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Determination of CO_2 in gaseous samples using a monosegmented flow system and conductimetric detection

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Abstract

The monosegmented approach to flow analysis was employed for determination of low contents (100–1000 ppmv) of CO_2 in gaseous samples. The front bubble of the flow pattern constitutes the gaseous sample. The sample is pumped through a glass tube (2 mm i.d., 80 cm long) by deionised water. The film of water present in the tube wall absorbs the CO_2 present in the sample. The liquid monosegment collects, by convection movement of the fluid, the layer containing the partially ionized CO_2, while the second bubble restricts the dispersion of the collected specimens. The conductivity of the liquid monosegment is monitored at the end of the glass tubing and is proportional to the CO_2 content in the gaseous sample. The system has been optimized for determination of CO_2 in the 50–1000 ppmv range. For the experiment, 100 µl of sample is employed and the system can perform 60 determination per hour. The relative standard deviation for the signals of standards in the 100–900 ppmv range was ca. 3%. Comparison with a gas chromatographic method revealed a mean relative difference of 7% for samples containing CO_2 in the 20–700 ppmv range. The system employing conductimetric detection does not employ any reagent, is very simple and suitable for field monitoring of CO_2 present in the atmosphere, indoors and outdoors. © 1998 Elsevier Science B.V.

Keywords: Gaseous samples; Conductimetric detection of CO_2; Monosegmented flow system

1. Introduction

Interest in rapid determinations of CO_2 in gaseous samples has recently increased. Estimates of CO_2 contents of urban and indoor environments and clinical breath monitors are but a few examples of current demands for automated systems.

A number of physicochemical approaches have been employed for CO_2 determinations in the range usually found in the atmosphere (100–800 ppmv). These include acid–base titration, chromatography, and IR adsorption [1–3]. Electrochemical detection of CO_2 in gaseous samples include potentiometry [4] and conductimetry [5,6]. These techniques employ membrane permeation to isolate the sensor from sample matrices. The use of membranes causes a significant reduction in sensitivity and introduces an additional source of error in the determination as long term stability of the membrane to gas permeation is not easy to achieve.

The literature reports on a few flow systems developed for the determination of gaseous specimens in gaseous samples. Early papers include a system, where the gaseous sample occupies the loop of a

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flow-injection device [7]. The sample was introduced into a reagent stream and the gaseous specimen reacts, producing a coloured compound. Because the system did not employ a second bubble, the dispersion of the compound formed could be large.

More recently, Dasgupta et al. [8,9] described a hanging drop system that can be considered a hybrid between the flow and batch approaches. The system has been applied to the determination of gaseous specimens in large volumes of gaseous samples admitted to a chamber where a hanging drop of the reagent solution is kept in the path of a spectrophotometric detection system. Finally, a flow system that employs the enhancement of luminol-cobalt(II) phthalocyanine chemiluminescence has been described for the determination of CO_2 in atmospheric samples and human breath [10]. This system presents a fast response and is capable of reaching detection limits down to 1.5 ppmv when working at steady state conditions with the gaseous sample being continuously pumped. However, the system employs an expensive reagent mixture, the signal is pH-dependent and the chemiluminescence detection system is somewhat complex.

This paper describes a monosegmented system [11] developed for the determination of CO_2, directly in outdoor and indoor atmospheric samples. The system does not employ either reagents or membrane permeation and the increase of conductivity generated by CO_2 dissolution and ionisation in a water monosegment is used as the analytical response proportional to the content of that gaseous specimen in the sample. The effect of various physical parameters on the performance of the flow system and the relevant effect of the second gaseous bubble on the sensitivity of the proposed methodology were investigated.

