

User Benefits

- ◆ Trace amounts of Ar, O₂, and N₂ contained in solutions can be quantified.
- ◆ Autoinjector measurement is possible in the processes from preparation of calibration curves to measurement of the actual samples.
- ◆ Low cost analysis is possible by using air as a substitute standard gas.

Introduction

The amount of gas dissolved in a solution controls the functionality of the solution, and in some cases, the gas concentration may affect the stability and reactivity of other solution components. Since the concentration of dissolved gases in solutions is generally on the trace level, the barrier discharge ionization detector (BID) is an effective analysis technique for those gases. However, it is not possible to measure the oxygen (O₂) and nitrogen (N₂) contained in liquids by the headspace method due to their high concentrations in the atmosphere. Although these gases in liquids must be measured directly, it was difficult to prepare calibration curves. Application News (01-00182-EN) introduced a simple calibration curve preparation method for O₂ and N₂ using air as a substitute standard gas. In this article, calibration curves were prepared by that method, and quantitative analyses of argon (Ar), N₂, and O₂ in various organic solvents and water were conducted.

Analysis Conditions

Tables 1 and 2 show the analysis conditions. In this experiment, the insert (P/N: 221-41444-01) was filled to a position 20 mm from the top with about 20 mg of quartz wool (P/N: 201-47616-01), and a plunger-in-needle syringe (P/N: 227-35002-01) with a 0.5 μL capacity was used as the autoinjector syringe.

Table 1 GC Analysis Conditions

Model	: Nexis GC-2030 / AOC-30i
Injection Temp.	: 250 °C
Injection Mode	: Split
Split Ratio	: 1 : 25
Carrier Gas	: He
Carrier Gas Control	: Linear velocity 50 cm/s
Purge gas	: 20 mL/min
Column	: SH-MSieve 5A (30 m × 0.32 mm I.D., 30 μm) ^{*1} With 2.5 m particle trap
Column Temp.	: 35 °C
Detector	: BID-2030
Detector Temp.	: 300 °C
Detector Gas.	: 50 mL/min
Filter Time Constant	: 50 ms ^{*2}

*1 P/N: 227-36611-02

*2 Double-click BID under environment settings and change the filter time constant.

Table 2 Autoinjector Analysis Conditions

	Calibration curve	Sample measurement
Injection Volume	: See Table 3	0.5 μL
Pumping Times	: 0	5
Pre Solvent Wash Times	: 2	0
Post Solvent Wash Times	: 0	0
Sample Wash Times	: 0	2
Solvent	: Water	

Preparation of Calculation Curves

Empty vials were set in the autoinjector, and the calibration curves were prepared using water as the rinse solvent. The calibration curves were prepared by measuring air with different injection volumes of 0.05, 0.1, 0.25, and 0.5 μL.

Table 3 shows the relationship between the syringe injection volume and the amount of each compound injected. The values used for the concentrations of the compounds in air were Ar: 0.0934 %, O₂: 20.9 %, and N₂: 78.1 %. Fig. 1 shows the calibration curves of Ar, O₂, and N₂. All calibration curves passed through the origin, and good linearity was obtained.

Table 3 Relationship of Syringe Injection Volume (μL) and Volume of Gas Injected (nL)

Syringe injection volume (μL)	0.05	0.1	0.25	0.5
Ar (nL)	0.467	0.934	2.34	4.67
O ₂ (nL)	10.5	20.9	52.4	105
N ₂ (nL)	39.0	78.1	195	390

