Errors in atmospheric CO_2 concentration measurements arising from the use of reference gas mixtures different in composition to the sample air

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ABSTRACT

Comparisons have been made between the URAS 2, UNOR 2 and Grubb Parson's SB2 non-dispersive infra-red gas analysers, involving the measurement of CO_2 concentration in gas mixtures containing N_2 and O_2 in varying proportions. The results imply that the CO_2 concentration in air when using CO_2/N_2 mixtures as references, is under-estimated by 3.7 and 2.3 ppmv for the URAS and Grubb Parson's instruments respectively and over-estimated by 4.5 ppmv by the UNOR. The measurement of CO_2 concentration in air is not affected if CO_2/air mixtures are used as references. The indicated CO_2 concentration of air relative to a CO_2/N_2 reference mixture is found to depend on ambient pressure for both the UNOR and URAS analysers. Thus aircraft or high altitude *in situ* measurements need an additional correction, to be comparable with measurements made relative to the same CO_2/N_2 reference mixtures at a standard (near sea-level) pressure of 1 000 mb. The results are similar to those obtained by Bischof (1973) and have important implications on the interpretation of carbon dioxide concentration measurements made at monitoring stations.

Introduction

For more than a decade now, the Scripps Institute of Oceanography has provided reference gas mixtures of CO_2 in N_2 for the calibration of "working" gas mixtures used in the various atmospheric CO_2 monitoring programmes. The CO_2 concentration of the reference mixtures have been determined by a manometric technique (C.D. Keeling, unpublished report).

Recently the authors commenced an atmospheric CO_2 monitoring programme aimed at providing data for the mid-latitudes of the Southern Hemisphere (Pearman & Garratt, 1973). Early measurements were made with a URAS 2 non-dispersive infrared (NDIR) gas analyser,[1] whilst since July 1972 we have additionally used a UNOR 2 analyser.[2] The CO_2 measurements were made differentially with respect to the reference CO_2/N_2 mixtures. Both instruments were found to give identical CO_2 concentration differences when two CO_2/N_2 mixtures were compared. However, when the CO_2 concentration of an air sample was measured relative to a reference CO_2/N_2 mixture, the UNOR 2 analyser gave a consistently higher (indicated) concentration of approximately 8 parts per million by volume (ppmv).

The UNOR 2 analyser was also operated in an aircraft up to a height of 3 km during a number of field experiments over S.E. Australia. Calibration of the analyser (viz. to determine the analyser output in millivolts per ppmv of CO_2 difference between measuring and reference cell) was necessary as both the sensitivity and differential zero of the analyser changed with altitude (or pressure). Air samples in flasks obtained simultaneously with the *in situ* measurements were analysed on the URAS 2 in the laboratory at surface pressure. Comparison of the two sets of data showed a relative variation of 2 ppmv in indicated CO_2 concentration for the UNOR 2, as pressure varied between sur-

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[1] URAS 2: Hartman and Braun, AG Frankfurt/Main.

[2] UNOR 2: H. Maihak, AG. 2000 Hamburg 39.

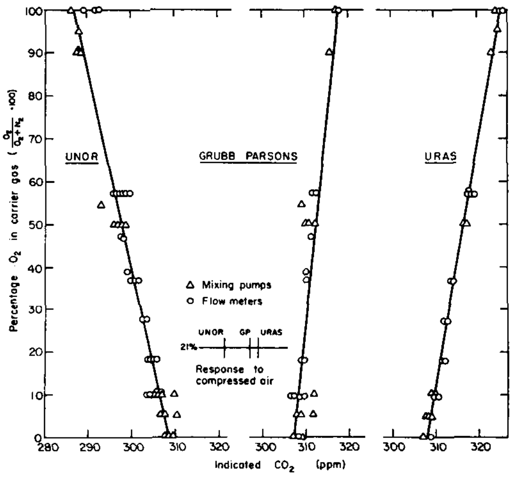

Fig. 1. Indicated CO_2 concentration vs. fraction of O_2 in the carrier gas: experimental data for URAS 2, Grubb Parson's SB2 and UNOR 2 NDIR gas analysers. Varying proportions of O_2 and N_2 comprising the carrier gas were produced using either flowmeters (○) or 'Wostoff' gas mixing pumps (△). The relative response of each analyser to air from a compressed air cylinder (assumed ~21 % O_2) is also shown.

face (1010 mb approximately) and 3 km (about 700 mb).

