Technology

Development of a highly sensitive analytical method for detecting impurities in CO_2 using gas separation membrane

KOJIMA Yuta*　　TOUKAIRIN Susumu**

1. Introduction

In our company, analysis of various impurity components in product gases is performed as part of the quality assurance for industrial gases. In recent years, the demand for high-purity gases has been increasing alongside advancements in semiconductor miniaturization. Users are also demanding strict quality assurance, and high-sensitivity analysis technology that meets these requirements is needed accordingly.

In the ultra-trace range where impurity concentrations are at the sub-ppb level, measurement with commercially available analyzers such as gas chromatographs is difficult. For this reason, as a pretreatment, impurity concentration analysis using a low-temperature trap with liquid nitrogen or similar substances is performed. While this method enables sub-ppb analysis, it presents the following challenges:

(1) Since the method needs repeated cooling and heating cycles, analysis time and running costs increase.

(2) If the main component of the sample has a higher boiling point than the impurities, the main component solidifies or liquefies during the cooling process, causing the flow path of the concentrating section to become blocked.

In recent years, the demand for high-purity CO_2 has been increasing as supercritical CO_2 drying technology is increasingly utilized as a wafer cleaning technique in semiconductor manufacturing processes. However, applying the technology to impurity concentration analysis using a low-temperature trap has been difficult because it causes CO_2 to solidify.

Accordingly, as a new method to enable the analysis of ultra-trace impurities even in samples containing CO_2 as its main component, we have developed an impurity concentration analysis technology using a separation membrane. The following introduces this technology.

2. Methods for Impurity Concentration Analysis

2.1 Concentration Analysis Using a Low-Temperature Trap

As previously stated, in our company, an ultra-trace impurity concentration analysis technology using a low-temperature trap has been established, and analysis of ultra-trace impurities at the sub-ppb level is performed. The concentration system used in this method consists of a concentrating column for capturing and concentrating impurities, and a cooling/heating device that repeatedly controls the cooling and heating processes. As shown in Fig. 1, this system captures ultra-trace impurities in a cooled concentrating column for a certain period and then heats the column to introduce the concentrated impurities into an analyzer for ultra-trace impurity analysis.

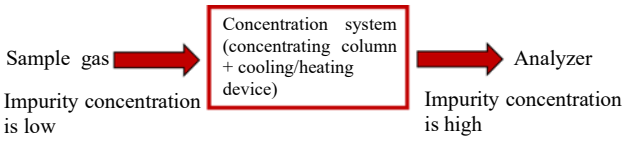

Fig. 1 Overview of impurity concentration analysis using a low-temperature trap

2.2 Concentration Analysis Using a Gas Separation Membrane

On the other hand, gas separation membranes possess the property of selectively permeating specific components in a multi-component mixed gas, which allows for the separation of impurities in the gas. The permeation of gas molecules through a polymer membrane consists of three steps (Fig. 2): (1) dissolution of gas molecules into the membrane, (2) diffusion of the dissolved gas molecules through the membrane, and (3) desorption of the gas molecules from the opposite side of the membrane.

* Evaluation Technology Development, Electronics Development Department, Tsukuba Laboratory, R&D Unit
** Analysis Development, Analysis technology Department, Tsukuba Laboratory, R&D Unit

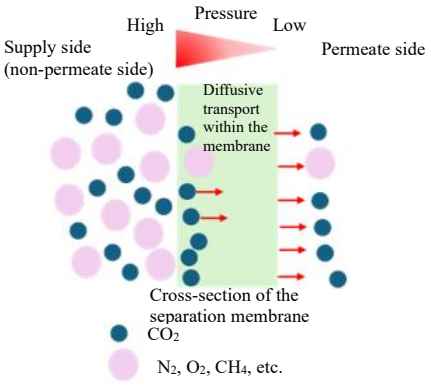

Fig. 2 Permeation of gas molecules through a separation membrane

For the permeating gas components in a given membrane, when the permeation flux is defined as N_A, the membrane thickness as δ, and the partial pressure difference across the membrane as ΔP, the permeability coefficient P is represented by the following equation[1]:

$$P = N_A \delta / \Delta P$$

The permeation rate of gas molecules through a gas separation membrane varies depending on factors such as molecular size, polarity, and affinity with the membrane material. Generally, gas species with smaller molecular diameters or those with higher affinity with the membrane tend to move to the permeate side more easily.

In concentration analysis using a separation membrane, by concentrating impurities using a membrane selected based on the permeability coefficient and then introducing the obtained concentrated gas into an analyzer, it is possible that ultra-trace impurity analysis at the sub-ppb level can be performed, similar to the method using a low-temperature trap.

3. Development of Impurity Concentration Analysis

3.1 Selection of Gas Separation Membranes and Analysis Object Impurities

In a user request for CO_2 gas analysis, the C_3H_8 component was identified as an impurity. Additionally, a user requested assurance regarding concentrations below the detection limit of the current analytical method. In this case, we considered that a method using a separation membrane might be feasible for the analysis and therefore selected the C_3H_8 component as the target for analysis.

Since C_3H_8 generally has a large molecular diameter and is difficult to permeate through membranes, we considered that a separation membrane through which CO_2 easily permeates should be selected. Since polyimide membranes have a high affinity for CO_2, making it easier for CO_2 to permeate them compared to C_3H_8, we selected a polyimide membrane for this study.

3.2 Construction of an Impurity Concentration System Using a Separation Membrane

A system as shown in Fig. 3 was constructed to perform impurity C_3H_8 concentration analysis using a polyimide separation membrane. Upstream of the separation membrane, a line for diluting and mixing CO_2 gas and C_3H_8 standard gas was installed, enabling the introduction of CO_2 with arbitrary impurity concentrations. An automatic pressure regulator (hereafter referred to as APR) was installed at the non-permeate side outlet downstream of the separation membrane to control the non-permeate side at a constant pressure. Meanwhile, the permeate side outlet was opened to atmospheric pressure. In this study, gases from the permeate and non-permeate side outlets were introduced into a gas chromatograph-hydrogen flame ionization detector (hereafter referred to as GC-FID) for analysis of C_3H_8.

