

A CHEMICAL AMPLIFICATION SYSTEM FOR CONDUCTIMETRIC MONITORING OF AIRBORNE CO₂ PARTIAL PRESSURES

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ABSTRACT

A novel method for the detection and quantitation of airborne carbon dioxide is described. The method is based upon membrane transport, chemical amplification, and conductimetric detection. Gas phase CO₂ is equilibrated across a hydrophobic hollow fiber membrane with a primary, secondary, or tertiary alkanolamine containing aqueous phase. The resulting dissolved carbon dioxide reacts reversibly with both water and the alkanolamines to form a variety of ionic species, including: carbonate, bicarbonate, carbamates, and protonated amines. At equilibrium, the CO₂ holding capacities of the alkanolamine solutions are several orders of magnitude greater than that of pure water, resulting in a substantial amplification of the conductivity signal for solutions in equilibrium with a given atmospheric pCO₂.

INTRODUCTION

Gas phase carbon dioxide readily permeates both non-porous and microporous hydrophobic membranes. If the membrane separates a gaseous and an aqueous phase, CO₂ will equilibrate across the membrane as described by Henry's Law.¹

$$H_{\text{CO}_2} = \frac{p_{\text{CO}_2} \text{ atm} - \text{kg}}{m_{\text{CO}_2} \text{ mol}}, \quad (1)$$

where p_{CO_2} is the partial pressure of CO₂ in the gas phase (atmospheres), m is the molality (moles/kg) of CO₂ in the aqueous phase, and H is the Henry's Law¹ constant for CO₂.

In water, ionic species originate from dissolved CO_2 via dissociation reactions,



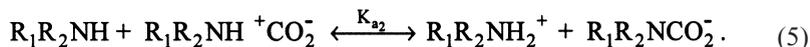
The extent of the resulting ionization is strongly pH dependent.² The dissociation of CO_2 produces hydrogen ions, which in the absence of buffering counter-ions, acidify the aqueous phase. For example, 300 μatm of CO_2 (g) equilibrating with pure water of an initial $\text{pH} = 7$ will produce a final pH of approximately 5.8. The ions formed by the dissociation of dissolved CO_2 increase the specific conductance (κ) of the aqueous medium proportional to their concentrations.

Following equilibrium transport of CO_2 vapor across a membrane into deionized water, the conductivity increase resulting from CO_2 induced ionization reactions will be proportional to the CO_2 concentration on the opposite side of the membrane. The equilibrium constants K_1 , K_2 corresponding to the two dissociation reactions, the Henry's Law constant H , and the equivalent conductances (Λ°) for the ionic species are all functions of temperature. Fortunately, both temperature and specific conductance can be measured very precisely using simple and reliable instruments.

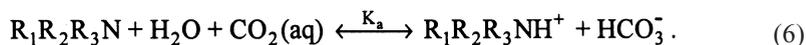
The inherent weakness in using the conductivity of deionized water to monitor CO_2 stems from the very low levels of specific conductance which arise due to equilibration with CO_2 . This can be overcome by chemical amplification of the basic signal. Chemical amplification is achieved using aqueous alkanolamines which increase the solubility of CO_2 through the ionization reactions shown below. Primary and secondary alkanolamines react with dissolved CO_2 in a two step sequence,³⁻⁸ forming first a zwitterion,



which then transfers a proton to an un-ionized amine, forming the corresponding carbamate.



The reaction of tertiary alkanolamines with CO_2 proceeds by the formation of a protonated amine and a bicarbonate anion,



Conductivity is enhanced by the greater equilibrium concentrations of the ionic products for these reactions as compared to those for the dissociation of CO_2 in pure water.

