Batchwise Collection-Flow Injection Method for the Determination of Carbon Dioxide in Ambient Air

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Abstract

A sensitive and reliable FIA method for the determination of CO_2 in ambient air, coupled with a simple batchwise absorption collection method, was developed. Carbon dioxide in the ambient air could be collected in a 5 ml syringe containing 2 ml of 1×10^{-3} M triethanolamine (TEA), and the carbonate in the absorbing solution was measured by a newly designed FIA system equipped a gas diffusion system (GDS) on line. The color change of cresol red solution was measured at 450 nm with a calibration graph prepared by using standard sodium hydrogen carbonate solutions could be used for the calculation of carbonate concentration in ambient air. The determination range was 0 to 9×10^{-5} M, sample through-put was 12 /h. The average CO_2 concentration of six replicates of an outdoor air sample was 380 ppm; standard deviation (SD) and relative standard deviation (RSD) were 1 ppm and 0.31%, respectively.

Keywords flow injection, carbon dioxide, ambient air, batchwise collection

1. Introduction

Carbon dioxide (CO_2) is the most effective greenhouse gas, which can lead to the result of abnormal climate changes. Carbon dioxide in the atmosphere has gradually increased by 0.3% of the average CO_2 concentration of 360 ppm in air, and to 0.05% of 2000 mol kg^{-1} total carbonate (TC) in seawater [1], which is mainly due to the combustion of a great deal of fossil fuels. The concentration of CO_2 in the atmosphere is equilibrated in surface waters, and more than 98% of the carbon is stored in the oceans dissolved as inorganic carbonate. Therefore, it is very important for better understanding of the change in the concentration of CO_2 in the atmosphere in the future, as well as in the past, to know the role of the ocean and the atmosphere as the carbon reservoirs and to analyze the dynamics of a carbon cycle on the earth. The study on the equilibrium of CO_2 between the atmospheric and the aquatic environment is very interesting for analyzing the global carbon cycle, for which precise and sensitive methods for the determination of CO_2 in air and water samples are urgently required.

The determination of CO_2 in air samples has been carried out so far by the absorption of CO_2 in an alkaline solution and subsequent acid-base titration, an infrared absorption spectroscopy, an electrochemical method, and a thermal conductivity method [2-4].

In JIS (Japanese Industrial Standards) methods [5-7], a non-disperse infrared gas analysis (IR) and a gas chromatographic analysis (GC) were adopted for the determination of CO_2 in air. The main disadvantages of these methods are as follows: (1) the sampling and the pretreatment of air samples are complicated, (2) the moisture in the air must be removed before introducing the air sample to the analyzer and (3) analyte gas standards are necessary for calibrating analyzers.

In recent years, an increasing interest in the development of inexpensive and portable-type sensors for CO_2 determination in air such as capacitor-type sensors using polycrystalline ceramics [8], sodium ionic conductor-based electrochemical cells [9] and lithium ionic conductor-based sensors [10]. Usually, these CO_2 sensors have wide dynamic ranges and their response times are in the ranges of 8 to 40 s. However, they usually have to be operated at high temperature (600-1100K), and their response is sensitive to temperature changes.

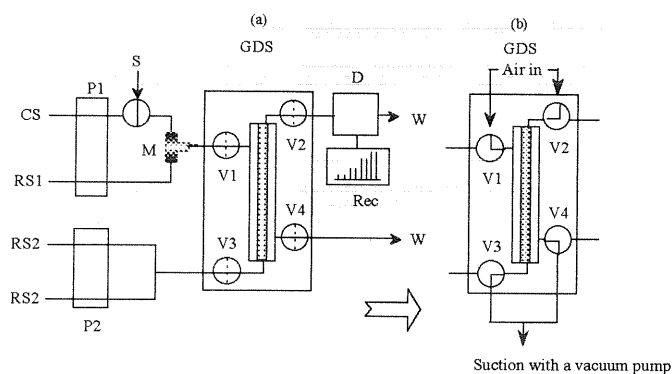*Corresponding author.
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Fig.1 Flow diagram of three-line system incorporating gas diffusion unit for the determination of total carbonate
CS: 1×10^{-3} M TEA; RS1: 3.6×10^{-3} M H_2SO_4 solution; RS2: 2.5×10^{-5} M cresol red solution; P1, P2: double-plunger micro pump; S: sample injection; M: mixing joint; GDS: gas diffusion system ($35°C$); V1, V2, V3 and V4: 3-way valve; D: detector; Rec: recorder; W: waste.
(a) flow diagram during measurement, (b) flow diagram of GDS after measurement.

