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Application News

CGT-7100 Transportable Gas Analyzer and the TOC-L Total Organic Carbon Analyzer

Evaluation of the Quantity of CO_2 Absorbed by an Aqueous Amine Solution

—Evaluation of the Quantity of CO_2 Absorbed Using the CGT-7100 and TOC-L—

M. Tanaka and T. Iharada

User Benefits

- Combining the CGT-7100 and the TOC-L can be used to obtain information useful for the development of CO_2 separation and recovery techniques using aqueous amine solutions, which is indispensable for carbon recycling.
- The CGT-7100 is compatible with a wide range of sample gas flowrates, so it can be utilized for a variety of tests and evaluations at scales ranging from laboratories to factories.
- The concentration of inorganic carbon like the dissolved CO_2 and HCO_3^- ions in CO_2 absorption liquids can be measured with the TOC-L.

■ Introduction

The search for techniques for the separation, recovery, reuse, and storage of CO_2 is being pursued energetically as a means of attaining a carbon neutral society.

Various physical and chemical approaches are being investigated for CO_2 separation and recovery, one of which is technology that utilizes aqueous amine solutions. In addition to quickly reacting with CO_2, the amines playing a leading part in this technology must provide low cost CO_2 recovery after absorption, as well as excellent stability and safety. Accordingly, research and development is being performed with the aim of achieving better characteristics.

Against this background, this article introduces CO_2 absorption tests using an aqueous amine solution using the Shimadzu CGT-7100 Transportable Gas Analyzer and the Shimadzu TOC-L Total Organic Carbon Analyzer.

■ Measurement Methods

A schematic for the flow line system in this experiment is shown in Fig. 1, and an overview of the equipment is shown in Fig. 2.

CO_2 gas was introduced to an impinger (Fig. 3) at a flowrate of 100 mL/min from a 4.78 vol% CO_2 (in N_2) cylinder, and the CO_2 concentration of the gas at the outlet was measured continuously with the CGT-7100.

The difference between the flowrate for the CO_2 gas delivered under pressure from the CO_2 cylinder and the flowrate of the CO_2 gas suctioned by the pump built into the CGT-7100 was released as "overflow," and its flowrate was set at approximately 30 mL/min. A 3-way valve was used to bypass the impinger.

The amine used was 2-Amino-2-methyl-1-propanol (abbreviated as AMP, chemical formula $(CH_3)_2C(NH_2)CH_2OH$), and this was diluted with pure water to a concentration of 20 wt%.

Two routes, shown below in (1) and (2), are known for the reaction of CO_2 with amines (for primary amines R-NH_2).

$$2(R\text{-}NH_2) + CO_2 \Leftrightarrow R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^- \quad \cdots (1)$$

$$R\text{-}NH_2 + CO_2 + H_2O \Leftrightarrow R\text{-}NH_3^+ + HCO_3^- \quad \cdots (2)$$

Separation and recovery of CO_2 by reaction (2) is preferable because the amine molecules and CO_2 molecules react in a 1 to 1 ratio (as opposed to a 2 to 1 ratio in reaction (1)), and the thermal energy required for CO_2 recovery is less than in reaction (1). Reaction (2) is the primary reaction for AMP, which is the amine used in this experiment.[1,2)]

In addition, in reaction (2), the CO_2 absorbed by the aqueous AMP solution exists as HCO_3^- ions. In this experiment, the concentration of this HCO_3^- was measured with the TOC-L.

The TOC-L is equipped with a function for separately quantifying the total organic carbon (TOC) and the inorganic carbon (IC). In this approach to IC measurement, the sample is acidified so that the HCO_3^- and CO_3^{2-} therein are changed to dissolved CO_2. After this, it is extracted using pure gas, and then quantified by an IR CO_2 detector. Using this function, the amount of HCO_3^- carbon can be quantified without being affected by the carbon from the amines included in large quantities in the CO_2 absorption liquid.