The simple three-step process for determining pCO_2 levels in air has been evaluated in the two prime configurations illustrated schematically in Figure 1. These differ only in the flow characteristics of the alkanolamine solution. The *Closed Circuit* con-

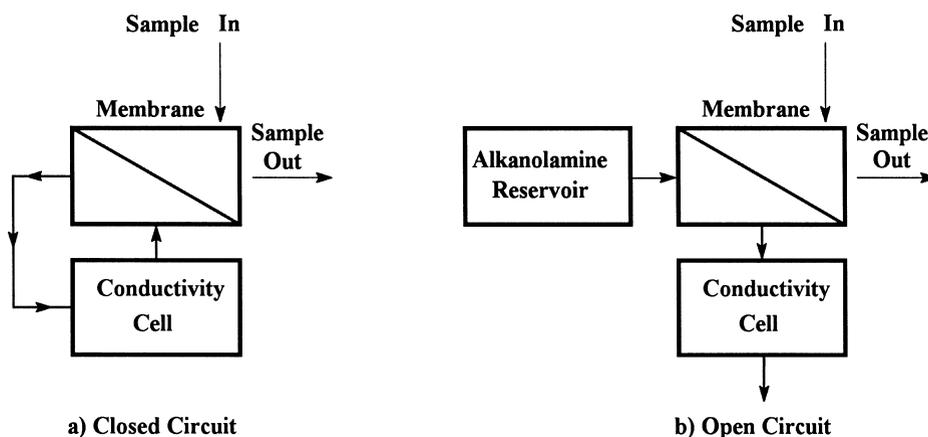


Figure 1. Open circuit and closed circuit primary CO₂ analyzer configurations.

figuration consists of an alkanolamine solution which continuously recirculates through the conductivity cell. This represents an equilibrium detection mode in which the alkanolamine solution gains or loses CO₂ across the membrane in order to equilibrate with a rising or falling pCO₂ in the surrounding air.

In the *Open Circuit* configuration the alkanolamine solution flows from a feed reservoir, first through the membrane contactor, then into the conductivity cell, and then to waste. In this configuration the expendable alkanolamine solution makes a single pass through the system. This mode of detection may or may not be an equilibrium process, depending upon the kinetics of CO₂ transport into the alkanolamine in the membrane contactor.

EXPERIMENTAL

Closed Circuit (Recirculating) CO₂ Vapor Analyzer

The closed circuit test apparatus used to determine atmospheric pCO₂ is illustrated schematically in Figure 2. The system consists of a manifold of valve selectable calibration gas mixtures and ambient air inlet, a membrane contactor, a recirculating pump, an in-line conductivity cell and bridge, a non-dispersive infrared (NDIR) CO₂ detector, and a Molytek model 3702 data logger. Separate contactors were prepared using polypropylene and PTFE membranes. The non-porous PTFE gas-liquid membrane contactor consists of a single 2438 cm fiber (0.051 cm ID x 0.061 cm OD) in a glass shell with an internal liquid volume of 5.0 cm³, an external gas volume of 1000 cm³, and a membrane gas-liquid contacting surface area of 391 cm². The polypropylene gas-liquid membrane contactor consists of a single 610 cm microporous fiber (0.040 cm ID x 0.046 cm OD) in a polyethylene shell with an internal liquid volume of 0.8 cm³, an external gas volume of 12.1 cm³, and a membrane gas-liquid contacting surface area of 24.4 cm².

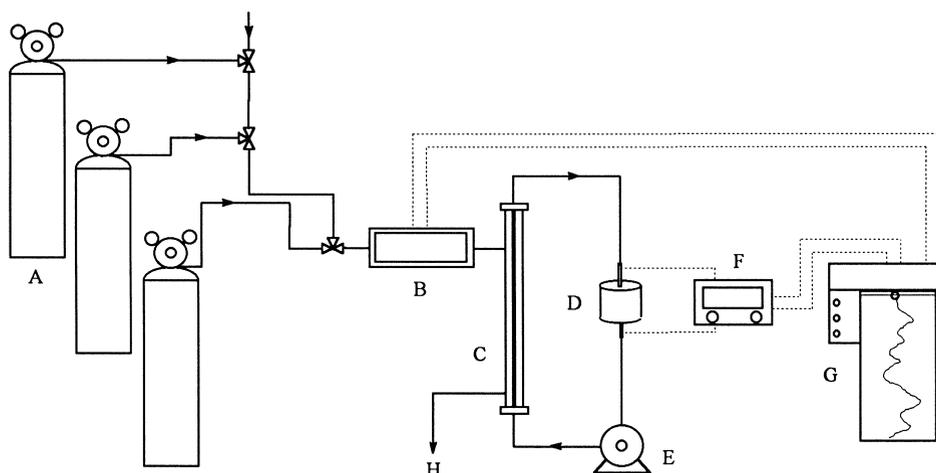


Figure 2. Closed circuit configuration: A - feed gas mixtures/ambient inlet, B - non-dispersive IR analyzer, C - membrane contactor, D - conductivity cell, E - recirculation pump, F - conductivity bridge, G - data logger, H - vent to atmosphere.

