CORRECTION FACTORS FOR INFRARED CARBON DIOXIDE PRESSURE BROADENING BY NITROGEN, NITROUS OXIDE AND CYCLOPROPANE

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PRESSURE (or collision) broadening introduces errors in infrared analysis of CO_2 when nitrogen, nitrous oxide or cyclopropane are present in the sample but not in the calibrating gas. Correction for this error requires the use of accurately known mixtures of CO_2 in these gases. In previous reports on pressure broadening [1-6] workers have utilized either chemical analysis or volumetric mixing methods. Chemical analysis of CO_2 in anesthetic gases is somewhat difficult due to absorption of the anesthetic into the CO_2 absorber. The CO_2 electrode,[7] being unaffected by anesthetics, permits greater accuracy and speed in preparing correction factors for this effect. Since the relatively new Beckman-Spinco LB-1 CO_2 analyzer has not been studied in the published reports, it seemed wise to draw attention to its considerably reduced broadening effect in comparison with older instruments.

We also wish to introduce a simple method of correcting for the pressure broadening effect involving a constant multiplier for the apparent CO_2 concentration given a constant background gas.

METHOD

Two Beckman Spinco LB-1 infrared CO_2 analyzers with microcatheter sampling cells were used. The detector cells were charged with CO_2 to a pressure of 50 mm. of mercury. The analyzer heads were flushed and filled with N_2O under slight positive pressure to eliminate the error due to the overlapping absorption bands of N_2O and CO_2. Regulated negative pressure of -100 mm. of mercury was applied to the sample cell outlet. Flow through the cell was controlled to 5–10 ml./second by an orifice at the sampling tip. Most of this 100 mm. pressure drop occurred at the inlet orifice, so pressure in the sample cell approximated -100 mm. of mercury. In end-tidal sampling, this modification reduces the effect of pressure fluctuations in the airway, eliminates condensation of water vapor in the sampling catheter, and improves response time. The use of low pressure in the sample cell also increases linearity.[8] Readings were obtained directly from the meter on the amplifier in order to eliminate possible errors arising in further amplification and direct writing instruments. Full scale sensitivity was approximately 10 per cent CO_2 in O_2.

Calibration gases (CO_2 in air and CO_2 in O_2) in cylinders were analyzed chemically (Scholander 0.5 ml.) and redetermined against each other on the CO_2 electrode. Response curves for CO_2 in air and CO_2 in O_2 were then prepared.

Anesthetic test mixtures and additional CO_2 in air or O_2 mixtures were prepared volumetrically in a 1,500 ml. plastic syringe. After mixing, they were analyzed simultaneously in the electrode and infrared analyzer. The infrared analyzer sampling was from an open ended rubber tubing through which the syringe was slowly emptied, producing a flowing stream of gas at atmospheric pressure.

A number of the anesthetic mixtures were analyzed both in the electrode and in duplicate with the Scholander technique, using a correction for anesthetic gas solution described in a previous publication.[8]

The CO_2 electrode (National Welding Co.) was mounted in a 37 C water bath. The output was read on an Instrumentation Laboratory blood gas analyzer with a Tapot readout calibrated logarithmically from 1.0 to 100 per cent (or 10 to 1,000 mm. P_{CO_2}) having 1,000 divisions over the range. Readings over the entire range could be read to 0.5 per cent of the value (not of full scale). That is, 2 per cent CO_2 could be read to $2.00 \pm .01$ per cent. Drift of the entire system was less than 1 per cent in 8 hours, *i.e.*, 0.05 per cent CO_2 at 5 per cent CO_2. Reproducibility and linearity

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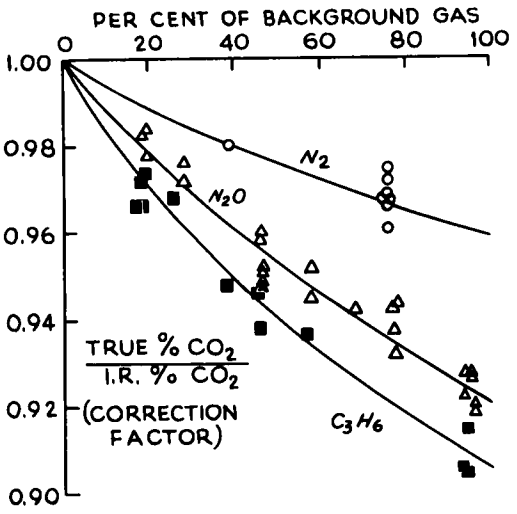

FIG. 1. "True % CO_2" is the value obtained from CO_2 electrode analysis, supplemented in some instances by Scholander analysis. "IR % CO_2" is the value obtained from a calibration curve plotting meter deflection against CO_2 in oxygen. The ratio of these readings when background gases other than oxygen are present is a correction factor. The IR percentage CO_2 multiplied by the correction factor gives the true percentage CO_2.

were both better than 0.5 per cent. Response time was about two minutes.