2. Experimental

Fig. 1 depicts the flow system employed for CO_2 determinations. The system employs a peristaltic pump (Ismatec MP-13) that impels two deionised water streams through two columns filled with mixed-bed ion-exchange resin used for final purification of the deionised water. A homemade, acrylic injection port is simultaneously used to introduce the contents of three loops into a deionised water carrier stream. In the sampling position (Fig. 1(a)), loop L_1 is filled with synthetic air free of CO_2, L_3 with deionised water and L_2 with the gaseous sample containing CO_2. When the central slice of the injection device is moved to the injection position (Fig. 1(b)), the monosegmented pattern is carried, by a deionised water stream through a glass tube, 2 mm i.d. (see Fig. 1), to the conductimetric flow cell, described elsewhere [12]. Simultaneously, the computer receives a digital TTL signal generated at the optical switch OS_1 that indicates the injection of a sample. The computer programme watches the logical state of OS_2 and triggers the data acquisition routine when the first liquid–gas interface of the sample bubble passes through it. The analogue output of the conductivity meter (Micronal, model B331) is digitised for a previously defined time interval, sufficiently long to allow the second bubble to leave the flow cell. Typical signals generated by the system can be observed in Fig. 2.

2.1. Signal generation principle

After injection (Fig. 1(b)) the gaseous sample and the monosegmented flow pattern are impelled through the glass tube whose wall is wetted with deionised water. The CO_2 dissolves and ionises in the water film. This film is transported into the monosegment by convection forces generated by the movement of the fluid held between the two gas bubbles. The increase in the conductivity of this monosegment is proportional to the CO_2 content of the gaseous sample (Fig. 2). The role of the second bubble is to restrict the dispersion of the collected specimens. Fig. 3 shows the reduction in signal and how large is the dispersion of the specimens if the second bubble is removed by filling the L_1 loop with deionised water.

2.2. Gaseous standards

Certified gaseous standards of synthetic air containing CO_2 (used to simulate samples to evaluate accuracy of the method) in the 140–900 ppmv range were supplied by Air Liquide, Brazil. Additional standard mixtures, used for the construction of analytical curves, were prepared by volumetrically sampling the atmosphere of a bottle containing Dry Ice (solid CO_2) followed by dilution using CO_2-free synthetic air in a sealed, calibrated Erlenmeyer flask.

