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Application News

TOC-L Total Organic Carbon Analyzer

Evaluation of Amine Solutions for CO_2 Absorption by TOC/TN

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User Benefits

- Separation and recovery processes for the greenhouse effect gas (GHG) CO_2 by amine solutions can be evaluated by using the TOC-L analyzer.
- The concentration of inorganic carbon, such as the concentrations of dissolved CO_2 and hydrogen carbonate ions, can be obtained by inorganic carbon (IC) measurement of amine solutions.
- Concentration control of amine solutions is possible by TOC/TN measurement.

■ Introduction

Global warming, which has become an issue in recent years, is caused by the increasing concentration of greenhouse effect gases (GHG) in the atmosphere. In particular, it is feared that the effects of CO_2 may affect ecosystems at the global scale. As a countermeasure for this problem, research on technologies such as CCS (carbon capture and storage) and CCUS (carbon capture, utilization, and storage) for separation and recovery of CO_2 and reuse of CO_2 by conversion to valuable substances is underway with the aim of realizing carbon neutrality.

CO_2 recovery techniques include chemical absorption methods, physical absorption methods, and membrane separation methods. The optimum method is selected based on the physical properties of the discharge source, such as the CO_2 concentration and pressure.

Among these various approaches, chemical absorption methods utilizing amine-based solutions, which bond strongly with CO_2 by chemical reaction, have the advantage of applicability to low partial pressures such as combustion off-gas and other sources of CO_2 because of their high reactivity, and various research efforts are in progress.

This article introduces an example of measurement of CO_2 capture by amine-based solutions and TN measurement and TOC measurement of the amine solutions by adding a TNM-L total nitrogen measurement unit to Shimadzu TOC-L total organic carbon analyzer.

■ Measurement Method

Two types of amine solutions were prepared using 2-amino-2-methyl-1-propanol [abbreviation: AMP, chemical formula: $(CH_3)_2C(NH_2)CH_2OH$] or monoethanolamine [abbreviation: MEA, chemical formula: $HOCH_2CH_2NH_2$]. The AMP and MEA were diluted with pure water to prepare solutions having concentrations of 20 wt% of AMP and 30 wt% of MEA.

It is known that there are two paths in the reaction of amine and CO_2, as shown in ① and ② below (for the case of Class 1 amine $R\text{-}NH_2$).

$$2(R\text{-}NH_2) + CO_2 \Leftrightarrow R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^- \quad \cdots ①$$
$$R\text{-}NH_2 + CO_2 + H_2O \Leftrightarrow R\text{-}NH_3^+ + HCO_3^- \quad \cdots ②$$

MEA is widely used because it is inexpensive and has high reactivity with CO_2. However, since reaction ① is the main reaction, the stoichiometric ratio of the amine molecule and CO_2 molecule is 2:1. As a result, the heat of reaction with CO_2 is large, and the energy consumption required in CO_2 recovery is also large.

On the other hand, when using AMP, reaction ① is difficult because a bulky substituent is bonded around the amine group, and reaction ② becomes the main reaction, but because the stoichiometric ratio of the amine molecule and CO_2 molecule is 1:1, energy consumption for CO_2 recovery can be reduced. In addition, AMP also has the advantage of a large CO_2 absorption rate.

In this experiment, samples were prepared by flowing CO_2 gas through these two types of amine solutions, as shown in Fig. 1, to cause CO_2 absorption.

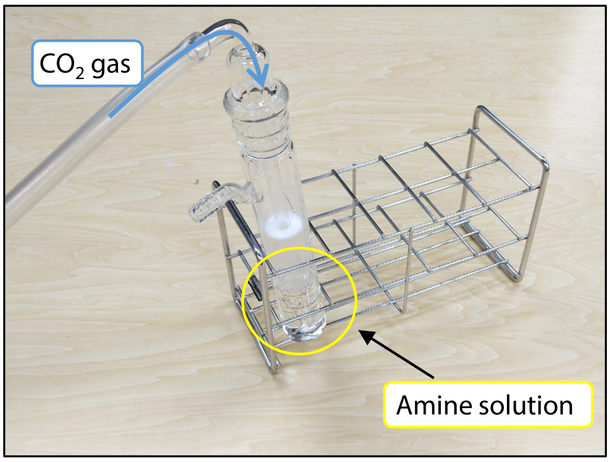

Fig. 1 Experimental Setup for CO_2 Absorption in Amine Solutions

First, 20.6 mL of the amine solution was introduced into an impinger, and CO_2 gas was flowed for approximately 2 h at a flowrate of 100 mL/min from a 4.74 vol% CO_2 (in N_2) cylinder to absorb CO_2 in the solution. Due to reaction ②, part of the CO_2 captured by the amine solution exists in the form of hydrogen carbonate ions.