Motomizu et al. developed various types of gas diffusion units (GDU) for the separation of gaseous analytes, and applied them to the determination of ammonia (ammonium) [11], carbon dioxide (carbonate) [12-13], iodine and chlorine [14], as well as to the indirected determination of hydrogen peroxide [15], in aqueous solutions. Recently, the newly designed GDU was developed, and the sensitivity and reproducibility of the determination of gaseous analytes were improved by installing the GDU in a thermostated compartment. The gas diffusion system (GDS) with the GDU was applied to the sensitive determination of ammonia [16-18] and carbon dioxide [19-21] in water samples. These gas diffusion systems are promising as a useful apparatus for the determination of carbon dioxide in the atmosphere, when some adequate collection techniques are available.

In this work, we developed a reliable and sensitive determination method for CO_2 in air by developing a reproducible batch-wise method for gaseous CO_2 collection and a flow injection analysis (FIA) coupled with a improved gas diffusion system with the GDU.

2.Experimental

2.1 Apparatus

The flow diagram is shown in Fig. 1. Two double-plunger micro pumps, P1 and P2 (F.I.A. Instrument Co., PFA-3000), were used for propelling a carrier, a reaction solution (dil. H_2SO_4) and a receptor/color-developing solution. The GDU was assembled with two deformed

Y-shaped connectors, a glass tubing (2.0 mm i.d., 5.0 mm o.d., x 10 cm) as the outer tubing, a polytetrafluoroethylene (PTFE) membrane tubing (GORE-TEX TA001: 1.0 mm i.d.; 1.8 mm o.d.; pore size, 2 mm; porosity, 50%) as the inner tubing, PTFE tubing (0.5 mm i.d., 1.0 mm o.d.), two O-rings, two ferrules made of silicone rubber and two fittings, which are the same as in the previous paper [21]. A gas diffusion system (GDS) consisting of GDU and valves (V1, V2, V3 and V4) were kept in a temperature-controlled box. After measurements were finished, each valve was turned, and the solutions in the GDU were removed and replaced with air by aspirating air from V3 and V4 for about 5 min (Fig. 1, (b)). By the procedure of replacing solution with air, the gas-permeability of the PTFE membrane can be refreshed and used for more than six months.

Absorbance changes of the receptor/color-developing solution (cresol red, pH 9.0) at 450 nm were measured using a absorptiometric detector consisting of a light emitting diode (LED) as a light source, an interference filter (450 nm) and a micro flow cell (light path 10 mm; volume 8 µl) which was installed in PFA-3000. Flow signals were recorded with a strip chart recorder (Toa Dempa FBR-251A) or a note-type personal computer by using FIA monitor (F.I.A. Instrument).

2.2 Reagents

Chemicals used were of analytical reagent grade (Kanto Chemical Co., Inc.). Purified water was prepared by purifying tap water with a Elix 3 / Milli-Q Element (Millipore Co., Japan), and then

CO_2 in the ultrapurified water was removed by bubbling N_2 for 1.5 h in a water bath at 50°C under ultrasonic radiation. The less-carbonate water thus prepared was used for preparing the carrier (CS), the reaction solution (RS1), the receptor solution (RS2), and the standard carbonate ($NaHCO_3$) solutions.