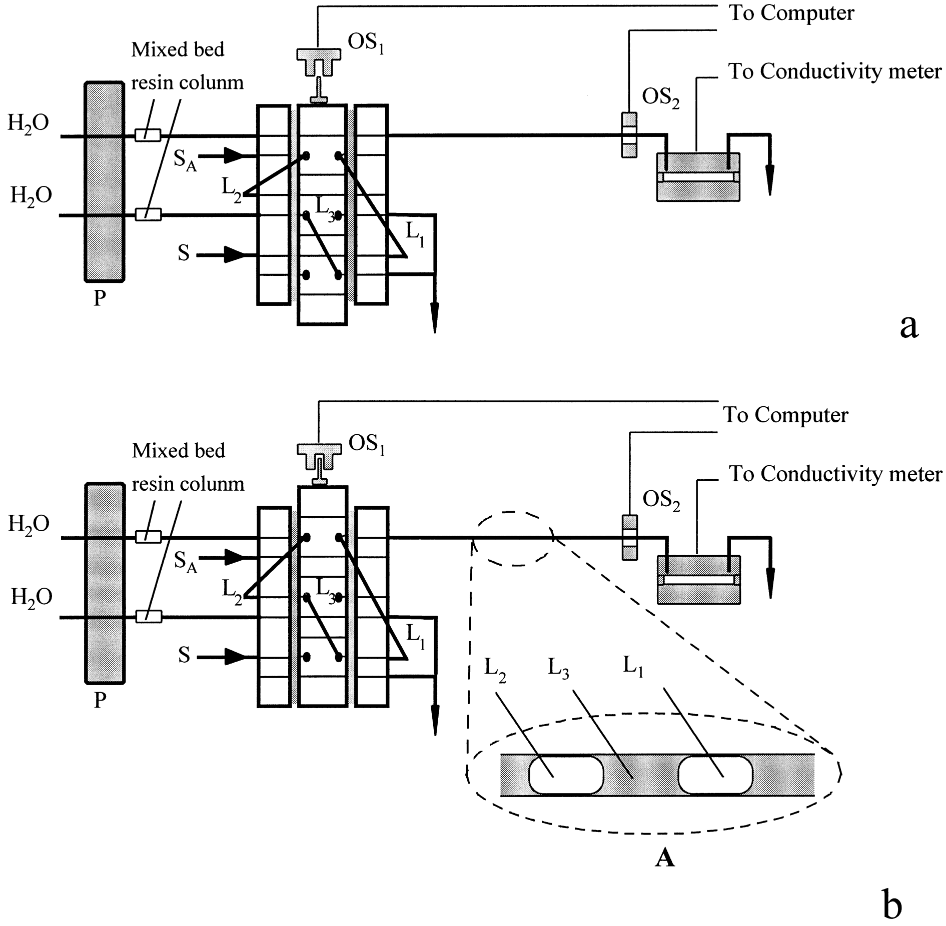

Fig. 1. Monosegmented flow manifold for conductimetric determination of CO_2 in gaseous samples. P, peristaltic pump; $OS_{1,2}$, optical switches; C, conductimetric flow cell; L_1, L_2 and L_3 the loops for the synthetic air free CO_2 (S_A), gaseous sample (S) and deionised water monosegment, respectively. A is a zoomed view showing the flow pattern generated after introduction of the contents of the three loops. (a) and (b), Injector in the sampling and injecting position, respectively.

2.3. Gas-chromatography procedure

Chromatographic determination of CO_2 in the above-mentioned commercial standards of synthetic air were made for comparison purposes, following a previously described procedure [13]. A Hewlett–Packard 5890A chromatograph equipped with a 1-ml sampling loop, a pre-column of molecular sieve 13X, 45/60 mesh, 3 m×2 mm i.d., a working column of Poropak N 80/100 mesh, 3 m×2 mm i.d. and a TCD operating at 100°C, the injector and oven temperature both being fixed at 40°C and an H_2 mobile phase employed at a flow rate of 25 ml min^{-1}. Additional standards (other than for the conductimetric method) were employed for calibration of the chromatography method.

3. Results and discussion

3.1. Effect of flow parameters

Fig. 4 shows the effect of changing the glass tube length (L), the gaseous sample volume (S_v), the liquid monosegment volume (M_v) and the carrier flow rate (r) on the analytical conductimetric signal.

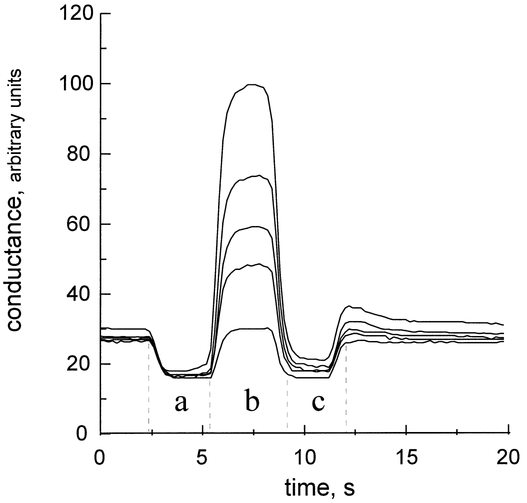

Fig. 2. Typical signals obtained for the determination of CO_2 in gaseous samples: (a) first gas bubble (sample); (b) liquid monosegment; and (c) second inert gas bubble. The signals, read from bottom to top, are: blank (synthetic air free CO_2), 143, 248, 450 and 888 ppmv, respectively.

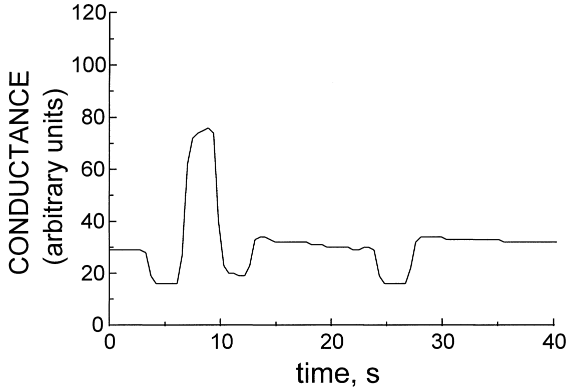

Fig. 3. Analytical signals obtained from a 450 ppmv sample by: (A) using the conventional (two bubbles) monosegmented system; and (B) removing the second bubble.