The electrode membrane was 0.001 inch Teflon. Instead of the usual cellophane, 8 denier nylon stocking mesh was used to hold the 0.01*M* $NaHCO_3$ and saturated KCl electrolyte layer. With this modification, the electrode is linear down to 0.5 per cent CO_2. The electrode cuvette was kept wet to insure that the gas samples would be saturated at 37 C. Readings were made with gas stationary in the cuvette, to avoid cooling and drying effects.

Calculation

Readings from the microammeter on the infrared analyzer amplifier were converted to percentage CO_2 from a CO_2 in O_2 calibration curve. All readings were considered as dry gas readings. The dilution effect of water vapor has been shown [2, 8] to be almost counterbalanced by a presumed pressure broadening effect of water vapor. The remaining effect of water vapor is "ironed out" by the tendency of water vapor to cling to sample cell walls. The electrode scale readings were also read as percentage dry gas. (Since both calibration gas and test gas are saturated at the same temperatures in the electrode cuvette, the reading is independent of the water vapor in the sample just as it is in the Scholander apparatus.)

Results

We computed the ratio of the correct concentration (from Scholander and CO_2 electrode) to the concentration value obtained from the infrared analyzer using a CO_2 in O_2 calibration curve. This ratio is a correction factor, and is plotted in figure 1 as a function of N_2, N_2O and cyclopropane concentration. The factor for CO_2 in O_2 is 1.0.

There was no detectable variation of the correction factor over the range of 1.5–9 per cent CO_2. The two instruments appeared to have identical broadening effects.

Varying the total pressure in the sample cell has an effect on pressure broadening. Figure 2 presents data on 95 per cent N_2O and 5 per cent CO_2. The effect is relatively unimportant if sample cell pressure is within 100 mm. of mercury of atmospheric pressure.

Discussion

Several workers [3, 5] have noted that the error in percentage CO_2 incurred by pressure broadening, is proportional to the CO_2 concentration. If this is true, then the ratio of true CO_2 to the apparent CO_2 (based on a CO_2 in O_2 calibra-

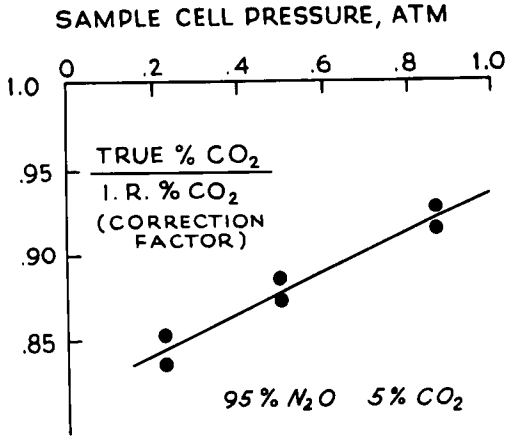

FIG. 2. The pressure broadening effect increases as the total pressure in sample cell is reduced. The effect is negligible at usual sampling pressures of 0.87 to 1.0 atmosphere. (− 100 mm. of mercury to zero negative pressure).

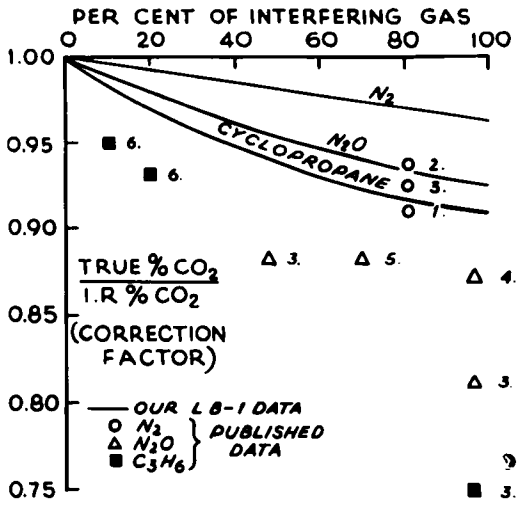

FIG. 3. Correction ratios computed from published data compared with the present study. Liston Becker Model 16 was used by Collier,[2] Bergman [4] and Linde.[6] Infrared Development Co. meter was used by Ramwell [3] and Cooper.[5] Stow [1] constructed his own instrument.

tion curve) would be independent of CO_2 concentration. Our data support the constancy of this ratio. This is also in accord with the theoretical basis for pressure broadening as described by Lorenz.[9] Therefore, this ratio may be used as a correction factor for readings taken from a CO_2 in O_2 calibration curve. This also makes it unnecessary to prepare separate calibration curves for mixtures containing the anesthetic gas.

