Calibration of Infra-red CO₂ Gas Analyzers[1]

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Abstract. Precision gas mixing pumps produce CO_2 gas mixtures for the calibration of infra-red CO_2 gas analyzers equivalent in accuracy to the standard CO_2 gas mixtures ($\pm$ 1 %) supplied by the National Bureau of Standards, Washington, D. C.

The calibration of infra-red gas analyzers by the pressure difference method and by concentration differences did not agree. A factor of 0.709 was necessary to correct the pressure difference method for the effects of pressure broadening with our analyzer.

Since it is frequently necessary to measure a small change in CO_2 concentration, the IRGA is often calibrated to detect a small CO_2 differential, with a reference base considerably above zero. To do this the reference and measuring cells of the IRGA are flushed using 2 calibration gases with CO_2 concentrations at or near the limits of the desired differential. In such a case the standard error of the differential will be a function of the mean error of each calibration gas. *i.e.,* Differential $= A - B \pm \sqrt{a^2 + b^2}$ where A and B are the mean CO_2 contents of the gases and a and b their respective mean standard errors. The maximum error potential will be the sum of the errors of each calibration gas (11). Since the use of 2 calibration gases increases the error of the differential, some workers (1, 5, 7) have used a single calibration gas and increased the pressure in the measuring cell to achieve an increase in the CO_2 concentration (14) and thus a CO_2 differential. However, as Legg and Parkinson (11) have recently pointed out, there can be a considerable error in the latter method of calibration due to pressure broadening of the absorption bands of CO_2.

Recently the National Bureau of Standards, Washington, D.C. have made available standard CO_2 calibration gases with a tolerance of less than 1 % at the 99 % confidence level (12). Using an NBS calibrated gas as a prime standard, we have investigated sources of calibration gases from commercial firms and from precision gas mixing pumps and the calibration of the IRGA at atmospheric and above atmospheric pressures.

Materials and Methods

All calibration measurements were done using a Beckman Infra-Red Gas Analyzer (Model 215) equipped with 13 and one-half inch flow through cells and detector filling pressure of 50 torr CO_2.

The IRGA was calibrated for the range 270 ppm to 360 ppm CO_2 using high precision gas-mixing pumps. (H. Wosthoff o. H. G., 463 Bochum, Germany, Type NA27/3A and NA18/3A). Dry carbon dioxide (99.99 %) and dry CO_2-free air were mixed in a set ratio by the first pump (Fig. 1) and the gas mixture from this pump was further diluted with dry CO_2-free air in the second pump. By using 4 pumps in series 2 gas streams containing 360 ppm CO_2 and 270 ppm CO_2 respectively were generated. To zero the IRGA, the 270 ppm CO_2 gas mixture flowed through a pressure regulator, drier (magnesium perchlorate) and flow meter (Manostat Corporation, New York, New York 10013, Type 36-541-13) to both cells of the analyzer. After setting zero, the 360 ppm CO_2 gas mixture was passed through the measuring cell of the IRGA and the IRGA gain and recorder span adjusted so that 1 ppm CO_2 elicited a response of 1 % full scale on a Sargent potentiometric recorder (Model DSRG).

The IRGA was also calibrated using nitrogen instead of CO_2-free air as the carrier gas and in addition, calibration gases were generated using several different mixing ratios in the pumps to ascertain the possible error due to gear ratios (table I). Each measurement was replicated 3 times and the results were statistically analyzed using analysis of variance.

