

Analysis of Dissolved Oxygen and Nitrogen in Water

E. Shimbo and S. Uchiyama

User Benefits

- ◆ Trace amounts of oxygen (O₂) and Nitrogen (N₂) contained in water can be quantified.
- ◆ Both calibration curve preparation and sample analysis can be performed with an autoinjector.
- ◆ Analysis at low cost is realized by using air as a substitute for standard gas.

Introduction

The amount of gas dissolved in a solution controls its functionality and the gas concentration may affect the stability and reactivity of other dissolved components. Fine bubble is a technology that makes the gas in bubbles dissolve into solution more than the saturation concentration, so it is applied to growing agricultural products and preserving the freshness of foods. Therefore, interest in analysis of gas dissolved in water is increasing.

A previous Application News (01-00183) introduced the analysis of dissolved gases in the split mode using a capillary column, but the reproducibility of water analysis was not very good. In this article, the quantitation of O₂ and N₂ in water was performed using a thermal conductivity detector (TCD) and packed column, which enabled satisfactory reproducibility to be achieved.

Measurement Conditions

Tables 1 and 2 show the analytical conditions. Xtra Life micro syringe 10 µL (P/N: 227-35400-01) was used.

Table 1 Analytical Conditions of GC

Model	: Nexis GC-2030APT/AOC-30i	
Injection Temp.	: 300 °C	
Carrier Gas	: He	
Carrier Gas Control	: 50 mL/min	
Column	: MS-5A 60/80 (4 m × 3 mm I.D.) Reference line directly connected by stainless steel pipe	
Column Temp.	: 50 °C	
Detector	: TCD	
Detector Temp.	: 100 °C	
Current	: 150 mA	
Preamp*1	: × 10 ¹	

*1 PTC D Preamp is modified in Apparatus Configuration.

Table 2 Analytical Conditions of Autoinjector

	Calibration curve preparation	Sample analysis
Injection Volume	: 0.5 µL	8 µL
Pumping	: 0	5
Solvent Wash before Injection	: 2	0
Solvent Wash after Injection	: 0	0
Sample Wash before Injection	: 0	2
Solvent	: Water	

Check of Air Contamination by Injection

In order to check the air contamination during injection, the plunger-fixing knurled screw of the autoinjector was loosened and the plunger holder was removed, as shown in Fig. 1. Then an analysis was executed with the syringe without any samples. Fig. 2 shows the chromatograms of the analysis with an empty syringe and 0.1 µL of air. It was confirmed that there was no air contamination when just the syringe was inserted.

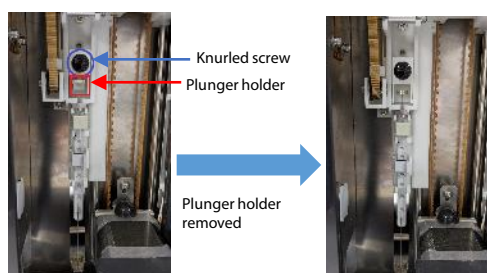


Fig. 1 Positions of Knurled Screw and Plunger Holder

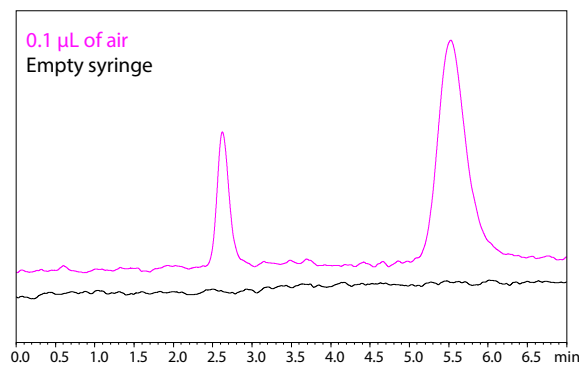


Fig. 2 Chromatograms of Empty Syringe Injection and 0.1 µL of Air

Sample Analysis

Milli-Q water (hereinafter abbreviated 'Water') was used as a sample. In addition to Water, samples of He- and N₂-purged Water were prepared to imitate samples whose concentrations of He and N₂ were different from normal Water. They were prepared by purging water with 5 mL/min of He and N₂ gas for 30 minutes and then used for analysis. Since the concentrations of dissolved O₂ and N₂ were relatively low, 8 µL of samples were injected.

Fig. 3 shows the chromatograms of each sample that was continuously analyzed 5 times, in which peaks indicating O₂ and N₂ were detected. Table 3 shows the results of quantitation of the continuous analysis. The reproducibility was sufficient in the Water sample. On the other hand, the concentrations of O₂ and N₂ changed with time in He- and N₂-purged Water. It is assumed that the concentration of dissolved O₂ and N₂ in the samples changed because of the gas-liquid distribution between those in atmosphere and the sample. It is recommended that the samples be analyzed immediately after dispensing them to the vials.

