p.m.)	APC index† J (index units)		Carrier gas shifts: observed Δ_{obs} (index units)	Carrier gas shifts: calculated Δ_{calc} (index units)
(a)	CO_2-in-air mixtures				
	334.11	330.22		−3.91	−3.93
	336.99	332.86		−4.04	−3.96
	338.55	334.36		−4.03	−3.98
	352.96	347.76		−4.20	−4.12
	355.64	350.26		−4.18	−4.16
(b)	CO_2-in-N_2, O_2 mixtures				
			$\%O_2$		
	323.86	320.88	18.8	−3.28	−3.22
	323.91	320.98	18.8	−3.23	−3.22
	335.36	331.35	20.9	−3.98	−3.68
	351.92	346.92	21.7	−4.07	−4.01
	309.57	306.36	22.4	−3.56	−3.66
	332.04	324.95	40.2	−7.18	−7.23
	327.02	316.41	60.0	−10.84	−10.91
	339.06	323.36	79.9	−15.51	−15.41
	340.39	320.22	100.0	−19.92	−19.90
	361.50	339.34	100.0	−20.49	−20.96

* Determined manometrically.
† Determined with APC analyzer 55 at SIO.

($F(N_2) = 1.0$ by definition), and for O_2, N_2 mixtures from

$$F(O_2, N_2) = (1 - x_{O_2}) \cdot F(N_2) + x_{O_2} \cdot F(O_2) \qquad (8)$$

where x_{O_2} denotes the mole fraction of O_2 in the mixture. A line broadening coefficient, $F(O_2) = 0.840$ gave the optimal fit to all the manometric data. In Fig. 3, carrier gas shifts are plotted against percent O_2. The smooth line connects the model calculated points. The shifts have been scaled to those of a standard mole fraction of 330 p.p.m. CO_2 sample assuming the shift to be proportional to the concentration. Although this is not strictly true as is evident from calculated Δ versus $J(X)$ curves (e.g. Fig. 2), it is a sufficiently good approximation in comparing these mixtures with varying concentrations of O_2 since the range in concentration is small.

2.3. *Data at reduced pressure*

In a further study carried out in 1974, some of the same gas mixtures, measured with APC analyzer 55 at ambient pressure, were also analyzed at reduced sample cell pressures by using a manostat installed in series with the sample

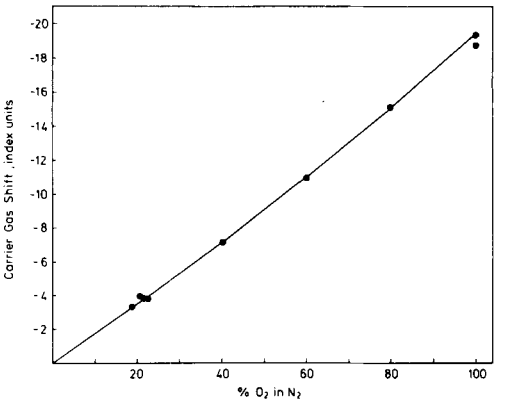

Fig. 3. Calculated and observed carrier gas shifts versus O_2 content of the carrier gas in 330 p.p.m. CO_2-in-N_2, O_2 mixtures. Points are experimental, the line is calculated with $F(O_2) = 0.84$.

chamber of the analyzer. Carrier gas shifts from CO_2-in-N_2 were established at ~350 and 700 mb for two and six CO_2-in-air mixtures respectively, and for the 40% O_2 and 60% O_2 mixtures analyzed in the previously-described work. The mole fractions were between 300 and 350 p.p.m. The pressure effects were computed by comparing shifts at low pressure with the corresponding shifts at one atmosphere pressure. The results are summarized in Table 4 along with model calculated values using $F(O_2) = 0.840$. The CO_2-in-air measurements, being for mixtures of nearly the same CO_2 concentration, show no significant correlation with CO_2 concentration and are grouped under their means.

Decreasing sample cell pressure increases the magnitude of the carrier gas shift. Agreement between observed and calculated shifts is good, except for the two CO_2-in-air mixtures at 350 mb. The pressure data have particular relevance because analyzers at baseline stations are often located at high altitude (e.g. Mauna Loa, Hawaii and South Pole). Carrier gas effects at such stations clearly must be determined in situ, not in a sea level laboratory.