These samples were evaluated by using a TOC-L analyzer, which has a function that enables separate quantitation of the total organic carbon (TOC) and inorganic carbon (IC) in the sample. IC measurements are carried out by the acidification and sparging method, in which the sample is first acidified to convert HCO_3^- and CO_3^{2-} to the form of dissolved CO_2, and this CO_2 is then extracted (sparged) with a clean gas and quantified using an infrared CO_2 detector. This method makes it possible to determine the carbon content of HCO_3^- unaffected by carbon originating from the amine, even though the CO_2 capture solution contains a large amount of amine. If the optional TNM-L total nitrogen measurement unit is added to the system, it is also possible to measure the total nitrogen (TN) content, which can be used to control the concentration of the amine solution.

By using the TOC-L analyzer, it was possible to obtain the quantity of CO_2 captured by the amine solutions based on the IC measurements and the TN concentration and TOC concentration of the amine solutions from the TN and TOC measurements.

■ Measurement Conditions

The IC, TN, and TOC concentrations were measured before and after absorption of CO_2 by the amine solution. The samples for the IC measurements were diluted 100x and the samples for the TN and TOC measurements were diluted 500x with pure water. Table 1 shows the measurement conditions.

Table 1 Measurement Conditions

Instruments	: TOC-L_{CPH} total organic carbon analyzer, TNM-L total nitrogen measurement unit
Catalyst	: TOC/TN catalyst
Measurement items	: IC, TN, TOC (= TOC after acidification and sparging)
Calibration curves	: IC: One-point calibration curve by 200 mgC/L of sodium carbonate/sodium bicarbonate (aq) TN: One-point calibration curve by 200 mgN/L of potassium nitrate (aq) TOC: One-point calibration curve by 400 mgC/L of potassium biphthalate (aq)
Injection volume	: 40 µL
Samples	: AMP (2-amino-2-methyl-1-propanol), concentration 20 wt% solution MEA (monoethanolamine), concentration 30 wt% solution
CO_2 absorption conditions	: Absorption of 4.74 Vol% CO_2 (in N_2) by approximately 20 mL of sample at flowrate of 100 mL/min for approximately 2 h
Sample dilution rates	: IC measurements: 100x TN measurements: 500x TOC measurements: 500x

■ Measurement Results

Table 2 shows the results of the measurements of the IC, TN, and TOC of the amine solution before and after CO_2 gas absorption. All measurement values have been corrected for the dilution rate.

Table 2 Measurement Results

Sample	IC measurements values (%C)	
	AMP solution	MEA solution
Before CO_2 absorption	0.00118	0.0006
After CO_2 absorption	1.26	1.07

Sample	TN measurements values (%N)	
	AMP solution	MEA solution
Before CO_2 absorption	3.37	7.18
After CO_2 absorption	3.34	7.08

Sample	TOC measurements values (%C)	
	AMP solution	MEA solution
Before CO_2 absorption	11.7	12.2
After CO_2 absorption	11.4	12.1

From Table 2, it can be understood that the IC concentrations of both the AMP solution and the MEA solution increased greatly, by more than 1000 times, as a result of absorption of CO_2 gas. From this, it is clear that the IC concentration increases because the amine solutions capture CO_2 gas and this CO_2 is dissolved in the solutions as hydrogen carbonate ions.

On the other hand, no large changes were detected in the TOC and TN concentrations, indicating that there was no significant effect on the concentration of the amine solutions in this CO_2 gas capture experiment.

■ Conclusion

This experiment demonstrated that the amount of CO_2 captured by amine solutions can be quantified and the concentration of the amine solutions can be controlled by using the TOC-L analyzer. At present, various research projects on low cost, energy saving CO_2 separation and recovery technologies are underway with the aim of realizing carbon neutrality. Among those efforts, chemical adsorption methods using amine solutions have attracted considerable attention, and the TOC analyzer is expected to be useful in that research.

Fig. 2 Shimadzu TOC-L Total Organic Carbon Analyzer and TNM-L Total Nitrogen Measurement Unit

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