In order to explain the observed behaviour of the conductimetric signal as a function of these parameters, one should consider that this signal is the result of three processes occurring in the dynamic conditions of the flow system. First, the CO_2 present

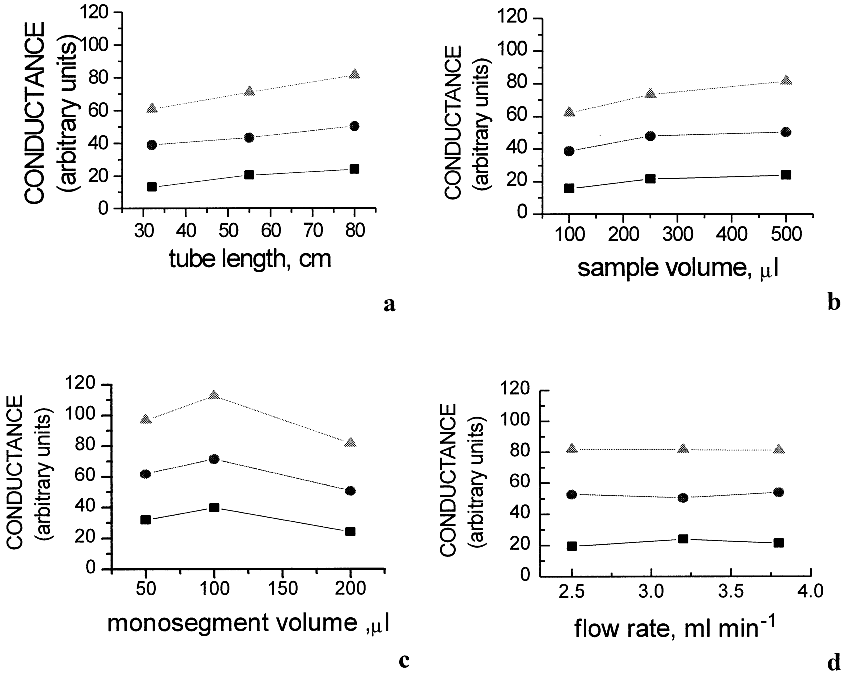

Fig. 4. Effect of some flow parameters on the analytical conductimetric signal: (a) effect of tube length (M_v=200 μl, S_v=500 μl and r=3.2 ml min^{-1}); (b) effect of sample volume (M_v=200 μl, L=80 cm and r=3.2 ml min^{-1}); (c) effect of the monosegment volume (S_v=500 μl, L=80 cm and r=3.2 ml min^{-1}); and (d) effect of flow rate (M_v=200 μl, S_v=500 μl and L=80 cm), $[CO_2]=\Upsilon$90, 360, 720 ppmv.

in the gaseous sample, in contact with a fresh (CO_2-free) water film, held in the glass tube wall, dissolves in that layer. There are evidences that this process is very rapid because a high surface of liquid is exposed to the gaseous sample, the layer is thin and the gas transport is made under turbulent conditions [14]. Assuming that equilibrium is achieved very rapidly, the gas content of the liquid layer is governed by the Henry law, being proportional to the partial pressure of CO_2 (or its concentration) in the gaseous sample. The total amount of CO_2 transferred to the whole liquid layer formed along the glass tube is not easy to calculate because each new fresh portion of the liquid layer will be in contact with a gaseous sample which had its CO_2 content previously reduced by absorption. It was experimentally observed that after running on the liquid layer produced by a 80 cm long glass tube, ca. 50% of the initial CO_2 present in a 250 μl sample, with an initial concentration of 400 ppmv, remains in the gaseous phase leaving the flow cell.