These results stimulated the work described in this paper. It is by no means complete, requiring further refined measurements using additional analysers

Method

To investigate the effects of the carrier gas on indicated CO_2 concentration, mixtures of O_2 and N_2 with a constant CO_2 mixing ratio of approximately 310 ppmv were passed through the measuring cell of each of the three gas analysers available (UNOR 2, URAS 2 and Grubb Parson's SB2[1]) and compared with a reference CO_2/N_2 mixture passed through the comparison (or reference) cell. Each analyser was calibrated before each measurement by comparison of two reference CO_2/N_2 mixtures. The results are shown in Fig. 1, where the relative response of the three analysers to a varying fraction of O_2 in the carrier gas is clearly demonstrated. We also show the CO_2 concentration of air in a compressed air cylinder (approximately 21% O_2) as indicated by each of the three analysers. The observed differences in indicated concentration are consistent with those at comparable O_2 ratios shown by the other experimental results.

To investigate the effect of ambient pressure, URAS and UNOR analysers were operated in a large decompression chamber at a number of pressures intermediate between 1 000 and 700 mb, equivalent to a change in altitude from near-surface to 3 km. For each pressure, the two analysers were calibrated and then measurements made of the CO_2 concentration in air (from a compressed air cylinder) relative to a CO_2/N_2 reference mixture. The results are shown in Fig. 2, for both analysers, and indicate a near linear relation between CO_2 and pressure change over the range considered.

Discussion

The differential measurement of CO_2 concentration by NDIR gas analysers appears to

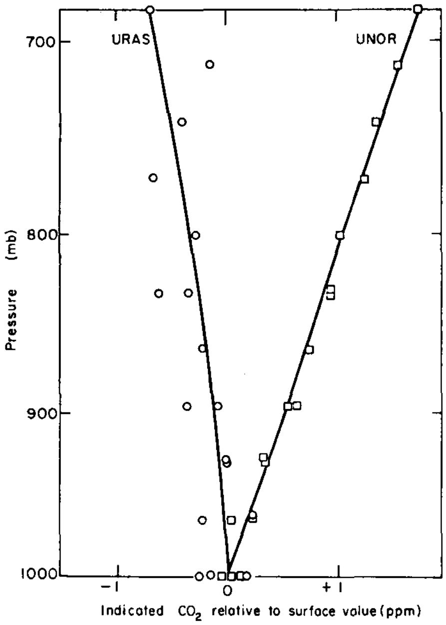

Fig. 2. Indicated CO_2 concentration of an air sample relative to the 1 000 mb (surface) value vs. pressure; experimental data are for the URAS 2 (○) and the UNOR 2 (□). The mean curves have been drawn by eye.

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[1] Grubb Parson's SB2: Grubb Parsons, Walkergate, Newcastle-Upon-Tyne 6.

be affected by different pressure (or collision) broadening effects of O_2 and N_2 on the absorption of the CO_2 vibrational band (at 4.3 μm). The absorption is thus sensitive to the ambient pressure as well as the O_2/N_2 proportion. The problem arises only when the sample mixture differs from the reference mixture in carrier gas composition, and thus use of CO_2/air reference mixtures does not affect the measurement of CO_2 concentration in air. In the context of the space and time variations of CO_2 concentration in the atmosphere such effects have until recently been unappreciated. Fig. 2 indicates the effect of pressure (for the UNOR and URAS analysers) on the indicated CO_2 concentration of an air sample relative to a reference CO_2/N_2 mixture. Thus normal synoptic fluctuations in surface (sealevel) pressure, of order 1% or less, give less than 0.2 ppmv and 0.1 ppmv variation in a measurement made with the UNOR and URAS respectively. These are close to the limit of resolution for a differential measurement on both analysers and are therefore not significant. *In situ* measurements made in aircraft or at high altitude stations would however require appropriate correction, depending on the analyser used, for comparison with sea-level measurements. Thus each analyser would require a correction curve similar to those shown in Fig. 2.