Immediately after each of these instrument calibrations, the 360 ppm CO_2 gas mixture was replaced by the prime standard (308 $\pm$ 3 ppm CO_2) obtained from the National Bureau of Standards, Washington, D.C. (12).
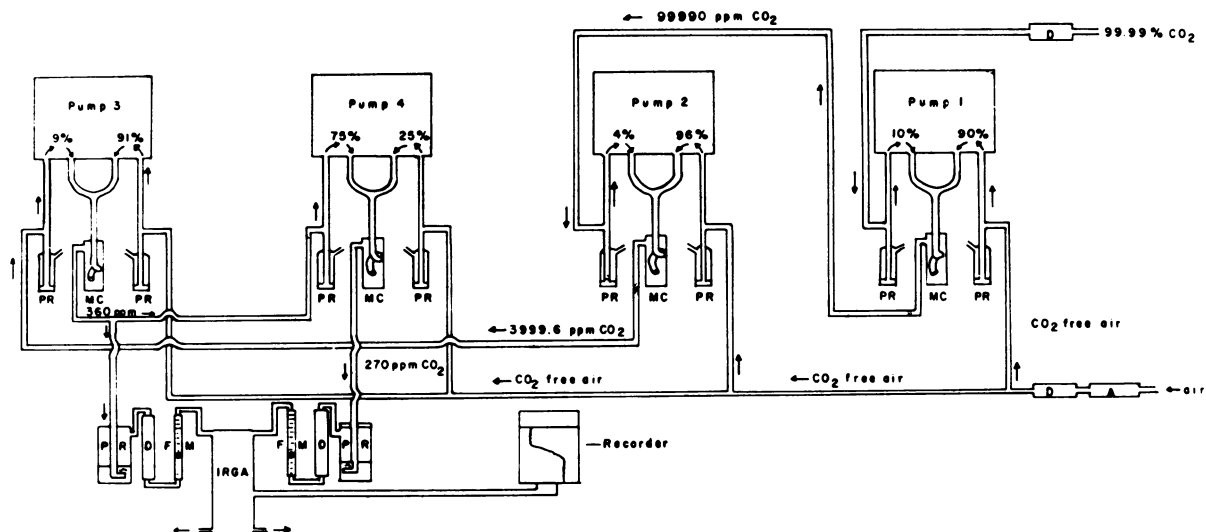
FIG. 1. Schematic diagram of precision gas mixing pump arrangement for generating gas mixtures with 270 and 360 ppm CO_2 for the calibration of the infra-red gas analyzer. A — CO_2 absorber. D — Magnesium Perchlorate drying column. PR — Pressure regulator. MC — Mixing chamber. FM — Flowmeter.

Table I. *Pump Ratios for Production of CO_2 Gas Mixtures and CO_2 Content of The NBS Standard* The NBS standard contained 308 ± 3 ppm CO_2.

Mixture[1]	Pump No.				CO_2 Concn of NBS standard		
	1	2	3	4		Carrier gas	
No.		Mixing ratio			CO_2-free air	N_2	Mean
	%	%	%	%	ppm	ppm	ppm
1	10	4	9	75	306.4[2]	304.7	305.6
2	4	9	10	75	308.4	308 0	308.2
3	6	6	10	75	307.4	304.4	305.9
Mean					307.4	305.7	306.6

[1] Each mixture was produced using CO_2-free air or nitrogen as carrier gas and in every case the CO_2 concentration at the outlet of pump 3 was 360 ppm CO_2 and at the outlet of pump 4, 270 ppm CO_2. (See Fig. 1).

[2] Standard error calculated from analysis of variance as ± 0.7 ppm ($n = 3$) from S. E. of treatment mean =

$$\sqrt{\text{EMS} \times \frac{1}{n}}$$ where EMS = Error mean square and n = number of replications.

Two further calibrations of the IRGA were performed with CO_2-free air or nitrogen in the reference cell and gas mixtures (from the precision gas mixing pumps) of known CO_2 content in the measuring cell. This calibration curve was then checked with the prime standard from NBS.

To 'pressure' calibrate, the IRGA was first calibrated using gas-mixtures from the pumps for a differential range of 210 to 330 ppm CO_2. A gas stream from a commercial tank containing 212 ppm CO_2 in air (CO_2 content determined by an IRGA that was calibrated with the precision mixing pumps) was then passed through both cells of the analyzer. The exit port of the measuring cell was connected to a manometer with a T-joint and by restricting the flow to the atmosphere the gas pressure in this cell was increased. The theoretical increase in CO_2 content was calculated (14) and compared to the observed response.