RS2 contained 2.5×10^{-5} M cresol red (Wako Chemicals, Osaka) and 3×10^{-3} M sodium hydrogen carbonate; the pH of RS2 was adjusted to 9.0 with sodium hydroxide.

RS1 was prepared by diluting a 1.8 M H_2SO_4 stock solution to 3.6×10^{-3} M with the less-carbonate water.

Triethanolamine (TEA) stock solution, 0.5 M, was prepared by dissolving 7.5 g of triethanolamine (Wako Chemicals, assay 98.0-102.0 %) into 100 ml of the purified water. This stock solution was diluted with less-carbonate water and used as CS and an absorbing solution of CO_2 in air samples.

The stock solution of the standard carbonate solution was prepared by dissolving 0.420 g of sodium hydrogen carbonate in 100 ml of water to give a 5.00×10^{-2} M solution. This solution was diluted accurately with the less-carbonate water.

All of the absorbing solutions and the standard carbonate solutions were prepared in a N_2 (min. 99.99%)-filled glove box and stored in a N_2-filled desiccator.

2.3 Standard Procedures for CO_2 collection from air and measurement by FIA

The collection of CO_2 from air samples was carried out with a plastic syringe, whose volume was measured accurately to be 7.012 ± 0.008 ml by weighing the water fulfilled in the syringe till pistons stopped. Into the syringe, 2 ml of absorbing solution (TEA) was transferred from the injection port of the syringe by using a piston-type pipette (Eppendorf, Germany) in the N_2-filled glove box, and then an airtight cap was fixed. The syringes filled with TEA were carried to sampling sites, and the air samples were introduced into the syringes on site, and brought back to a laboratory for the measurement. The air sample syringes were shaken vigorously by hand or with a shaking apparatus (Iwaki KM Shaker Model V-S, Iwaki Co., Tokyo) for required times. After shaking, the absorbing solutions were introduced into the FIA system using a six-way injection valve (Fig.1, S). The concentrations of CO_2 in air samples can be calculated from the measured concentrations in the absorbing solutions by using the collection efficiency and the concentration factor of CO_2. In

this experiment, the concentration factor was $V_{air}/V_1 = 2.506$, where V_{air} and V_1 represent the volume of the air sample (7.012-2.000 = 5.012 ml) and the absorbing solution (2.000 ml), respectively.

The calibration graph was made by using the standard solutions prepared by diluting 1.000×10^{-3} M $NaHCO_3$ accurately with 1×10^{-3} M of TEA. A linear calibration graph was obtained from 0 to 9×10^{-5} M and can be represented as $H = 1.000 \times C$ ($r = 1.000$), where H and C are the peak height of flow signals in centimeter and the concentration of total carbonate in mole per liter, respectively.

3. Results and Discussion

3.1 Shaking time for the collection of CO_2 from air to the absorbing solution

The effect of shaking time on the absorption efficiency of CO_2 in practical air samples was examined using the TEA solution as an absorbing solution by varying the shaking time from 0.5 to 10 min. The results obtained are shown in Fig. 2. The peak height became almost constant at longer than 2 min, where the transfer of CO_2 from the air into the absorbing solution can reach to almost 100 %. In further experiments, 5 min was selected for the complete collection of CO_2 from air.
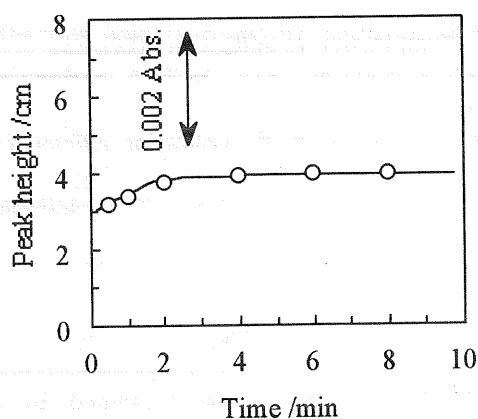

Fig. 2 Effect of shaking time on peak height of total carbonate in the absorbing solution
Air sample; sampled at the campus of Okayama University on December 10, 2001; absorbing solution: TEA (1×10^{-3} M); peak height was obtained by using the flow injection system in Fig. 1.