In general, the good agreement between the three sets of data and the calculations gives us confidence that the model can reliably predict differences in APC analyzer behavior as carrier gas composition is varied. The only serious inconsistency is the different line-broadening factors for oxygen, 0.85 and 0.84, which give the best fits to the volumetric and manometric data, respectively. The cause of this anomaly, however, is clearly related to the experimental data since the analyzer optical system was unchanged during the two sets of measurements, made concurrently in 1974. We suspect the presence of a few percent of a contaminant in the commercial grade O_2 used in the volumetric study: 5% N_2 would be sufficient to bring the two sets of data into agreement. The rather large disagreement in the manometric results between the two 100% O_2 mixtures in 1980 also may have a chemical cause, although no contaminant could be found in either mixture by mass spectrometric analysis. Unfortunately, the oxygen gas used in the volumetric study was used up before a discrepancy with the manometric study was discovered. No check on its composition could be made.

Table 4. *Experimental and calculated effects of pressure on carrier gas shifts for APC analyzer 55*

CO_2 mol. frac.* X (p.p.m.)		Difference in carrier gas shift when pressure reduced from 1013 mb to: 700 mb obs (index units)	700 mb calc (index units)	350 mb obs (index units)	350 mb calc (index units)
CO_2-in-air mixtures					
300.00			−0.36		−0.82
325.00			−0.39		−0.89
350.00			−0.41		−0.94
326.82†		−0.39 + 0.09†			
322.69‡				−0.56 + 0.04‡	
CO_2-in-N_2, O_2 mixtures					
	%O_2				
332.04	40.2	−0.80	−0.70	−1.61	−1.58
327.02	60.0	−1.10	−1.02	−2.05	−2.32

* Determined manometrically.
† Average of measurements for 6 gas mixtures.
‡ Average of measurements for 2 gas mixtures. Standard deviation not significant.

3. URAS[1] analyzers at CSIRO

Since 1972, Pearman and co-workers have maintained a base-line CO_2 monitoring program in the Southern Hemisphere with a central calibrating laboratory at CSIRO, Melbourne, Australia (Beardsmore et al., 1978). Both URAS and UNOR analyzers have been used for which carrier gas shifts have been determined experimentally. Earlier measurements (Pearman and Garratt, 1975; Pearman, 1977) have been supplemented recently by new measurements using SIO-calibrated CO_2-in-air gas mixtures. The mole fractions of these were determined by comparison with CO_2-in-N_2 standards at SIO using analyzer 55 and assuming eqs. (1) and (3) to be valid. The instrument response of each CSIRO analyzer is calibrated in the mole fraction scale, X, by periodically determining the response for a suite of ~ ten SIO-calibrated CO_2-in-N_2 mixtures and using a quadratic function to fit response and mole fraction data. Thus all CSIRO data in this paper are quoted directly in the mole fraction scale, X.

For URAS analyzers, measurements of the carrier gas shifts, defined for CSIRO data as:

$$\Delta_{obs} = X_{URAS} - X \tag{9}$$

for four CO_2-in-air mixtures with mole fractions between 300 and 350 p.p.m., are tabulated in Table 5 along with calculations using an optimal line broadening coefficient, $F(O_2) = 0.82$. The agreement is not as good as that for the APC analyzer but is within ± 0.4 p.p.m., approximately the experimental error of the URAS analyzer. The calculated carrier gas shifts do not increase as quickly with concentration as do the experimental shifts, indicating a systematic discrepancy between the model predictions and the data. Furthermore, carrier gas shifts from other URAS-2 analyzers (D. Beardsmore (CSIRO) and W. Komhyr (GMCC-NOAA, Boulder, Colorado), personal communications), although of similar magnitude, are not the same, indicating that there are variations between analyzers of the same type. These latter data have not been treated here because of uncertainties in the analyzer parameters for calculation, but if the analyzers are nominally identical, the present model is unable to account for the differences. We can identify no obvious simplifying assumption in the model which may be the cause of this shortcoming.