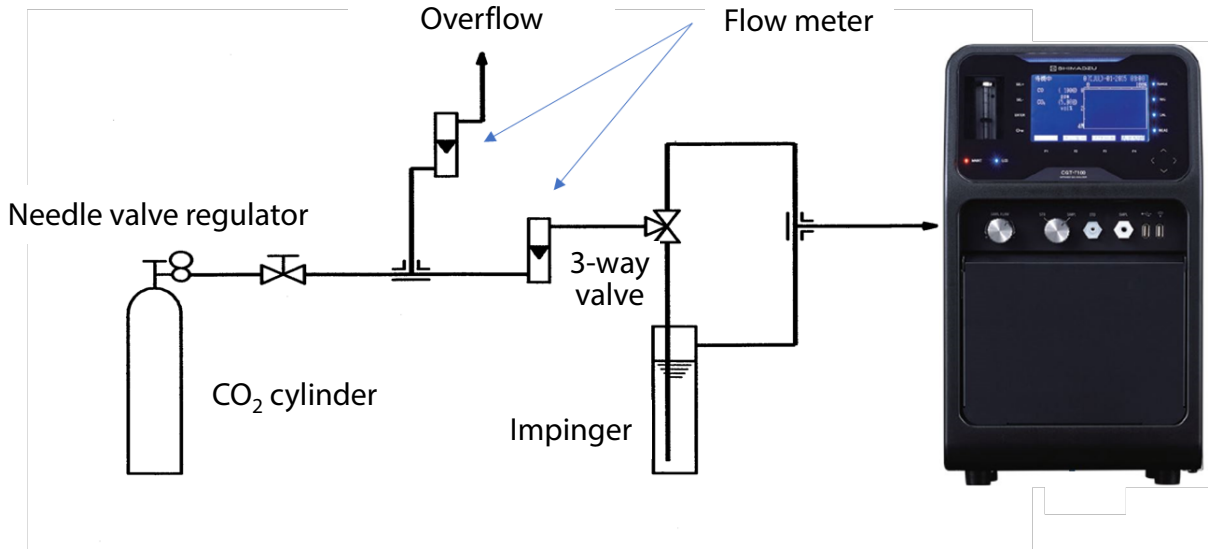

Fig. 1 Schematic of the Flow Line System for this Experiment

Table 1 Measurement Conditions

Analyzer:	CGT-7100	TOC-L
Measured Components:	CO_2	IC
Range:	10 vol%	1000 mg/L
Gas Flowrate:	100 mL/min	—
Amount of Sample Injected:	—	28 µL
AMP Concentration:	20 wt%	
Amount of Aqueous AMP Solution:	0.6 mL	
Room Temperature:	26 °C	

■ Measurement Results and Discussion

The results of the CO_2 concentration measurements using the CGT-7100 are shown in Fig. 4. The regions in Fig. 4 denoted by red arrows (A) and (B) are the intervals in which the CO_2 gas passed through the impinger. Outside of these regions, the impinger was bypassed using the 3-way valve.

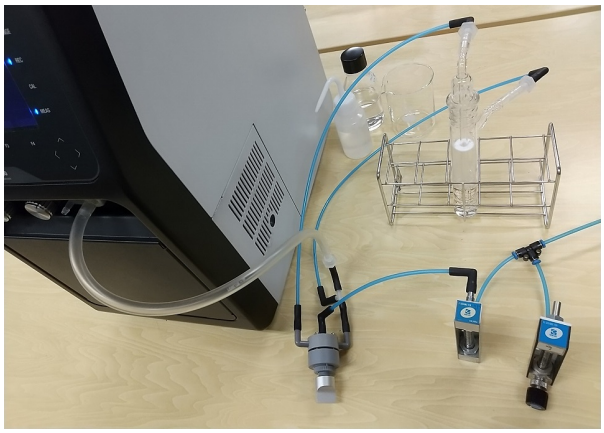

Fig. 2 Overview of the Experiment

The CO_2 gas concentration was not 0 vol% even when passing through the impinger, so with the conditions for this experiment, it is evident that the gas/liquid contact efficiency (including agitation) for the CO_2 gas and the aqueous AMP solution as well as the reaction rate were insufficient for complete CO_2 absorption. In addition, the CO_2 concentration rose with the time spent passing through the impinger, which means that the CO_2 absorption capacity decreased. This was likely due to a decrease in the concentration of unreacted AMP as reaction (2) progressed. This is also suggested by the fact that the changes in CO_2 concentration while passing through the impinger in regions (A) and (B) form a continuous curve when the points at both ends of the black curve (C) are connected.