Open Circuit (Single Pass) CO₂ Vapor Analyzer

The open circuit test apparatus used to determine atmospheric pCO₂ is illustrated schematically in Figure 3. The system consists of a manifold of valve selectable calibration gas mixtures and ambient air inlet, a membrane contactor, a peristaltic pump, a zero headspace Tedlar alkanolamine feed reservoir (Jensen Inert Products, Miami, FL), a feed conductivity cell and bridge, an in-line conductivity cell and bridge, a non-dispersive IR cell, and a data logger. In this configuration, specific conductance was determined as the differential between the properties of influent and effluent alkanolamine. Two gas-liquid contactor modules were used in this configuration. A microporous polypropylene membrane contactor was prepared using a single 90 cm long fiber (0.040 cm ID x 0.046 cm OD) in a glass shell. This module has an internal liquid volume of 0.1 cm³, an external gas volume of 1000 cm³ and a membrane gas-liquid contact area of 11.3 cm². The second contactor used in the open circuit configuration was the PTFE module described in the previous section.

RESULTS AND DISCUSSION

Based upon initial experiments, 0.001M aqueous solutions of monoethanolamine (MEA) and diethanolamine (DEA) were selected for the open circuit, and closed circuit CO₂ detector configurations, respectively. Prior to experimentation with alkanolamines, as a basis for comparison, the response of a recirculating deionized water loop was characterized when exposed to varying levels of atmospheric CO₂ ranging between 0 - 10,000 μatm. A microporous polypropylene membrane was used. As shown in Figure 4, the experimental results are in reasonable agreement with the theoretical values predicted by Henry's Law, the CO₂ dissociation equilibria, and equivalent conductances at infinite dilution for H⁺, OH⁻, HCO₃⁻, and CO₃⁻, indicating that equilibrium distribution of CO₂ was achieved.

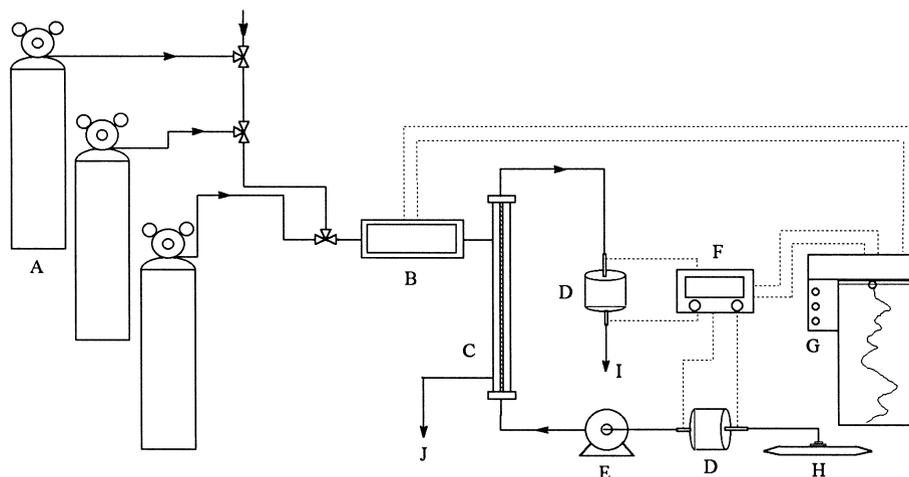


Figure 3. Open circuit configuration: A - feed gas/ambient inlet, B - non-dispersive IR, C - membrane contactor, D - conductivity cells, E - pump, F - conductivity bridge, G - data logger, H - alkanolamine feed reservoir, I - outlet to liquid waste, J - vent to atmosphere.