Table 5. *Experimental and calculated carrier gas shifts for CO_2-in-air for URAS-2 analyzer, serial no. 6933216,* of CSIRO, Melbourne*

CO_2 mol. frac.† X (p.p.m.)	Carrier gas shifts observed Δ_{obs} (p.p.m.)	Carrier gas shifts calculated Δ_{calc} (p.p.m.)
303.83	−3.28	−3.39
315.98	−3.53	−3.63
330.14	−4.02	−3.90
353.95	−4.75	−4.40

* Detector filling: 10% CO_2-in-Argon. Detector path length: 2.0 cm. Sample cell path length: 25.0 cm. Temperature: 333 K. Oxygen line-broadening factor: 0.820.

† Determined by NDIR analysis at SIO using APC analyzer 55 (see text).

4. UNOR[1] analyzers at CSIRO

UNOR analyzers with both long (20.0 cm) and short (6.0 cm) sample cells are also used by CSIRO, and data similar to those presented above for the URAS-2 analyzer are available for three UNOR analyzers. In the preceding paper it was shown that there are much larger uncertainties in the calculation of absolute carrier gas shifts for UNOR analyzers owing to the sensitivity of the calculation for the balanced detector to uncertainties in input parameters. Tables 6 and 7 contain the experimental carrier gas shifts and the calculations allowing $F(O_2)$ to vary for best-fit as previously. The instrument responses expressed as mole fractions were obtained in the same manner as for the URAS analyzer, as discussed above. The two short-cell UNOR analyzers are different models (UNOR-2 and UNOR-5B), but we have been obliged to assume the same nominal dimensions, detector fillings, sources etc. in the absence of better information. Variation of one or several of these parameters (e.g. due to slightly different

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detector construction) may explain the variations in prediction. Qualitatively the model correctly predicts the carrier gas shifts:

$$\Delta_{obs} = X_{UNOR} - X \quad (10)$$

to be positive compared with negative shifts for URAS and APC analyzers, and it predicts the relative magnitudes for long and short sample cells. Both effects are well described by the weak versus strong line properties discussed in the preceding paper. The quantitative agreement is also reasonable, and by varying some of the uncertain input parameters the agreement could presumably be made arbitrarily good; little would be gained from such an exercise, however. The best fit $F(O_2)$ values obtained were 0.86 (long cell) and 0.82 (short cell).

Table 6. *Experimental and calculated carrier gas shifts for CO_2-in-air for long-cell UNOR analyzer, serial no. 631693,* of CSIRO, Melbourne*

CO_2 mol. frac.† X (p.p.m.)	Carrier gas shifts observed Δ_{obs} (p.p.m.)	calculated Δ_{calc} (p.p.m.)
303.83	2.70	2.56
315.98	2.78	2.61
330.14	2.47	2.68
353.95	2.72	2.76

* Front detector path length: 0.9 cm. Rear detector path length: 5.0 cm. Detector volume ratio: 0.55. Detector filling: 2.1% CO_2-in-Argon. Sample cell 20.0 cm. Temperature: 296 K. Oxygen line-broadening factor: 0.858.

† Same analyses as for Table 5.

Table 7. *Experimental and calculated carrier gas shifts for CO_2-in-air for two short-cell UNOR analyzers* of CSIRO, Melbourne*

CO_2 mol. frac.† X (p.p.m.)	Carrier gas shifts observed Δ_{obs} (p.p.m.)		calculated Δ_{calc} (p.p.m.)
	Serial no. 631478	Serial no. 5.099	
303.83	4.77	5.62	4.48
315.98	4.68	5.89	4.64
330.14	4.66	5.85	4.81
353.95	4.21	5.87	5.10

* Front detector path length: 0.9 cm. Rear detector path length: 5.0 cm. Detector volume ratio: 0.55. Detector filling: 2.1% CO_2-in-Argon. Sample cell length: 6.0 cm. Temperature: 296 K. Oxygen line-broadening factor: 0.820.

† Same analyses as for Table 5.

