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

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Pressure (or collision) broadening introduces errors in infrared analysis of CO₂ 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 CO₂ in these gases. In previous reports on pressure broadening it workers have utilized either chemical analysis or volumetric mixing methods. Chemical analysis of CO₂ in anesthetic gases is somewhat difficult due to absorption of the anesthetic into the CO₂ absorber. The CO₂ electrode, being unaffected by anesthetics, permits greater accuracy and speed in preparing correction factors for this effect. Since the relatively new Beckman-Spinco LB-1 CO₂ 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 CO₂ concentration given a constant background gas.

METHOD

Two Beckman Spinco LB-1 infrared CO₂ analyzers with microcatheter sampling cells were used. The detector cells were charged with CO₂ to a pressure of 50 mm. of mercury. The analyzer heads were flushed and filled with N₂O under slight positive pressure to eliminate the error due to the overlapping absorption bands of N₂O and CO₂. 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. 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 CO₂ in O₂.

Calibration gases (CO₂ in air and CO₂ in O₂) in cylinders were analyzed chemically (Scholander 0.5 ml.) and redetermined against each other on the CO₂ electrode. Response curves for CO₂ in air and CO₂ in O₂ were then prepared.

Anesthetic test mixtures and additional CO₂ in air or O₂ 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.

The CO₂ 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 CO₂) 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 CO₂ could be read to 2.00 ± .01 per cent. Drift of the entire system was less than 1 per cent in 8 hours, i.e., 0.05 per cent CO₂ at 5 per cent CO₂. Reproducibility and linearity

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PER CENT OF BACKGROUND GAS
1.00
0.98
0.96
0.94
0.92
TRUE % CO₂
I.R. % CO₂
(CORRECTION FACTOR)
0.90

Fig. 1. "True % CO₂" is the value obtained from CO₂ electrode analysis, supplemented in some instances by Scholander analysis. "IR % CO₂" is the value obtained from a calibration curve plotting meter deflection against CO₂ in oxygen. The ratio of these readings when background gases other than oxygen are present is a correction factor. The IR percentage CO₂ multiplied by the correction factor gives the true percentage CO₂.

we 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 0.01M NaHCO₃ and saturated KCl electrolyte layer. With this modification, the electrode is linear down to 0.5 per cent CO₂. 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 CO₂ from a CO₂ in O₂ calibration curve. All readings were considered as dry gas readings. The dilution effect of water vapor has been shown 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 CO₂ electrode) to the concentration value obtained from the infrared analyzer using a CO₂ in O₂ calibration curve. This ratio is a correction factor, and is plotted in figure 1 as a function of N₂, N₂O and cyclopropane concentration. The factor for CO₂ in O₂ is 1.0.

There was no detectable variation of the correction factor over the range of 1.5–9 per cent CO₂. 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 N₂O and 5 per cent CO₂. The effect is relatively unimportant if sample cell pressure is within 100 mm. of mercury of atmospheric pressure.

DISCUSSION

Several workers have noted that the error in percentage CO₂ incurred by pressure broadening is proportional to the CO₂ concentration. If this is true, then the ratio of true CO₂ to the apparent CO₂ (based on a CO₂ in O₂ calibra-

SAMPLE CELL PRESSURE, ATM

0

1.0

0.95

0.90

0.85

95% N₂O 5% CO₂

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).
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 (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. have suggested a dependence on the detector cell CO$_2$ pressure. However, the detectors in the instruments used by Linde and Lurie and by Ramwell were all charged with 50 mm. of mercury F$_2$O 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$_2$O would

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$_2$O 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$_2$O has twice the broadening effect of N$_2$ and cyclopropane has about 25 per cent more effect than N$_2$O. 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.
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, N₂, N₂O 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 CO₂ in 95 per cent N₂O as compared with a CO₂ in O₂ 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 N₂O, 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 N₂O.

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

SUMMARY

The pressure broadening effect of N₂, N₂O and cyclopropane on two Beckman Spinco LB-1 infrared CO₂ analyzers with microcatheter sampling cells has been checked by using the CO₂ electrode which is unaffected by anesthetic gases. The LB-1 analyzer exhibits less than half the effect reported in other instruments. The CO₂ concentration value derived from infrared analyzer readings, with a CO₂ in O₂ 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 CO₂ concentration from 1.5 to 9 per cent and probably to 18 per cent CO₂. The correction factors in the LB-1 analyzer were found to be 0.97 for air, 0.94 for 70 per cent N₂O 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 CO₂ electrode is useful for analysis of CO₂ in anesthetic gases, since it is unaffected by such gases.

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REFERENCES