Closed circuit atmospheric CO₂ tracking experiments were conducted using the apparatus illustrated in Figure 2, containing 0.001M DEA, and gas-liquid contactors utilizing non-porous PTFE, and microporous polypropylene membranes. The CO₂ detection circuit was exposed to the ambient laboratory atmosphere and the change in conductivity versus time was monitored. In all cases a continuously increasing conductivity

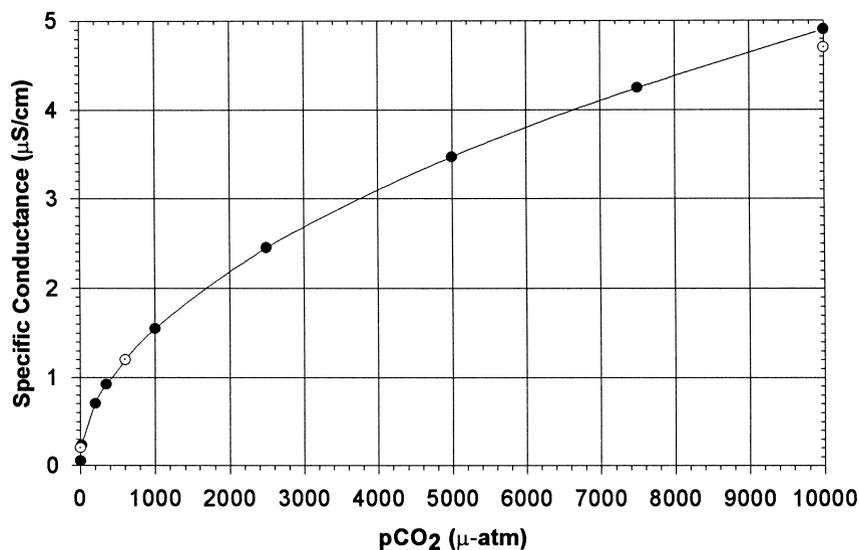


Figure 4. Equilibration of deionized water with CO₂ vapor using a polypropylene membrane contactor. Solid circles - theoretical at 25 C. Open circles - experimental.

baseline was observed due to transport of water vapor across the semipermeable membranes into the gaseous phase. This resulted in a net concentration of the DEA solution with a corresponding increase in baseline specific conductances. Of the two membranes examined, the polypropylene membrane was the most susceptible to water loss.

The rates of water loss across the PTFE membrane were sufficiently slow as to allow a reasonably accurate quantitative tracking of changing CO₂ concentrations. This was achieved by baseline compensation using a linear equation, and calibration of the closed circuit CO₂ sensor by comparison of IR derived CO₂ values and sensor derived specific conductances. The raw data, baseline corrected data, and pCO₂ vs. time in comparison to those derived by IR measurements are shown in Figure 5a, b, and c, respectively.

In this experiment, the Closed Circuit CO₂ monitor was operated continuously for a period of approximately 60 hours. Changing pCO₂ levels were tracked over this time period using the IR based CO₂ detector. The conductivity versus time traces of Figure 5 a and b, and the pCO₂ versus time trace of Figure 5 c, indicate cyclic fluctuations in atmospheric pCO₂, with a 24 hour periodicity. Each of these maxima correspond to levels of peak daytime activity within our laboratory and reflect maximum pCO₂ values in the range between 480 - 490atm. Periods of minimum pCO₂ correspond to evenings and nights. At these times pCO₂ within the laboratory fell to values between 380 - 400 μ atm.

Inspection of Figure 5 clearly indicates that the Closed Circuit apparatus faithfully tracked the relative fluctuations of the laboratory atmospheric p CO₂ over the full time course of this experiment. The two agreed to within 5 %. This level of accuracy was obtained under circumstances in which the deviation in specific conductance between pCO₂ maxima and minima was less than 1.5 S/cm. Atmospheric CO₂ tracking experiments, similar to those described in the preceding section, were conducted using a polypropylene membrane contactor and an open circuit atmospheric CO₂ detection configuration, similar to that illustrated in Figure 3, but with only a single in-line conductivity cell. In this configuration, 0.001 M MEA was used for chemical amplification. In the open circuit configuration the alkanolamine solution does not recirculate. Instead, it flows through the membrane contactor into the conductivity cell, and then to waste. For this reason, reversibility of the CO₂ absorption is not important, and hence the more active but less readily reversible MEA was used.