Finally, data are also available on the effects of pressure on the UNOR analyzers. The analyzers serial nos. 631693 and 631478 were operated in a large decompression chamber from 1000 to 600 mb. The analyzers were calibrated at several pressures with CO_2-in-N_2 mixtures followed by a single CO_2-in-air mixture having 328 p.p.m. CO_2. The observed carrier gas shift decreased markedly with pressure, at a rate of −0.87 p.p.m. per 100 mb for the long cell UNOR No. 631693 and −0.73 p.p.m. per 100 mb for the short cell UNOR No. 631478. Simulating the same experiment with the model and best-fit $F(O_2)$ values as determined above, the calculated effects at 328 p.p.m. are −0.66 p.p.m. per 100 mb (long cell) and −0.55 p.p.m. per 100 mb (short cell). Furthermore, the calculation indicates that the pressure effect is a strong function of concentration, i.e. the calculated rate of change differs by up to 0.1 p.p.m. per 100 mb around these values for concentrations between 300 and 360 p.p.m.

5. Discussion

The generally good agreement between calculated and experimental carrier gas shifts for the several sets of data and several analyzers strongly suggests that the spectral model is substantially correct, i.e. that the carrier gas effect is due principally to changes in pressure broadening in the sample cell. We feel that most, if not all, the variability in agreement between calculated and experimental data (as illustrated by the range of best-fit $F(O_2)$ values), can be explained by uncertainties in some of the analyzer parameters, and to a lesser extent by uncertainties in the experimental data.

In a sense, the procedure of varying the line broadening coefficients, $F(O_2)$ or $F(Ar)$, for best-fit to data is using the carrier gas effect as a means of

determining these factors. The values obtained for oxygen (0.85, 0.84, 0.82, 0.82, 0.86) are in fairly good agreement with themselves and are concordant within the range of Burch et al. (1962) (0.82 ± 0.05), but since they reflect other uncertainties in the calculations, they should not be collectively considered as a better estimate of the value of $F(O_2)$ than that of Burch et al.

Perhaps the most difficult and unsatisfactory part of this study has been attempting to gather the input parameters relevant to the analyzers from the manufacturers. The variability between analyzers of the same manufacturer and model is hard to explain, especially for the URAS analyzers. These were shown in the preceding paper to have carrier gas effects which were fairly insensitive to all the parameters (such as detector filling, effective optical path, and the source spectrum) which in practice may vary from analyzer to analyzer. We expect the spectrum of the source to change with age and from analyzer to analyzer, and this may partly explain slow changes in carrier gas effects with time.

There may be, of course, other factors not considered in this calculation which can lead to variability. An example is water vapor interferences; URAS-2 analyzers have considerable cross-sensitivity to water. Different gas drying techniques or ageing of the drying agent may lead to errors by causing variable amounts of water in the sample cell. The effect of water on the instrument could be calculated with the present model by including water lines from the AFGL listing in the sample cell, but the calculations are not worth attempting until corresponding experimental data are obtained.

Finally, we turn to practical applications of the model, which even if not sufficiently accurate to predict actual carrier gas effects *a priori*, should be useful to predict trends and perturbations related to analyzer conditions during their routine use. The Appendix contains tables of calculated instrument response for the analyzer types considered in this work for nitrogen and air carrier gases as a function of CO_2 concentration and sample cell pressure. All results in this paper for air carrier gas effects may be calculated from these tables.

1. *Pressure effects.* The carrier gas shifts for UNOR analyzers, as shown above, are quite strongly pressure sensitive: the order of −0.8 p.p.m. per 100 mb. The pressure effect even varies quite strongly with concentration. This sensitivity is sufficient for normal day-to-day variations in pressure to show up in the retrieved CO_2 mole fraction concentrations (X scale) unless a proper pressure correction is applied. For example a change of 50 mb, not unusual from day-to-day, will cause changes in carrier gas shifts of about 0.4 p.p.m. An initial look at UNOR carrier gas measurements at CSIRO during 1979 and 1980 indicates a correlation of measured carrier gas shifts against ambient pressure which is close to the predicted magnitude.