The second process is the ionisation of the dissolved CO_2 to produce the detected species (H^+ and HCO_3^-). This process is known to be slow [14]. About 20 s are necessary to reach the equilibrium after dissolution has occurred. The third process is the transference of the layer containing the dissolved gas (undergoing the ionisation process) to the liquid segment, where its ionisation could still be occurring while the segment travels to the conductimetric flow cell. Therefore, liquid layer portions transferred to the liquid segment, at the initial part of the glass tube, add to the liquid segment a portion of dissolved gas that will have ca. 60 s to complete the ionisation process while the portions transferred at the end of the tube, near the flow cell, will have a very short time interval to reach the ionisation equilibrium.

Fig. 4(d) gives some evidence that the Henry law is the limiting factor for the signal amplitude as little or no signal increase is observed by lowering the carrier flow rate from 3.8 to 2.5 ml min^{-1}. Apparently, it means that the gas/liquid equilibrium is very fast and that the gain that should be observed by allowing more time to elapse for the ionisation process to occur is not significant. Probably because only the last dissolved CO_2 entering the liquid monosegment, before the flow cell, is not nearly in ionisation equilibrium.

Fig. 4(a) shows that a liquid monosegment of 100 μl can still have its conductance increased, after 80 cm long glass tube. The ideal situation for the liquid monosegment is to reach a concentration of dissolved CO_2, equal to that of the absorbing layer. However, as described above, the concentration of the layer should decrease as the gaseous sample has part of its CO_2 removed by previous portions of liquid film. Due to the volume of the segment (100 μl, in the case of Fig. 4(a)), it is possible to predict that the liquid segment is not saturated in CO_2. Therefore, if the tube length is augmented the amount of dissolved CO_2 in the extra portion of liquid film will increase the conductance of the liquid segment due to an increase in the total amount of dissolved CO_2 it receives.

The fact that the Henry law is limiting the signal amplitude can also be observed in Fig. 4(b). Increasing the sample volume does not cause a significant increase in the analytical signal. It arises as a consequence of the fact that increasing the sample volume cannot much increase the total amount of CO_2 dissolved in the same liquid film volume, originated in a fixed tube length because that amount is primarily defined by the liquid/gas equilibrium. It is possible to infer that, if a gas volume equal to the glass-tube volume is introduced in the system the maximum signal will be obtained. However, reducing the volume to half will not cause the signal to be halved because only a fraction of the gas will be absorbed by the first portion of the liquid film. The gas sample is then transported to a new portion of the tube, where a fresh liquid layer is ready to further absorb an additional part of the remaining CO_2.

The fact the there is no remarkable influence of tube length and sample volume on the analytical signal can be taken as an advantage of the proposed method mainly because the precision in measuring the volume of gas sampled need not be very high.

The effect of the liquid monosegment volume (used to collect the CO_2 dissolved in the liquid film) is shown in Fig. 4(c). An optimum value of 100 μl was observed for the given flow manifold and carrier flow rate. The reason for the optimum value must be associated with the fact that lower liquid-segment volumes are not capable of removing the liquid layer containing the dissolved CO_2 with high efficiency while larger ones can do so, but which simultaneously cause a dilution of the resulting solution.

The foregoing explanations on the behaviour of the analytical signal as a function of flow parameters is oversimplified, mainly because no interaction between the glass surface and the gaseous sample is assumed and the dynamics of the dissolved transportation into, and out of the liquid segment was not considered in details.

The results permit the selection of the following values for the parameters: tube length=80 cm; sample volume=100 µl; monosegment volume=100 µl and carrier flow rate=3.2 ml min^{-1}. About 60 samples can be processed per hour if these flow parameters are employed.

Further investigation was carried out on the composition of the reactor tube by replacing the glass tube by a PTFE (1.5 mm i.d.) tube, keeping the internal tube volume the same as the 80 cm glass tube. In this case, a solid/gas equilibrium should be assumed. The results show that PTFE, due to its nonpolar character, causes significant tailing of the signal after the second bubble, thus slowing down the analytical rate.

3.2. Analytical curve, repeatability and accuracy

The analytical curve obtained by using the above-selected values for the parameters shows a quadratic dependence of the peak conductance with the CO_2 concentration in the gaseous sample. A typical analytical curve is: $(9.29\pm1.67)+(0.197\pm0.013)x+(-1.00180\ \text{E}-4\pm0.00002)x^2$, where x is the CO_2 concentration with a correlation coefficient of 0.99923. The behaviour of the calibration curve resembles the ionisation of the weak electrolyte CO_2.