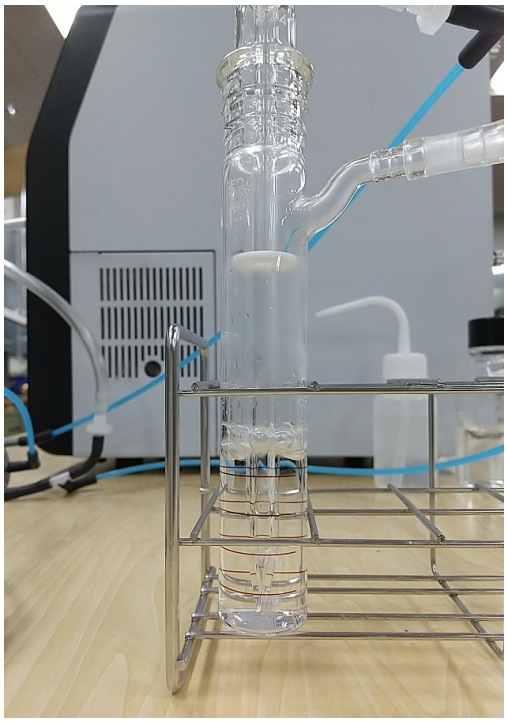

Fig. 3 Passing through the Impinger

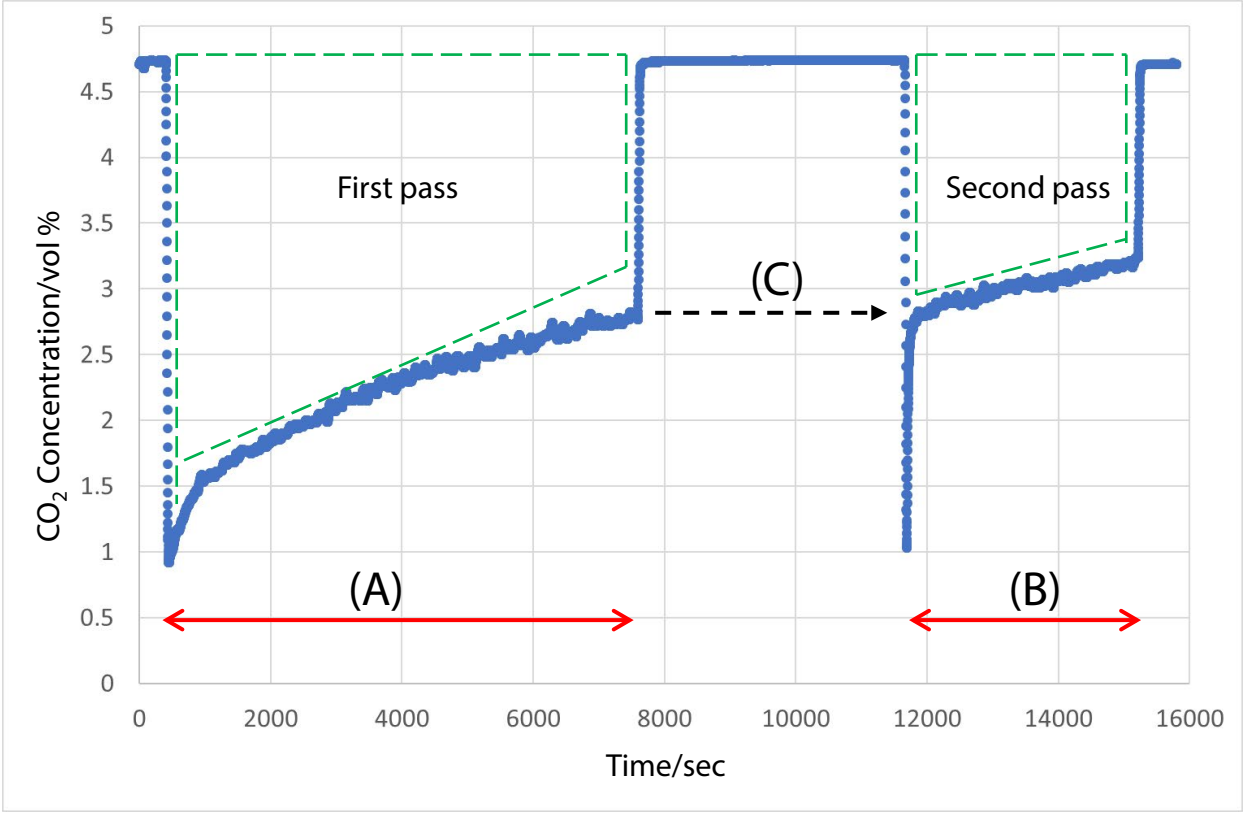

Fig. 4 CO_2 Measurement Results Using the CGT-7100

Next, the regions enclosed by the green dotted lines in Fig. 4 were taken to be the amount of CO_2 absorbed by the aqueous AMP solution. The value was determined to be 24,231 vol%•sec from a surface area calculation using spreadsheet software. If this is all assumed to exist as HCO_3^- in the aqueous AMP solution as the result of reaction (2), this represents an IC concentration of 10,502 mg/L. (Refer to the equation below.)

IC (mg/L) = 24,231 (vol%•sec)
× (100/60) × (1/100) ← Conversion to amount of CO_2 (mL)
× (1/22.4) ← Conversion to number of mols of CO_2 (mmol)
× 12 ← Conversion to carbon mass (mg)
× (1000/20.6) ← AMP absorption liquid amount correction
= 10,502 mg/L

The results of the IC measured using the TOC-L from the aqueous AMP solution diluted by a factor of 20 after the experiment in Fig. 4 was finished are shown in Fig. 5. If this measurement result of 561.6 mg/L is multiplied by 20 to find the IC concentration for the original aqueous AMP solution, a value of 11,232 mg/L is obtained. This is close to the value for the CO_2 absorption amount obtained from the above-mentioned CGT-7100 measurements.

This suggests the possibility that the AMP mainly reacted with CO_2 via reaction (2).

■ Conclusion

This experiment introduced the usage of two analyzers:

- Real time observations of CO_2 absorption by an aqueous AMP solution using the CGT-7100
- Quantitative determination of the CO_2 in the aqueous AMP solution using the TOC-L.

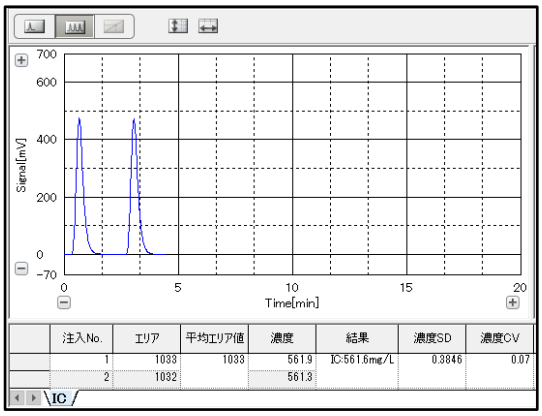