For APC analyzers the pressure effect is found to be 0.13 p.p.m. per 100 mb at 330 p.p.m. CO_2. Day-to-day variations in pressure will, therefore, produce an almost negligible effect. For URAS analyzers the model predicts even less pressure sensitivity, below 0.10 p.p.m. per 100 mb. No trend of carrier gas shift with pressure has been found in CSIRO data for URAS analyzers.

2. *Temperature effects.* URAS and APC analyzers are thermostatted and the neglect of small temperature variations, as are likely to occur, should not cause noticeable errors. UNOR analyzers, however, work at ambient temperature. In a variable temperature environment this will produce a variable carrier gas effect. The model predicts a 0.1 p.p.m. lowering of the carrier gas shift for a 5 °C rise in ambient temperature for both long and short-cell UNOR analyzers.

3. *Approximate correction factors.* It is common practice to use a factor G, defined as the quotient of the instrument response for CO_2-in-air to that of CO_2-in-N_2 (see eq. (2)) to correct observed data for carrier gas effects (Beardsmore et al., 1978; Keeling et al., 1976). If this approach were strictly correct, plots such as those in Fig. 2 would be straight lines passing through the origin. The calculated lines in Fig. 2 are actually slightly curved, and use of a single factor leads to errors of up to 0.2 p.p.m. for a range of 200 to 450 p.p.m. Nevertheless, when index values corrected for carrier gas are determined in the range of air variations (310 to 350 p.p.m.) the simple constant factor is adequate since predicted deviations from linearity are less than 0.10 p.p.m. in this range.

4. *Leaking detectors.* The sealed detector chambers of APC analyzers have been known to leak. Leakage causes a lower total filling amount either if the instrument is operated at higher altitude than that at which it was filled, or if the detector, filled at

ambient temperature and sealed, is warmed to the normal operating temperature. A prolonged leak can also cause exchange of filling gas with ambient air, driven by fluctuations in operating temperature or barometric pressure. Model simulations of the first type of leakage to an ambient pressure of 700 mb (the mean pressure at Mauna Loa) suggest a decrease in the magnitude of the carrier gas shift (increase in apparent CO_2-in-air relative to N_2) of 0.8 p.p.m. for APC analyzers, 0.4 p.p.m. for URAS analyzers and an increase in the error for UNOR analyzers of ~2 p.p.m. Thus, leaks could lead to noticeable effects on a CO_2 record.

The second problem is also serious. The loss of half of the CO_2 from the chamber at 700 mb leads to a further decrease in the magnitude of the carrier gas shifts of ~0.4 p.p.m. for URAS and APC analyzers and a further increase of ~4 p.p.m. for UNOR analyzers.

5. *Source changes.* Different infrared sources and the ageing of sources could cause variability due to changing the relative contribution of the 3650 cm^{-1} CO_2 bands to the absorption. However, calculations show that this effect (see preceding paper) should be less than 0.2 p.p.m. for URAS and APC analyzers and negligible for UNOR analyzers. The direction of change is hard to predict since we do not know how the source spectrum varies.

The above analysis illustrates that there are several possible ways in which day-to-day and year-to-year measurements of CO_2-in-air may be influenced to a few tenths of a p.p.m. by changes in ambient conditions and analyzer performance which influence the carrier-gas effect. These changes no doubt produce some of the scatter and long-term variations in the established CO_2 records. In this respect we would predict UNOR analyzers to show more variability than URAS or APC analyzers. Clearly, however, elimination of carrier gas effects altogether by using CO_2-in-air standards is a desirable step. Use of CO_2-in-air mixtures should lead to better CO_2 data when the technical problems in their production and maintenance are overcome.

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7. Appendix

Tables A-1 to A-4 contain, one for each analyzer, calculated analyzer responses (infrared absorptions in arbitrary units) for nitrogen and air carrier gases, CO_2 concentrations of 300–360 p.p.m. (true mole fraction scale), and ambient pressures of 1.0 to 0.7 atm. These tables can be used to deduce carrier gas shifts within these ranges as follows: For a prescribed mole fraction of CO_2-in-air, X_{air}, the instrument response R is calculated from the appropriate X versus R_{air} table by interpolation. The calculated response can then be related to the mole fraction, X_{N_2}, of a CO_2-in-N_2 mixture which gives the same response by interpolation of the appropriate X versus R_{N_2} table. The carrier gas shift is then $X_{N_2} - X_{air}$ in mole fraction units. Conversions to other scales than X must be made before and after use of the tables. Errors incurred by simple linear interpolation of the tables will be less than 0.03 p.p.m. More accurate fitting procedures may be used at the discretion of the user.