Results

The response of the IRGA to increasing CO_2 concentration over a differential range of 210 to 310 ppm CO_2 was linear (Fig. 2A) and an identical response curve was obtained for the range 270 to 370 ppm CO_2. This calibration response of the IRGA with either nitrogen or CO_2-free air as the carrier gas was used to "determine" the CO_2 content of the NBS standard and the results were statistically analyzed. The CO_2 content of the NBS standard was found to be 306.6 ± 0.7 ppm (S.E., $n=18$) which is within the 308 ± 3 ppm CO_2 ($P_{0.01}$) specified (12). The variations due to replications were non-significant ($P_{0.05}$). The pump ratios delivered significantly different ($P_{0.05}$) CO_2 concentrations but the mean determinations for the NBS standard of 305.6, 308.2, and 305.9 ppm CO_2 (table I) all fell within the prescribed limits. When
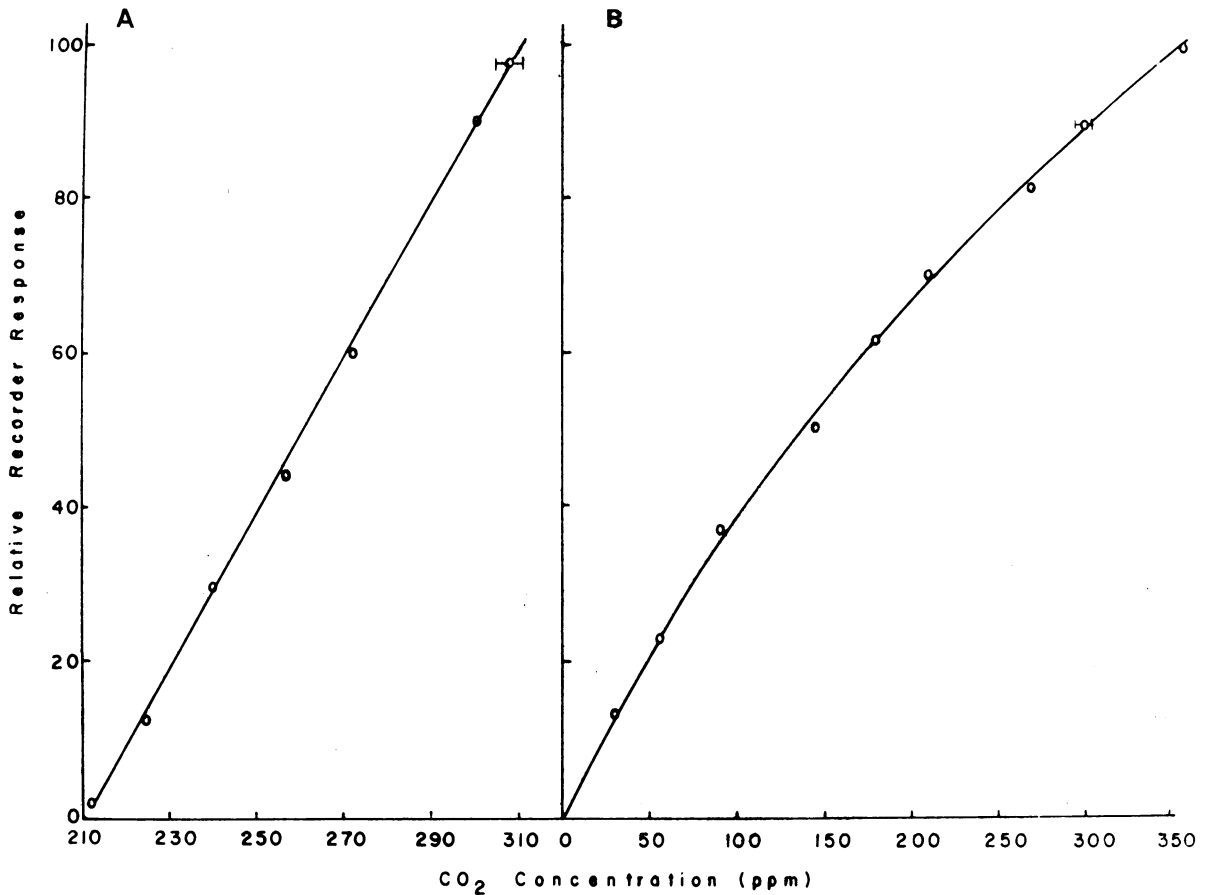
FIG. 2. Calibration curve of infra-red gas analyzer from (A) 210 to 310 ppm CO_2 (B) 0 to 350 ppm CO_2. Horizontal bars indicate the response from the NBS standard (308 ± 3 ppm CO_2).

the IRGA was calibrated with CO_2-free air as carrier gas the mean CO_2 content (307.4 ppm) of the NBS standard differed significantly ($P_{0\,05}$) from the mean CO_2 content (305.7 ppm) when the IRGA was calibrated with nitrogen as carrier gas (table I). This difference may be due to a difference in collision broadening due to the oxygen in CO_2-free air (4, 13). It should be emphasized that in every instance using CO_2-free air as the carrier, the variations encountered did not exceed the prescribed limits of the NBS standard (12).

The calibration response of the IRGA with either nitrogen or CO_2-free air in the reference cell was not linear (Fig. 2B) but again the concentration of the NBS standard agreed with the calibration curve.

With the IRGA calibrated (gas mixtures from the precision pumps) for a 100 ppm CO_2 differential in the appropriate range, the CO_2 content of several commercial cylinders was determined (table II). These cylinders were supplied with analyses and, as can be seen (table II), they all contained a higher CO_2 concentration than specified.