The preliminary open circuit atmospheric CO₂ tracking results are shown graphically in Figure 6. Figure 6 a, b, and c present IR derived pCO₂, baseline compensated detector response, and raw response data respectively. Inspection of Figure 6 c indicates a curvilinear rising baseline. This was due to absorption of CO₂ vapor into the alkanolamine feed solution prior to flow through the membrane contactor. These results prompted the modification of the open circuit atmospheric CO₂ detection circuit to the configuration illustrated in Figure 3. Two changes were incorporated into the new open circuit configuration. These were 1) storage of MEA feed solution in a gas-tight, zero headspace Tedlar bag, and 2) installation of a second in-line conductivity cell at the outlet of the MEA feed reservoir. All subsequent specific conductance measurements were taken as the differential between the two conductivity detectors.

The relative complexity of the curvilinear baseline elevation for this tracking experiment precluded the calculation of pCO₂ from the specific conductance data. An attempt at baseline compensation was made using a quadratic equation. The resulting

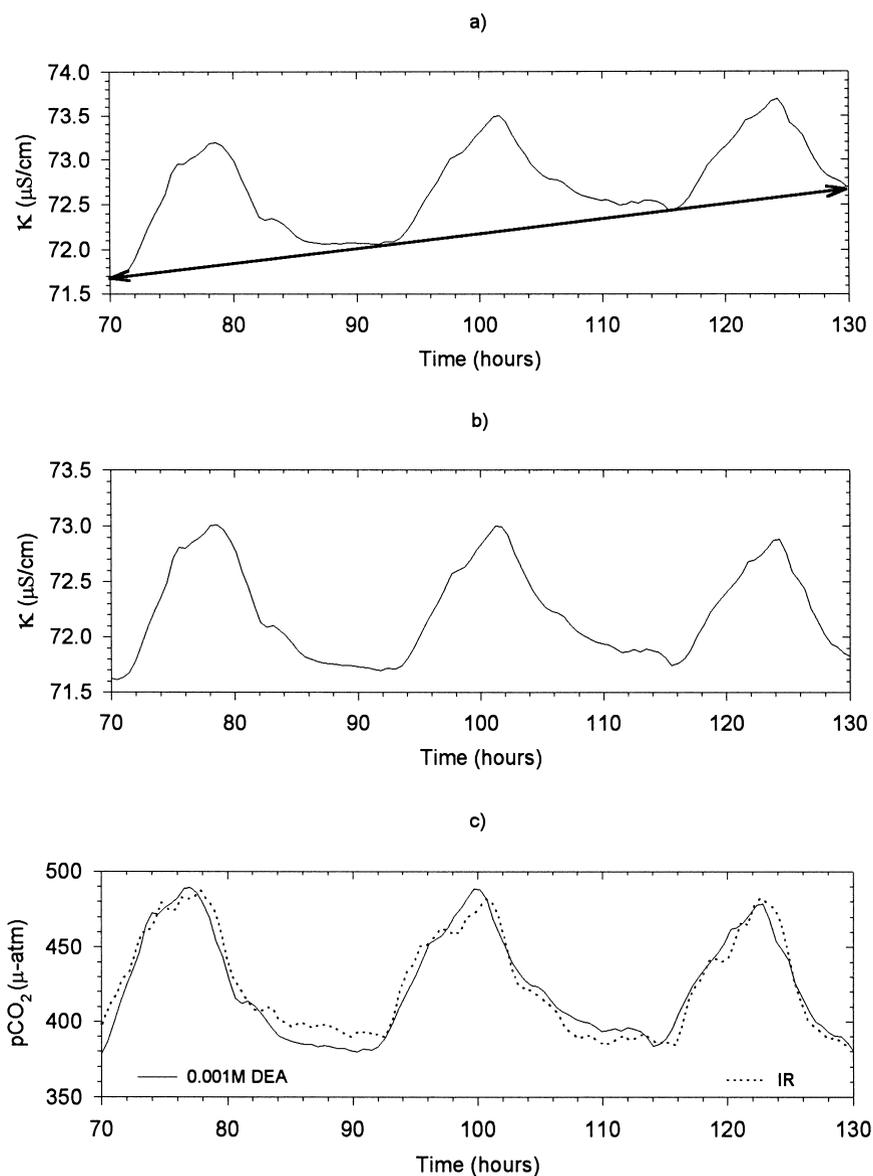


Figure 5. Closed circuit CO₂ vapor tracking - PTFE membrane - 0.001M DEA. a) Raw data, b) Baseline corrected data, c) pCO₂ vs. time.