The most important observation made in this study is that the pressure broadening in the Beckman Spinco LB-1 analyzer is less than half that reported by previous investigators using the Liston Becker Co. and the Infrared Development Co. (English) CO_2 analyzers. The correction ratios which we have calculated from published data are plotted in comparison with our data in figure 3. Ramwell gives values for N_2, N_2O and cyclopropane which all show about 2.5 times the broadening effect that we obtained, but bear about the same relationship to each other that our data do; that is, N_2O has twice the broadening effect of N_2 and cyclopropane has about 25 per cent more effect than N_2O. This suggests that while there are consistent differences between instruments, the relative effects of these gases on CO_2 may be the same in all instruments.

Further evidence that the Beckman Spinco instrument is less subject to pressure broadening than other instruments is found by recalculation of Linde and Lurie's data [6] (fig. 4), for cyclopropane. The original data * obtained by Linde and Lurie on the pressure broadening of cyclopropane in a Liston Becker Model 16 analyzer have been plotted in figure 3 and compared to our results with cyclopropane. It is evident that their analyzer had a larger broadening effect that the Beckman-Spinco LB-1 used in this investigation. The ratio appears to be independent of CO_2 concentration which in their data ranged from 3-18 per cent.

These findings suggest that the design of the infrared detector has some effect on the magnitude of pressure broadening. Bergman *et al.*[4] have suggested a dependence on the detector cell CO_2 pressure. However, the detectors in the instruments used by Linde and Lurie [6] and by Ramwell [3] were all charged with 50 mm. of mercury P_{CO_2} as were ours. This then cannot account for the difference. Variation of sample cell pressure appears to alter the correction ratio for pressure broadening, but none of the previous workers used as low a pressure in the cell as we did. By extrapolation to atmospheric pressure (fig. 2) the correction factor for CO_2 in N_2O would

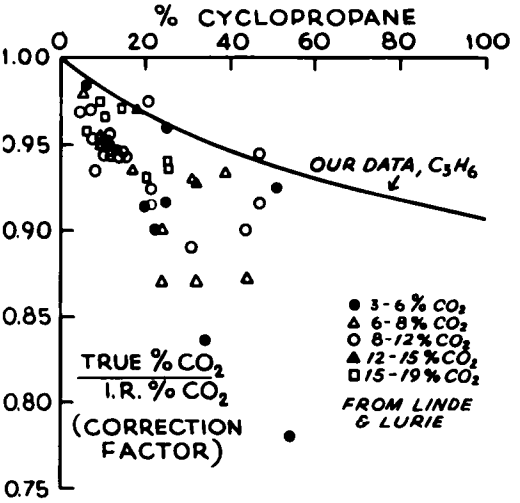

FIG. 4. Data supplied by Dr. Linde for cyclopropane show no correlation of the correction ratio with percentage CO_2.

* Kindly supplied by Dr. Linde.

be 0.94 in our instrument. Linde and Lurie found no difference between analyzers with optical path lengths in the sample cuvette of 0.1 inch and 0.5 inch although the scatter is too great to rule out such an effect. Ramwell's data agree with ours on the relative magnitude of the effect of the three gases, N_2, N_2O and cyclopropane. This relationship probably is transferrable to other instruments. This would suggest that other instruments could be checked at one point, for example 5 per cent CO_2 in 95 per cent N_2O as compared with a CO_2 in O_2 calibration curve and the remainder of the correction factors computed from our data. For example, if an instrument showed a ratio of 0.90 for 95 per cent N_2O, a set of curves could be prepared from our data by multiplying appropriate ratios from our curves by the ratio 0.90/0.92, 0.92 being our ratio for 95 per cent N_2O.

This approach indicates that previously obtained data can be corrected in retrospect (provided the anesthetic concentration is known).

Summary

The pressure broadening effect of N_2, N_2O and cyclopropane on two Beckman Spinco LB-1 infrared CO_2 analyzers with microcatheter sampling cells has been checked by using the CO_2 electrode which is unaffected by anesthetic gases. The LB-1 analyzer exhibits less than half the effect reported in other instruments. The CO_2 concentration value derived from infrared analyzer readings, with a CO_2 in O_2 calibration curve, may be corrected for the error due to these gases by multiplying the value by a factor depending on background gas concentration and sample cell pressure. This factor is independent of CO_2 concentration from 1.5 to 9 per cent and probably to 18 per cent CO_2. The correction factors in the LB-1 analyzer were found to be 0.97 for air, 0.94 for 70 per cent N_2O and 0.97 for 20 per cent cyclopropane. The relative broadening effect of these three gases is probably the same in other instruments but the absolute factor varies for unknown reasons related to detector head design. The CO_2 electrode is useful for analysis of CO_2 in anesthetic gases, since it is unaffected by such gases.

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