Suppliers' specifications for gas components of less than 1 % of the total mixture are usually ± 5 %. While few of the differences (B—A, table II) exceed these specifications, the gas mix-

Table II. *Analyses of CO_2-air Mixtures From Commercial Suppliers*

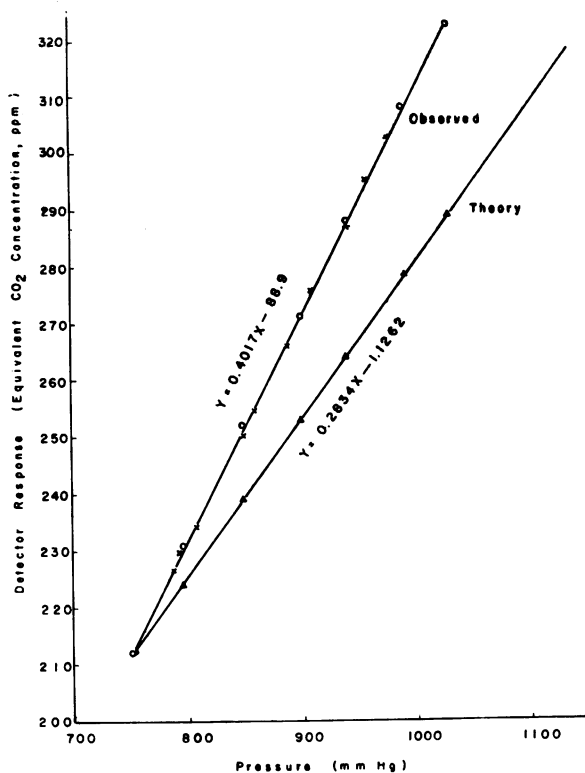|	Carbon dioxide concn		
Ordered	Suppliers analysis (A)	Our analysis (B)	B-A
ppm	*ppm*	*ppm*	*ppm*
250	255	259	+4
50-55	55	62	+7
95-100	98	113	+15
100	110	114	+4
350	348	362	+14
250-260	255	273	+18
360	355	369	+14
340	345	360	+15
290	285	293	+8
340	340	349	+9

FIG. 3. The theoretical CO_2 content of the measuring cell of the infra-red gas analyzer due to increased pressure and the observed detector response. O — Increasing pressure X — Decreasing pressure.

corroborate that the accuracy of the calibration CO_2 gas mixtures produced by the pumps was equivalent to that of the NBS standards. The 99 % confidence limits of 306.6 ± 2.3 ppm (S.E.) CO_2 for our calibration of the NBS standard would indicate that the pumps can deliver a CO_2 gas mixture with an accuracy of 2 ppm. If we assume this to be a constant error then the error of a 100 ppm CO_2 differential between 300 and 400 ppm would be 3.2 ppm or 3.2 %. The precision of this calibration is considerably better than that which can be achieved through the use of commercial gas mixtures.

The calibration of IRGA's by the 'pressure' method has been used previously (1, 5, 7). The authors, however, do not mention the potential errors that are introduced due to pressure broadening (2, 3 4) of the absorption bands of CO_2. Legg and Parkinson (11) have recently discussed this problem and compared the methods and showed that the results differed by 25 to 70 %. We have confirmed their findings as the response due to increased pressure exceeded the theoretical response by 41 % with a Beckman IRGA (Model 215). Thus, in order to use the 'pressure' calibration it is obligatory to first determine the required correction factor. Since this correction factor will vary with measuring cell length and detector gas content it must be determined for each instrument. It should also be mentioned that even the 'pressure' calibration will not be more accurate because, the error of 2 calibration gases will be included in the correction factor and any error of the calibration gas used to 'pressure' calibrate will be magnified by pressure.

Acknowledgments

tures are not acceptable for IRGA differential calibration.

The results of the 'pressure' calibration of the IRGA are shown in Fig. 3. The observed response, although linear as expected (Fig. 2A) exceeded the theoretical response by a factor of 1.41.

Discussion

Although the accuracy of calibration of the IRGA is only one factor of many that influence the determination of absolute rates of CO_2 exchange in plants, it can become a highly significant factor when very small CO_2 differentials are being measured. If the calibration accuracy of infra-red CO_2 gas analyzers are to be intercompared it is essential that a gas mixture of high precision be utilized.

While precision CO_2 mixtures had previously been produced (10), Hughes and Dorko (8, 9) have recently described the preparation and rapid mass spectrometric analysis of CO_2 mixtures. These latter precision CO_2 calibration standards are available from the National Bureau of Standards (12).

Precision gas mixing pumps can deliver many different gas mixtures (6) to a specified accuracy of less than 0.1 % (15). Our results certainly

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