partially baseline compensated conductivity trace is given in Figure 6 b. While calculation of pCO₂ from these data could not be accomplished with any degree of accuracy, the complimentary symmetry between the IR output and alkanolamine conductivity traces is taken as a strong indication of the potential for long term atmospheric CO₂ monitoring using the chemical amplification method. A calibration curve constructed at the beginning of the experiment is shown in Figure 7. Comparison of these data with

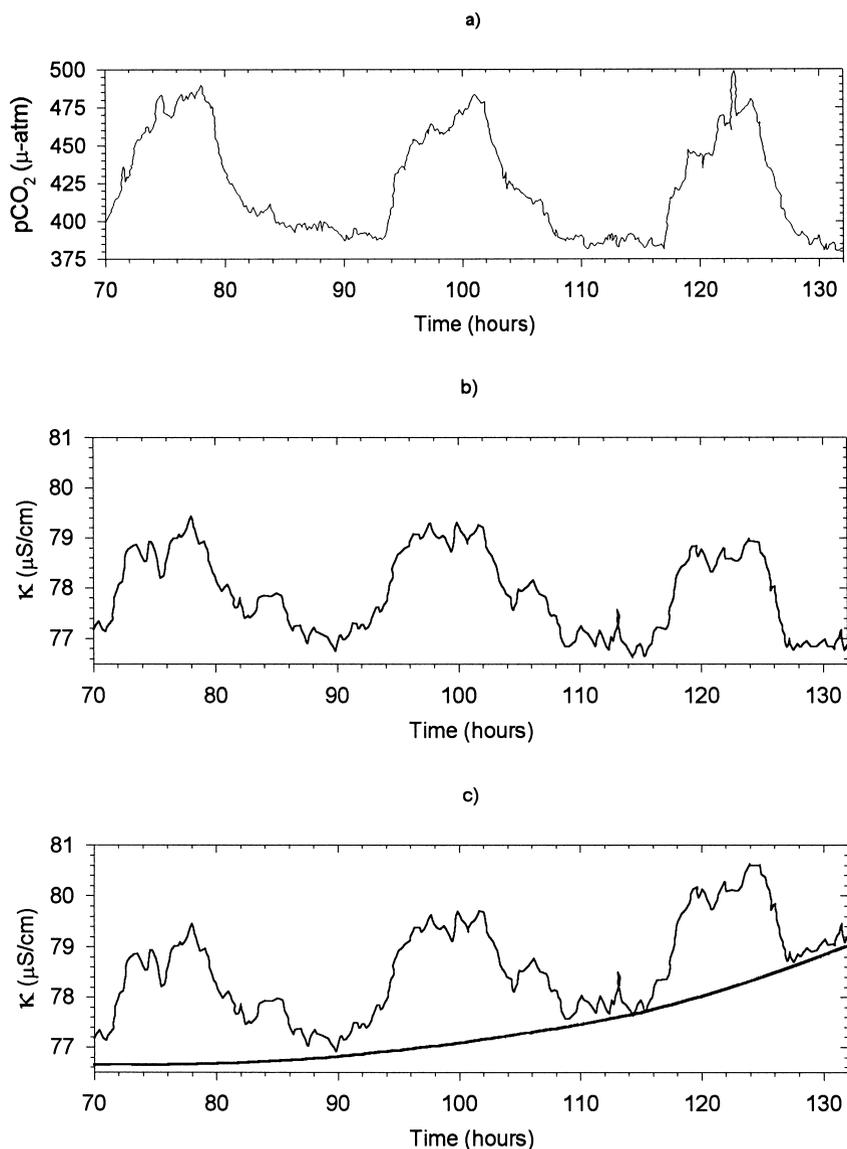


Figure 6. Open circuit CO_2 vapor detection - polypropylene membrane contactor. a) $p\text{CO}_2$ vs. time, b) baseline corrected data, c) raw data.

those of Figure 4 indicates an approximate 30-fold amplification of the specific conductance signal.