3.2 Collection efficiency of CO_2 from air into TEA absorbing solution

The collection efficiency was examined by three replicate with each 2 ml of 1×10^{-3} M TEA solution. The results were shown in Fig. 3. In the first collection procedure, the collection efficiency was more than 99.9 %: in the second and third collection procedure with the same air sample of the first absorption procedure was less than 0.1 %. The signals obtained in the second and the third procedure were almost the same as the noise of the background. These results mean that CO_2 in the air sample could be quantitatively absorbed into 2 ml of 1×10^{-3} M TEA solution in the first collection procedure.
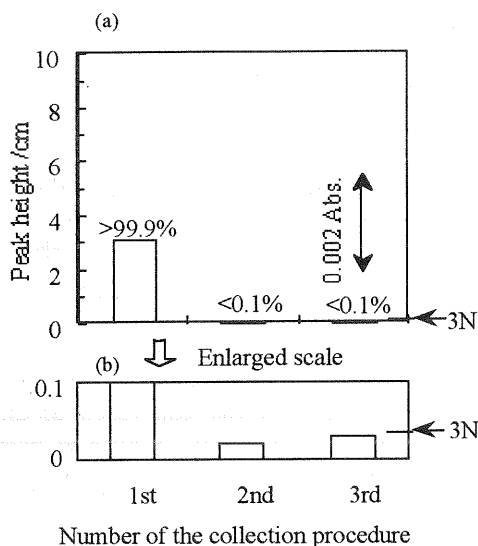

Fig. 3 Examination of collection efficiency.
Absorbing solution; 1×10^{-3} M TEA; shaking time; 5 min.
(a) percent (%) means the collection efficiency; (b) enlarged scale; concentration factor: 2.51.
3N : three times of a noise level of a background in FIA measurement.

3.3 Examination of sampling procedures

The reproducibility was examined by two sampling procedures: (a) the absorbing solution was transferred into the syringe before sampling of air as shown in the standard procedures, and (b) the absorbing solution was transferred into the syringe after sampling of air. The results of indoor (1) and outdoor (2) air samples were shown in Fig. 4. In the procedure (b), when the absorbing solution was transferred into the syringe, the identical volume of the air in the syringe was gone out, and the CO_2 in the discharged air was partly absorbed by the absorbing solution, causing a higher peak height. As a result, the reproducibility and the accuracy in the procedure (b) became worse than in the procedure (a). Therefore, the

procedure (a) was adopted in this work.

3.4 Absorbing solutions for the collection of CO_2 from air

Several absorbing solutions, such as TEA, less-carbonate water, NaOH and KOH solutions were examined for CO_2 collection. The results obtained for the collection efficiency were shown in Fig. 5. It was obvious that among these absorbing solutions, the TEA solution was the best for the collection of CO_2 in air samples.
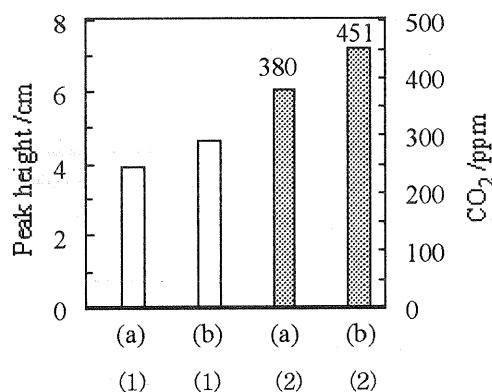