The relative standard deviation (N=6) of the analytical signals obtained for standard gaseous samples containing 90, 180, 360 and 720 ppmv of CO_2 are, respectively, 4.6, 3.5, 1.7 and 1.3%.

The accuracy of the method was assessed by comparison with chromatography, determining the CO_2 content of the certified standards supplied by Air Liquide using a calibration curve with standards prepared from the CO_2 atmosphere produced by solid CO_2. Different standards prepared were employed for the conductimetric and chromatographic methods. The results are summarised in Table 1. The results obtained for the proposed method are in good agreement with those expected for the certified standards and with those obtained by gas chromatography.

Table 1

CO_2 determination by monosegmented conductimetric flow analysis on gaseous standards

$[CO_2]$ expected (±rsd) (ppmv)	$[CO_2]$ found [c] (±rsd) (ppmv)	Relative difference (%)
20 [a] (±0.6)	16 (±31.3)	−20.0
207 [a] (±2.0)	219 (±3.9)	5.8
251 [a] (±1.0)	240 (±2.6)	−4.4
413 [a] (±0.6)	383 (±1.8)	−7.3
511 [a] (±0.6)	472 (±4.2)	−7.6
668 [a] (±1.0)	640 (±2.9)	−4.2
143 [b] (±3)	166 (±5.5)	16.1
248 [b] (±3)	265 (±0.5)	6.9
450 [b] (±3)	453 (±1.3)	0.7
888 [b] (±3)	882 (±3.9)	−0.7

[a] Determination by gas chromatography.

[b] CO_2 standards (Air Liquide), values reported for chromatographic analysis.

[c] Monosegmented conductimetric flow system rsd, expressed for the average of six determinations.

Long-term stability of the system was evaluated by following the variation of the signals obtained for certified standards containing 143, 248, 450 and 888 ppmv of CO_2. The results show relative standard deviations for an 8 h period of system operation, in a laboratory where the temperature was kept at (25±1)°C, of 12.6, 9.8, 7.2 and 3.9% respectively, for the CO_2 concentrations indicated above.

4. Conclusion

The proposed flow methodology for CO_2 determination based on the monosegmented system and conductimetric detection is very simple. It does not employ any reagent other than deionised water. Table 1 allows to infer for the conductimetric flow method a mean relative standard deviation of 3.0% and a mean relative difference of 6% when the results are compared with chromatography. These values were calculated by taking out the first row of Table 1 because such low CO_2 concentrations are difficult to find in the samples addressed by the proposed methodology. The mean precision achieved is ca. 1.5 times worse than that obtained by chromatography and the accuracy is enough to evaluate the CO_2 content in atmospheric air or in closed ambience for occupational health care control. A change in the conductimetric flow-cell constant can improve even more the sensitivity achieved. As the transference of the CO_2 to the acceptor water layer is made after direct contact with the gaseous sample, the sensitivity competes favourably with those flow methods that employ a permeation membrane before detection. The management of gaseous samples is conveniently made by the adapted sample-injection device usually employed in the monosegmented flow systems and the sampling process is, therefore, quite easy. The requirement for a second bubble in the approach herein adopted for CO_2 determination becomes evident from the higher gain in the signal obtained in a monosegmented system, when compared with the introduction of a gaseous sample (one bubble) in a carrier stream. Although the methodology is prone to interference from other gaseous specimens that can undergo ionisation in water, the potential interfering species (as SO_2, NO_2, NH_3) are usually present in very low relative concentrations compared to the usual average content of CO_2 in the air of indoor or outdoor ambience. The flow system presents some advantages for the determination of such kind of samples. It is a low-cost, simple system that can obtain the CO_2 content very rapidly and does not employ any hazardous substances when comparing with the help of chromatography.

The proposed system is also being investigated for use in determination of other gaseous specimens by promoting a colorimetric reaction between the gaseous analyte and a selective reagent, wherein the coloured product formed is maintained in the monosegment and detected by spectrophotometry.

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