The improved open circuit atmospheric CO_2 detection apparatus, in which differential specific conductance signals were monitored, was challenged with a multiple series of calibration gases to determine precision, accuracy and the time response characteristics of the system. These challenges took the form of step functions as illustrated

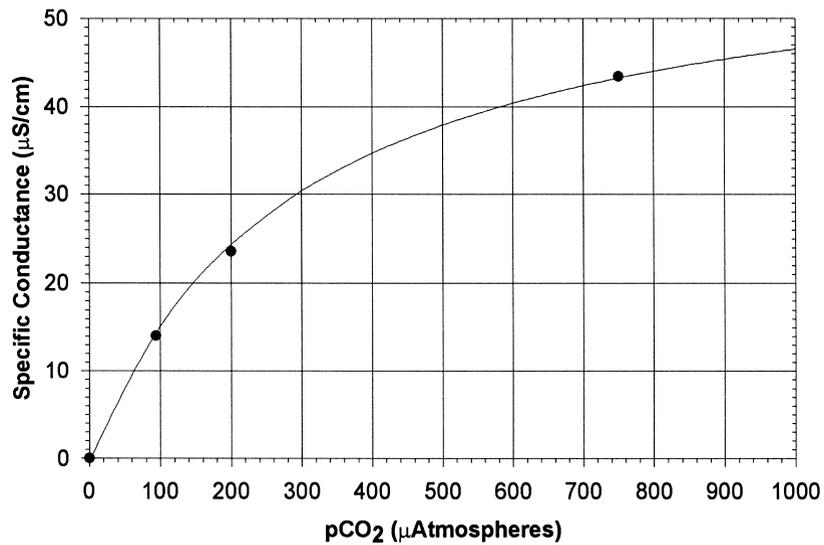


Figure 7. Open circuit calibration curve - 0.001 M monoethanolamine.

in Figure 8. Calibration air- CO₂ mixtures containing 80, 200, 510, and 750 atm pCO₂ were sequentially fed to the apparatus for times of approximately 45 minutes. During this time, differential specific conductance and IR derived pCO₂ were continuously monitored. Concentrations were increased stepwise from the 80 μatm minimum to the 750 atm maximum, and then decreased stepwise to the minimum.

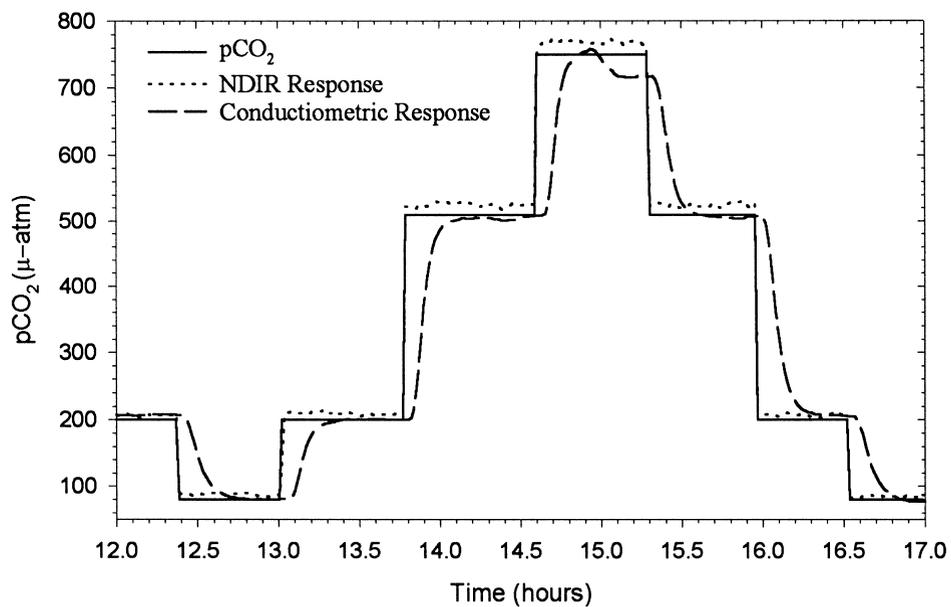


Figure 8. Open circuit dynamic response to calibration gases.