Table A-1. *Calculated instrument responses for an APC analyzer**

CO_2 conc. X (p.p.m.)	Calculated instrument response R (arbitrary units)							
	1.0 atm.		0.9 atm.		0.8 atm.		0.7 atm.	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
300.00	36.706802	36.812485	37.948807	38.051041	39.252090	39.349747	40.620087	40.711838
305.00	36.553619	36.660934	37.805328	37.909119	39.119308	39.218323	40.498917	40.592148
310.00	36.402222	36.511139	37.663422	37.768707	38.987823	39.088547	40.379028	40.473816
315.00	36.252441	36.363083	37.522873	37.629883	38.857788	38.959946	40.260391	40.356537
320.00	36.104340	36.216537	37.383942	37.492538	38.729050	38.832733	40.143005	40.240662
325.00	35.957916	36.071716	37.246475	37.356659	38.601608	38.706757	40.026733	40.125717
330.00	35.813248	35.928528	37.110504	37.222183	38.475433	38.582153	39.911713	40.012009
335.00	35.670074	35.786850	36.976028	37.089005	38.350647	38.458649	39.797562	39.899216
340.00	35.528397	35.646576	36.842697	36.957382	38.227020	38.336487	39.684540	39.787598
345.00	35.388153	35.507965	36.710983	36.827072	38.104599	38.215485	39.572556	39.677170
350.00	35.249420	35.370667	36.580490	36.697922	37.983292	38.095505	39.461792	39.567535
355.00	35.112228	35.234879	36.451355	36.570206	37.863205	37.976959	39.351852	39.459076
360.00	34.976303	35.100372	36.323456	36.443665	37.744278	37.859329	39.242996	39.351395

* Detector filling: 1.3% CO_2-in-Argon. Detector path length: 4.70 cm. Sample cell path length: 40.6 cm. Temperature: 323 K. Oxygen line-broadening factor: 0.840.

Table A-2. *Calculated instrument responses for a URAS-2 analyzer**

CO_2 conc. X (p.p.m.)	Calculated instrument response R (arbitrary units)							
	1.0 atm.		0.9 atm.		0.8 atm.		0.7 atm.	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
300.00	76.445450	76.554825	77.708679	77.810303	78.993423	79.087021	80.304306	80.386703
305.00	76.281647	76.393311	77.560135	77.663422	78.859299	78.953522	80.184570	80.269989
310.00	76.119049	76.232849	77.410919	77.515869	78.725403	78.822220	80.065918	80.152222
315.00	75.958633	76.074509	77.263580	77.370972	78.592789	78.691437	79.947174	80.035919
320.00	75.799301	75.917587	77.117645	77.227219	78.461288	78.560867	79.830185	79.920609
325.00	75.641281	75.762115	76.971802	77.083786	78.330719	78.432327	79.713531	79.805603
330.00	75.484665	75.606705	76.828217	76.942276	78.201019	78.304565	79.598999	79.691437
335.00	75.328064	75.453323	76.685822	76.801544	78.071747	78.177124	79.483414	79.579254
340.00	75.173111	75.300247	76.544250	76.661697	77.944412	78.051392	79.370239	79.467850
345.00	75.019623	75.148422	76.403778	76.523575	77.816803	77.925919	79.257019	79.355820
350.00	74.867538	74.998688	76.264313	76.386230	77.690918	77.801651	79.145767	79.244781
355.00	74.717117	74.849930	76.125870	76.249664	77.565613	77.678528	79.033112	79.136078
360.00	74.567123	74.701706	75.987640	76.113632	77.441177	77.556030	78.922592	79.026031

* Detector filling: 10% CO_2-in-Argon. Detector path length: 2.0 cm. Sample cell path length: 25.0 cm. Temperature: 333 K. Oxygen line-broadening factor: 0.820.