Fig. 4 Comparison of sampling methods
(a), 2 ml absorbing solution was transferred into the syringe before air sampling; (b), 2 ml absorbing solution was transferred into the syringe after air sampling; air sample was sampled at the campus of Okayama University on December 14, 2001; absorbing solution: 1×10^{-3} M TEA; full scale of measuring absorbance: 0.02 Abs. (1) outdoor; (2) indoor. Concentration efficiency: 2.51.
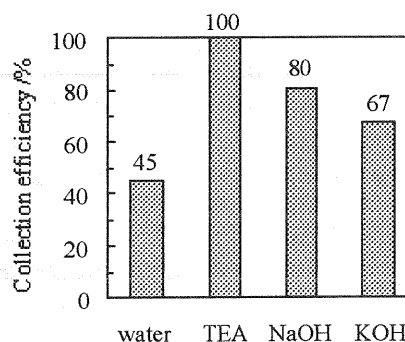

Fig. 5 Comparison of absorbing solutions for absorbing CO_2 in air sample.
Concentration of absorbing solution: 1×10^{-3} M, except for water. Concentration factor: 2.51.

3.5 Effect of TEA concentration in absorbing solution on CO_2 collection efficiency

The effect of TEA concentration on CO_2 collection efficiency was examined by varying its concentration from 1×10^{-4} to 1×10^{-2} M using a practical air sample. As shown in Fig. 6, the collection efficiency became constant at the concentration of TEA being larger than 1×10^{-5} M, and 1×10^{-3} M TEA solution was sufficient for the quantitative and complete collection of CO_2 in ambient air. In further experiments, 1×10^{-3} M TEA solution was used for CO_2 collection.
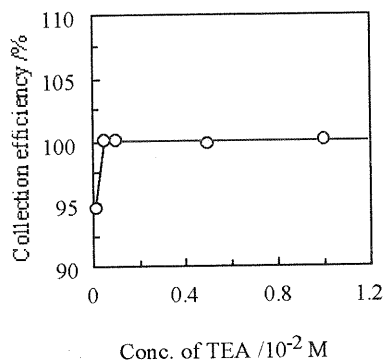

Fig. 6 Effect of TEA concentration on the collection efficiency of CO_2 from air samples.

3.6 Application to outdoor and indoor air

The proposed method was applied to the determination of CO_2 in outdoor and indoor air. The outdoor air was sampled at the campus of Okayama University on December 14, 2001 (pm 4:30; 18°C). The average CO_2 concentration of every two measurements for six replicate samples, was 380 ppm, and the standard deviation (SD) and the relative standard deviation (RSD) were 1 ppm and 0.31%, respectively. The flow signals for outdoor samples were shown in Fig. 7. The indoor air was sampled at our laboratory on the same day after a gas stove burned for 10 h; the CO_2 concentration was determined to be 853±1 ppm.

4. Conclusion

A sensitive and reliable method for the determination of CO_2 in ambient air was proposed. The method was achieved by developing a simple collection procedure with a small syringe, a small volume (2ml) of TEA solution and by using a FIA system coupled with GDS. The concentration of CO_2 in outdoor and indoor air was determined with sufficient accuracy and sensitivity. The method will be possibly used for studying on the CO_2

behavior in the atmosphere and the distribution behavior between the atmosphere and sea.
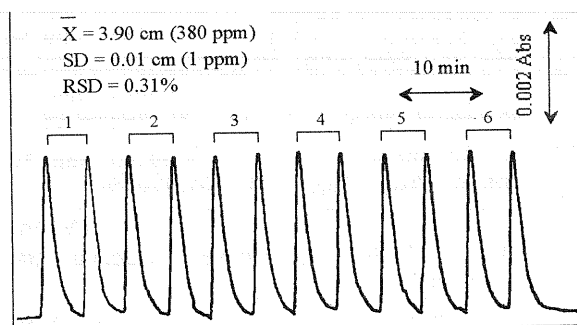

Fig. 7 Flow signals for carbonate measurement in absorbing solutions
Air sample was sampled at the campus of Okayama University on December 14: 2001; absorbing solution, 1×10^{-3} M TEA; shaking time, 5 min.
Six replicate sampling was done, and the carbonate in the absorbing solution was measured two times for each absorbing solution: (1)-(6): sample number.

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