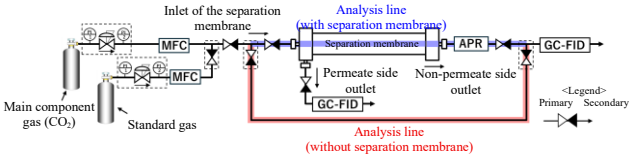

Fig. 3 Overview of the evaluation system

The non-permeate side outlet pressure was controlled at 120, 130, and 140 [kPaA] using the APR, and C_3H_8 in the gases from the permeate and non-permeate side outlets was analyzed by GC-FID.

Fig. 4 shows the chromatograms near the C_3H_8 retention time when the gases from the non-permeate and permeate side outlets were analyzed by GC-FID while varying the non-permeate side pressure.

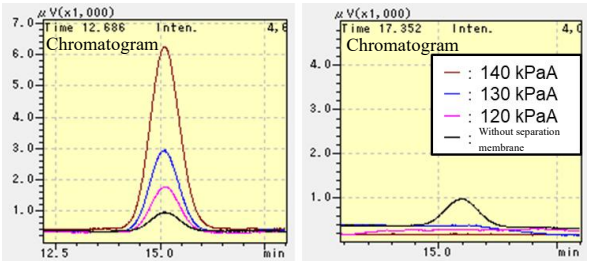

Fig. 4 Measurement results (Left: Non-permeate side; Right: Permeate side)

Analysis results of the gas from the permeate side outlet showed no peaks under any of the conditions, indicating that C_3H_8 did not permeate through the separation membrane. On the other hand, the analysis results of the gas from the non-permeate side outlet showed that the C_3H_8 peak increased as the control pressure increased, indicating that the C_3H_8 concentration in the non-permeate side outlet gas increased, i.e., C_3H_8 was concentrated.

The calculated detection limit (S/N = 2) for C_3H_8 was 10 [ppb] in the case of the method without a separation membrane, whereas it was 0.9 [ppb] at a control pressure of 140 [kPaA] in the case of the method with a separation membrane. This indicates that the use of a separation membrane enables high-sensitivity analysis of C_3H_8 in CO_2 gas.

It is considered that this is because the molecular sieving effect increased as the pressure difference ΔP between the permeate side and non-permeate side outlets became larger, thereby improving the separation ratio of the separation membrane, and that while the main component, CO_2, flowed more easily to the permeate side outlet, the C_3H_8 component flowed to the non-permeate side outlet without permeating the membrane, and consequently the C_3H_8 concentration in the non-permeate side outlet gas increased.

3.3 Verification of Mass Balance

To perform accurate impurity analysis using this concentration system, impurity components must not remain within the separation membrane, and the mass balance between the inlet and outlet sides of the separation membrane must be satisfied. In this verification, the mass balance was examined by controlling the non-permeate side outlet at 120 and 140 [kPaA]. The mass balance was calculated using the following equation:

$$\text{Mass balance (\%)} = \frac{\text{Gas flow rate (permeate side outlet)} \times \text{Peak area (permeate side outlet)} + \text{Gas flow rate (non-permeate side outlet)} \times \text{Peak area (non-permeate side outlet)}}{\text{Gas flow rate (separation membrane inlet)} \times \text{Peak area (separation membrane inlet)}} \times 100$$

Fig. 5 is a graph summarizing the C_3H_8 amounts in the inlet and outlet gases of the separation membrane obtained in this verification and the mass balance. Here, the C_3H_8 amount is calculated as the product of the gas flow rate and the C_3H_8 peak area measured by GC-FID.

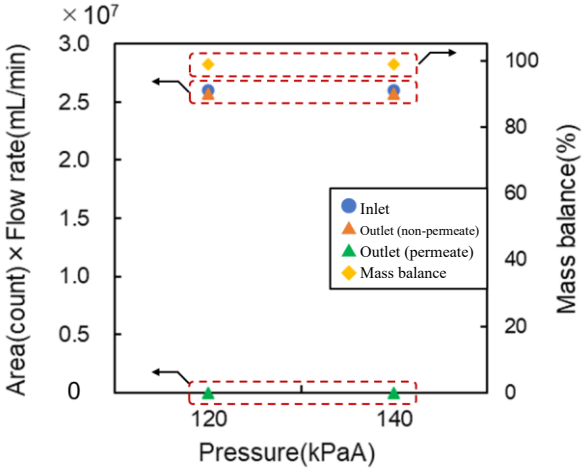

Fig. 5 Mass balance

As a result of this verification, the mass balance was 99% at a control pressure of 120 [kPaA] and 98% at 140 [kPaA], showing values close to 100%. From this, it was confirmed that the mass balance between the inlet and outlet sides of the separation membrane was maintained in this system, and the accuracy of this impurity concentration analysis is high.

4. Conclusion

This report has described that C_3H_8 in CO_2 gas can be concentrated and analyzed with high sensitivity using a separation membrane, and that the mass balance between the inlet and outlet sides of the separation membrane is maintained. This technology has demonstrated the feasibility for concentration analysis of high-boiling point gases, which could not be analyzed with conventional methods using a low-temperature trap. This technology can be applied to other than the combination of CO_2 and C_3H_8, so we will expand the range of applicable gas species in the future.

Reference:
1) The Society of Separation Process Engineers, Japan. Handbook of Separation Technology. 2010, p. 752.