Bischof (1973) has also investigated the effect of carrier gas composition (using N_2 and O_2) on the indicated CO_2 concentration. He tested 3 analysers commonly used to measure CO_2 concentration in the range 300–350 ppmv viz. a URAS 1, UNOR 2 and UNOR 5B, but with a CO_2/air reference mixture in the reference cell (the use of a CO_2/N_2 mixture was preferred by the authors). However, the effect on the observed CO_2 concentration for any one analyser due to a change in the carrier gas composition from 100% N_2 to 100% O_2 barely depends upon the composition of the reference mixture (so long as it is maintained constant—see Fig. 2, Bischof, 1973). His results are shown in Fig. 3, together with our own curves taken from Fig. 1. For the proportion of O_2 in the carrier gas varying from 0 to 100%, he found a linear response for the URAS analyser and a non-linear response for the two UNOR analysers.

No other published work on the effect of the carrier gas on the indicated CO_2 concentration is known, for concentrations in the range relevant to the problem of atmospheric CO_2 monitoring. However, work has been published on the effect of the pressure broadening of the CO_2 absorption band (4.3 μm) by O_2 and N_2 for a number of gas analysers used in medical research, covering the CO_2 concentration range from 1 to 10%.

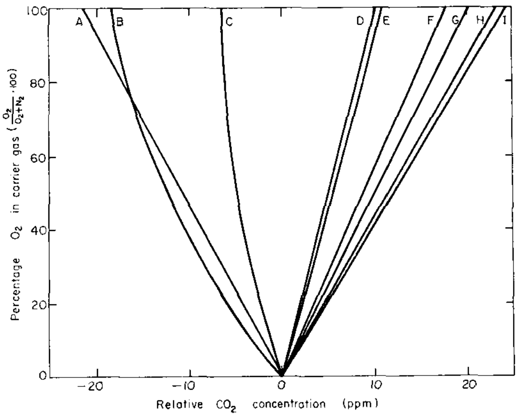

Fig. 3. Indicated CO_2 concentration relative to a CO_2/N_2 mixture vs. fraction of O_2 in the carrier gas: mean curves for a number of commercial NDIR gas analysers. *A* (UNOR 2), *E* (Grubb Parson's SB2), *F* (URAS 2) from Fig. 1 for CO_2 concentrations ~310 ppmv. *B* (UNOR 5B), *C* (UNOR 2), *H* (URAS 1) from Bischof (1973) for CO_2 concentration 322 ppmv. *D*, Beckman LB-1 (medical) from Severinghaus et al. (1961) extrapolated from a CO_2 concentration of 1 % in O_2 and N_2. *G* (URAS (medical)), *I* (M.S.A. 300 (medical)) from Hill & Powell (1968), both extrapolated from a CO_2 concentration of 1 % in O_2 and N_2.

In the absence of an appreciable effect of the CO_2 concentration upon the pressure broadening we have tentatively extrapolated these results to the case of a 0.03% CO_2 concentration.

The results of Severinghaus et al. (1961), who used Beckmann "Spinco" LB-1 analysers are shown in Fig. 3, the response being linear and about half the effect "reported by previous investigators" (Severinghaus et al., 1961).

Hill & Powell (1968) presented experimental data for two types of medical analyser—a URAS (model not given) and a M.S.A. 300; their results are also shown in Fig. 3.