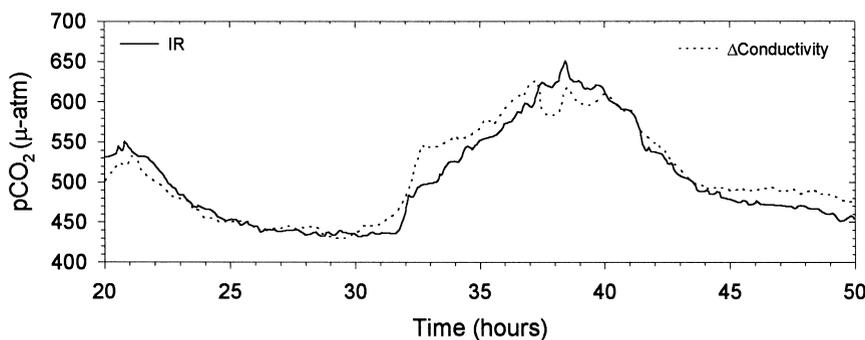


Figure 9. Modified open circuit configuration CO₂ vapor tracking.

Mean differential specific conductances were calculated for each incremental concentration step. The apparatus was challenged with each concentration several times, in both ascending and descending regimes. This resulted in the collection of multiple data points for each concentration. From these data a calibration curve was constructed. As expected, relative standard deviations (coefficients of variation) decreased with increasing sample concentrations. The values ranged from 6.4 % at 80 μatm to 4.0 % at 750 μatm . Significantly, it is evident from inspection of Figure 8 that, with the exception of the 750 μatm concentration, once the specific conductance stabilized at the new level, the experimental apparatus gave more precise results than the IR.

Following completion of the step function standard air-CO₂ gas challenges, the modified open circuit system was again allowed to track the changes in ambient laboratory pCO₂ over the course of approximately 30 hours. The results are indicated in Figure 9. The similarity of symmetry between the IR and experimental analyzer output is noteworthy, and again is taken as a strong indication of the potential for accurate pCO₂ quantitation using this approach.

CONCLUSIONS

The quantitative determination of atmospheric CO₂ using membrane transport, alkanolamine induced chemical amplification, and conductivity detection has been demonstrated. Two alkanolamine flow configurations have been evaluated: closed circuit with continuous alkanolamine recirculation, and open circuit with continuous alkanolamine flow in a single pass through the membrane contactor. Membranes were selected from which efficient vapor-liquid exchange modules were developed for mass transfer of CO₂ into alkanolamine solutions. The alkanolamine mediated chemical amplification of specific conductance, corresponding to typical environmental pCO₂ variations, was clearly demonstrated. This makes practical the use of simple, inexpensive and reliable conductivity cells and bridges in CO₂ analyzer design.

Non-porous PTFE and microporous polypropylene membranes were evaluated. Microporous polypropylene hollow fibers proved to be the most effective, primarily due to high CO₂ transport rates and large surface area to volume ratio. Monoethanolamine (MEA) was identified as a very responsive alkanolamine based on specific conductance changes corresponding to a fixed pCO₂. However, CO₂ absorption by Diethanolamine

(DEA) was found to be more readily reversible than for MEA. For these reasons, DEA was selected for use in the closed loop detector configuration, while MEA was used in the open circuit configuration where reversibility was not required.

Response times of approximately 15 minutes were obtained for step function changes in pCO₂. This value can be improved upon through optimization of the mass transport characteristics of the membrane contactor. Significantly, pCO₂ values provided by the open circuit CO₂ analyzer followed the known concentrations of standard CO₂-air mixtures during step changes more accurately than did our non-dispersive IR detector. The closed circuit (recirculating alkanolamine) configuration was found to be very susceptible to water loss across the membrane. Water was rapidly lost across the membrane into the vapor phase, resulting in an increasing concentration of the dissolved alkanolamine, and the consequent continual rise in baseline conductivity. For this reason, the open circuit configuration is preferred.

The sensitivity of both open and closed circuit CO₂ analyzer configurations can be attributed to the substantial chemical amplification of the conductivity signal. The innovation offers several distinct advantages over more conventional coulometric and infrared spectrometric methods of analysis. These advantages include: simplicity, reliability, instrumental stability, low cost, small size, modest power requirements, ease of automation, and capability for unattended operation over extended periods of deployment. A U. S. Patent has been issued, based in part, upon this work.¹¹

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