Fig. 5 IC Measurement Results Using the TOC-L for an Aqueous AMP Solution Diluted by a Factor of 20

As shown here, with the CGT-7100, information relating to the behavior of the aqueous amine solution and the absorption reactor could be obtained with the CGT-7100, and information relating to the CO_2 absorption reaction and the amount of absorption could be obtained using the TOC-L. Accordingly, combining these two analyzers makes it possible to obtain important information easily and in detail regarding the setting and evaluation of conditions for the CO_2 absorption process.

In addition, using the manual sample injection kit, an optional accessory for the TOC-L, makes it possible to measure the concentration of CO_2 contained in the gas collected in a gas tight syringe. This could be applied for example to applications for obtaining measurements of CO_2 concentrations at each component in a CO_2 separation and recovery system.

The CGT-7100 and the TOC-L can certainly be used for research and development of CO_2 separation and recovery techniques, at scales varying from laboratory to factory.

References

1) Computational Chemistry Studies on CO_2 Chemical Absorption Technique: Challenge on Energy and Environmental Issue, Kei Teranishi, Atsushi, Ishikawa, Hiromi Nakai, J. Comput. Chem. Jpn., Vol. 15, No. 2, pp. A15–A29 (2016).
2) CO_2 Capture Technology for Mitigating Global Warming and Climate Change, Masaki Iijima, Takahiko Endo, Daisuke Shimada, Mitsubishi Heavy Industries Technical Review Vol. 47 No. 1 (2010)

Shimadzu TOC-L Total Organic Carbon Analyzer

Shimadzu CGT-7100 Transportable Gas Analyzer

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