In general Fig. 3 demonstrates a remarkably wide variation in the response of the analysers investigated (indicated CO_2 concentration) due to varying proportions of O_2 and N_2 in the carrier gas. They cover the main types of NDIR gas analysers used in the various global CO_2 monitoring programmes except for the Applied Physics instrument used by the Scripps Institute. For the analysis of CO_2 in air (21% fraction of O_2, remainder N_2) the response curves show a range of 10.8 ppmv in the indicated CO_2 concentration; excluding the UNOR analysers, the range is 2.9 ppmv. The implication of Fig. 3 is that the analysis of an air sample (using CO_2 in N_2 as reference) leads to an overestimate of the CO_2 concentration for the UNOR analysers and an underestimate for all of the others. Thus for any one analyser the true CO_2 concentration of an air sample is given by the intersect of the response curve at zero O_2 concentration.

The range in the under-estimate of nearly 3 ppmv (1.9 ppmv for the Beckmann to 4.8 ppmv for the M.S.A.) is of the same order as the large-scale latitudinal and vertical variations occurring in the troposphere (Bolin & Keeling, 1963; Bischof & Bolin, 1965; Pearman & Garratt, 1973), and may have influenced interpretation of the small differences in CO_2 concentration reported between the various monitoring locations in the global network (e.g. Bolin & Keeling, 1963). This is difficult to assess because of lack of information on the types of analyser used; in addition there is the possibility of differences occurring even between analysers of the same make and model (see Fig. 3, for instance).

The magnitude of the pressure broadening effect of O_2 and N_2 is determined for any one analyser (even from the same manufacturer) by its design and filters (Severinghaus et al., 1961). Most analysers operate on a system of two parallel detection chambers (sample and reference cells) and these types tend to give positive slopes in Fig. 3. The UNOR analysers operate with the two detector chambers in series and these show negative slopes. Hill & Power (1968) have found that the pressure broadening effect is also dependent on the partial pressure of CO_2 in the detection chamber (if a mixture is used) or the total pressure if pure CO_2 is used.

What is urgently needed is the experimental determination of the carrier gas effect on the indicated CO_2 concentration for each analyser used in the various monitoring programmes (e.g. see Figs. 1 and 3). This would have to be repeated at regular intervals for each analyser when used over a period of many years. Such measurements have been commenced (in addition to our own) by the Swedish (Bischof, 1973) and Scripps' groups (P. Guenther, private communication). Only then will data from all stations be strictly comparable (assuming that any altitude effect is also suitably corrected for), and requiring, in publication, a record of the correction made and details of the type of analyser used.

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ОШИБКИ В ИЗМЕРЕНИЯХ КОНЦЕНТРАЦИИ АТМОСФЕРНОГО CO_2, ВОЗНИКАЮЩИЕ ПРИ ИСПОЛЬЗОВАНИИ ОТСЧЕТНЫХ СМЕСЕЙ ГАЗОВ, ОТЛИЧНЫХ ПО СОСТАВУ ОТ АНАЛИЗИРУЕМОГО ВОЗДУХА

Проведены сравнения между показаниями недисперсионных газовых анализаторов URAS 2, UNOR 2 и SB2 Грабба Парсонса при измерениях концентрации CO_2 в газовых смесях, содержащих N_2 и O_2 в изменяющихся пропорциях. Результаты показывают, что концентрации CO_2 в воздухе при использовании в качестве стандарта смеси CO_2/N_2 занижаются на 3,7 и 2,3 частей на миллион по объему (чмо) для приборов URAS и Грабба Парсонса, соответственно, и завышаются на 4,5 чмо для UNOR. Измерения концентрации CO_2 в воздухе не подвержены этому влиянию, если в качестве стандарта используются смеси CO_2/воздух. Найдено, что измеренные концентрации CO_2 в воздухе относительно стандартной смеси CO_2/N_2 зависят от окружающего давления для анализаторов UNOR и URAS. Таким образом, самолетные или наземные измерения на больших высотах над уровнем моря нуждаются в дополнительной коррекции, чтобы их можно было сопоставить с измерениями, сделанными относительно той же самой смеси CO_2/N_2 при давлении 1 000 *мб*. Результаты аналогичны полученным Бишофом (1973) и имеют важное значение для интерпретации измерений концентрации углекислого газа, сделанных на станциях слежения.