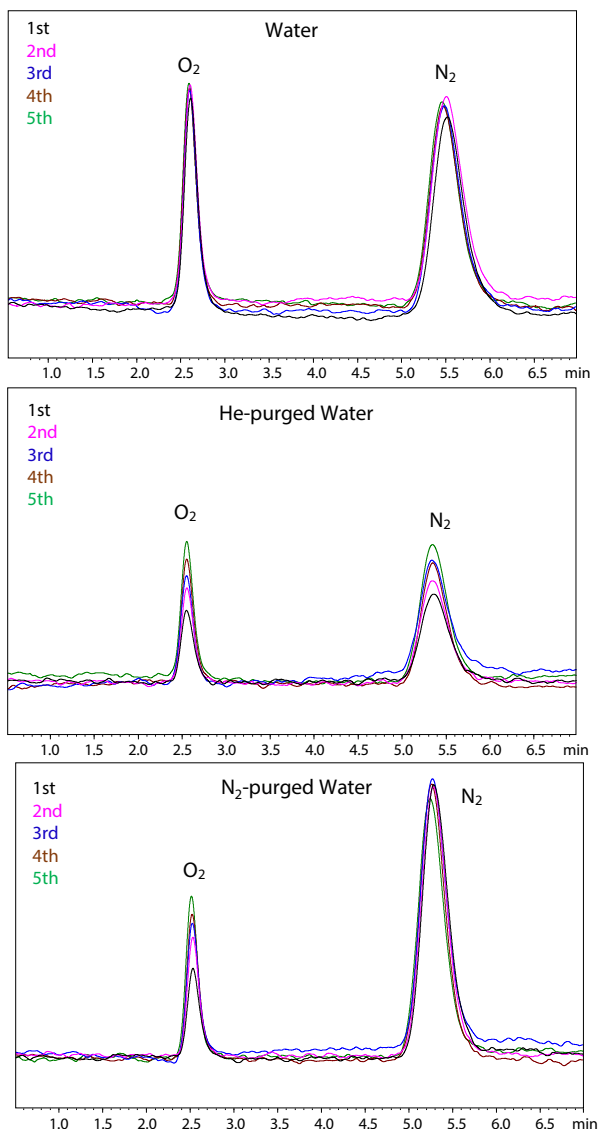


Fig. 3 Chromatograms of Each Sample Continuously Analyzed 5 Times
Top: Water, Middle: He-purged Water, Bottom: N₂-purged Water

Table 4 Area and Reproducibility (n = 5) of Each Sample

	O ₂			N ₂		
	Water	He-purged Water	N ₂ -purged Water	Water	He-purged Water	N ₂ -purged Water
1	2,184	755	822	4,303	1,631	5,124
2	2,214	858	1,051	4,486	2,163	4,950
3	2,288	1,076	1,244	4,559	2,222	4,951
4	2,225	1,233	1,309	4,510	2,511	4,991
5	2,131	1,354	1,413	4,374	2,938	4,679
Average	2,208	—*2	—*2	4,446	—*2	—*2
%RSD	2.60	—*2	—*2	2.36	—*2	—*2

*2 The average area and reproducibility of He- and N₂-purged Water were not calculated since the concentrations changed because of the gas-liquid distribution with the atmosphere.

Nexis is a trademark of Shimadzu Corporation in Japan and/or other countries.

Sample Quantitation

A micro syringe can be used as if it is a gastight syringe by washing with Water to improve its hermeticity (see Application News 01- 00182 for details). Water as washing solvent and an empty vial as a sample were set in the autoinjector, then 0.5 μL of the air was measured to prepare the calibration curves. The concentrations of each component in the air were assumed to be 20.9 % (O₂) and 78.1 % (N₂), so the theoretical volumes were 104.5 nL (O₂) and 390.5 nL (N₂) when 0.5 μL was injected. The first measurement of each sample was used for the quantitation. Fig. 4 and Table 4 show the chromatograms and the results of quantitation, respectively. The quantitative values were close to the theoretical values, that is, 8.5 ng/μL (O₂) and 14.3 ng/μL (N₂), which are the solubility of air-saturated aqueous solution at 25 °C calculated based on those values given in Handbook of Chemistry.¹⁾

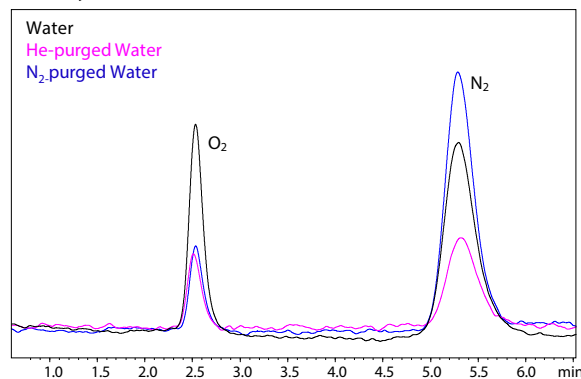


Fig. 4 Chromatograms of the First Analysis of Each Sample

Table 5 Quantitative Values of O₂ and N₂ in the First Analysis of Each Sample

	O ₂			N ₂		
	Water	He-purged water	N ₂ -purged water	Water	He-purged water	N ₂ -purged water
Volume (nL)	51.9	17.9	19.5	101.9	38.6	121.3
Quantitative Value (nL/μL)	6.5	2.2	2.4	12.7	4.8	15.2
Quantitative Value ^{*3} (ng/μL)	8.5	2.9	3.2	15.0	5.5	17.4

*3 Calculated as perfect gas at room temperature (25 °C)

Conclusion

The quantitation of O₂ and N₂ in water was performed with GC using TCD and a packed column. The peaks of dissolved O₂ and N₂ were confirmed and the continuous analysis had satisfactory reproducibility when 8 μL of the sample was injected. The quantitative values were close to the theoretical values.

In isothermal analysis as described in this article, accumulation of the water introduced to the column is unavoidable. This may cause the reduced retention of target components, earlier retention time, and worse shape of peaks, so conditioning of column is regularly required.

<Reference>

1) The Chemical Society of Japan: Handbook of Chemistry: Pure Chemistry II, 4th ed., Maruzen, 762 (1993)