Table A.3. *Calculated instrument responses for a long cell UNOR analyzer**

CO_2 conc. X (p.p.m.)	Calculated instrument response R (arbitrary units)							
	1.0 atm.		0.9 atm.		0.8 atm.		0.7 atm.	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
300.00	3.444303	3.468645	3.216234	3.234877	2.947409	2.960311	2.631320	2.638604
305.00	3.491982	3.516115	3.263144	3.281566	2.993064	3.005732	2.675149	2.682167
310.00	3.538866	3.562815	3.309325	3.327525	3.038054	3.050482	2.718375	2.725130
315.00	3.584996	3.608772	3.354785	3.372779	3.082393	3.094573	2.761013	2.767506
320.00	3.630390	3.653938	3.399552	3.417261	3.126087	3.138022	2.803073	2.809297
325.00	3.675029	3.698365	3.443573	3.461106	3.169147	3.180848	2.844563	2.850528
330.00	3.718928	3.742079	3.486975	3.504286	3.211603	3.223052	2.885500	2.891193
335.00	3.762135	3.785070	3.529719	3.546800	3.253452	3.264647	2.925893	2.931313
340.00	3.804670	3.827398	3.571809	3.588668	3.294707	3.305652	2.965741	2.970897
345.00	3.846483	3.869006	3.613290	3.629921	3.335362	3.346066	3.005063	3.009949
350.00	3.887652	3.909937	3.654127	3.670529	3.375451	3.385897	3.043872	3.048492
355.00	3.928150	3.950253	3.694361	3.710543	3.414914	3.425113	3.082161	3.086515
360.00	3.968019	3.989904	3.733983	3.749950	3.453863	3.463834	3.119954	3.124038

* Front detector path length: 0.9 cm. Rear detector path length: 5.0 cm. Detector volume ratio: 0.55. Detector filling: 2.1% CO_2-in-Argon. Sample cell length: 20.0 cm. Temperature: 296 K. Oxygen line broadening factor: 0.858.

Table A-4. *Calculated instrument responses for a short cell UNOR analyzer**

CO_2 conc. X (p.p.m.)	Calculated instrument response R (arbitrary units)							
	1.0 atm.		0.9 atm.		0.8 atm.		0.7 atm.	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
300.00	0.473477	0.500307	0.352055	0.374750	0.215654	0.234217	0.062352	0.076870
305.00	0.503710	0.530778	0.380797	0.403672	0.242668	0.261373	0.087380	0.101988
310.00	0.533786	0.561073	0.409386	0.432441	0.269546	0.288387	0.112291	0.126981
315.00	0.563681	0.591196	0.437815	0.461048	0.296284	0.315250	0.137073	0.151844
320.00	0.593415	0.621138	0.466085	0.489491	0.322885	0.341975	0.161729	0.176594
325.00	0.622971	0.650901	0.494210	0.517777	0.349340	0.368552	0.186266	0.201212
330.00	0.652364	0.680497	0.522178	0.545905	0.375657	0.394991	0.210675	0.225700
335.00	0.681592	0.709927	0.549994	0.573880	0.401840	0.421282	0.234968	0.250057
340.00	0.710663	0.739189	0.577660	0.601697	0.427891	0.447441	0.259136	0.274305
345.00	0.739563	0.768279	0.605181	0.629367	0.453803	0.473467	0.283188	0.298417
350.00	0.768304	0.797206	0.632552	0.656882	0.479582	0.499345	0.307119	0.322418
355.00	0.796879	0.825958	0.659776	0.684242	0.505224	0.525088	0.330934	0.346286
360.00	0.825306	0.854554	0.686847	0.711449	0.530741	0.550697	0.354628	0.370044

* Front detector path length: 0.9 cm. Rear detector path length: 5.0 cm. Detector volume ratio: 0.55. Detector filling: 2.1% CO_2-in-Argon. Sample cell length: 6.0 cm. Temperature: 296 K. Oxygen line broadening factor: 0.820.

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