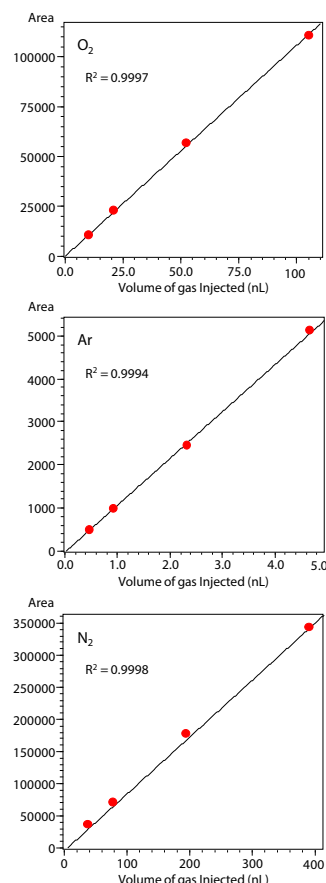


Fig. 1 Calibration Curves

■ Calculation of Quantitative Values of Real Samples

A quantitative analysis of the Ar, O₂, and N₂ contained in solutions was conducted using hexane, toluene, ethanol, acetone, and water as real samples. When changing the type of sample being measured, conditioning was carried out at 300 °C for 30 min because retention of the target component will be weak and the elution time will be rapid if the solution accumulates in the column. Fig. 2 shows a comparison of the chromatograms of each solution. Table 4(a), (b), and (c) show the quantitation results calculated using the calibration curves as in Fig. 1. The results for water are shown as reference values because water was outside the range of the calibration curve. While satisfactory repeatability was obtained for hexane, toluene, ethanol, and acetone, repeatability for water exceeded 10%.

Fig. 3 shows the chromatogram of N₂ in a continuous measurement of acetone, and Fig. 4 shows the chromatogram of N₂ in acetone after conditioning. Collapse of the peak shape of N₂ was observed in the continuous measurement of acetone, but area repeatability was good. Although the peak shape was improved by baking the column, the retention time shifted depending on the condition of the column.

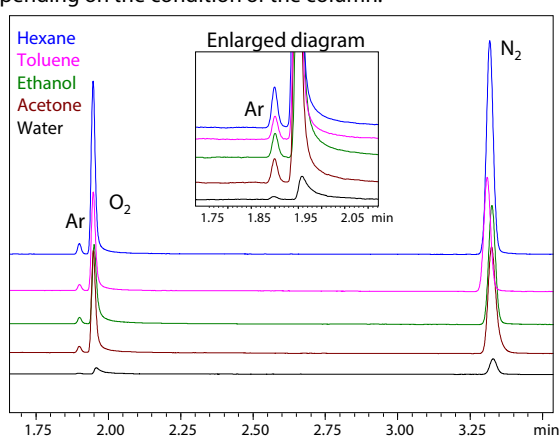


Fig. 2 Comparison of Chromatograms of Solutions

Table 4(a) Area Repeatability and Quantitative Values of Ar in Solutions (n = 5)

Solution	water	Hexane	Toluene	Ethanol	Acetone
Area repeatability (%RSD)	-	0.72	0.87	1.38	3.26
Volume (nL)	-	1.85	1.03	1.08	1.10
Quantitative value (nL/μL)	-	3.69	2.05	2.17	2.21
Quantitative value *1 (ng/μL)	-	6.04	3.35	3.54	3.61

*1 Calculated as an ideal gas at room temperature (25 °C).

Table 4(b) Area Repeatability and Quantitative Values of O₂ in Solutions (n = 5)

Solution	water	Hexane	Toluene	Ethanol	Acetone
Area repeatability (%RSD)	11.80	0.62	1.48	1.26	0.75
Volume (nL)	2.00 *2	37.53	22.51	21.45	23.92
Quantitative value (nL/μL)	3.99 *2	75.05	45.03	42.91	47.85
Quantitative value *1 (ng/μL)	5.22 *2	98.22	58.93	56.15	62.62

*1 Calculated as an ideal gas at room temperature (25 °C).

*2 Regarded as a reference value because water exceeded the range of the calibration curve.

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Table 4(c) Area Repeatability and Quantitative Values of N₂ in Solutions (n = 5)

Solution	water	Hexane	Toluene	Ethanol	Acetone
Area repeatability (%RSD)	16.99	0.91	0.99	0.29	1.34
Volume (nL)	6.66 *2	88.04	46.53	48.81	51.46
Quantitative value (nL/μL)	13.32 *2	176.08	93.06	97.63	102.93
Quantitative value *1 (ng/μL)	15.25 *2	201.63	106.56	111.80	117.86

*1 Calculated as an ideal gas at room temperature (25 °C).

*2 Regarded as a reference value because water exceeded the range of the calibration curve.

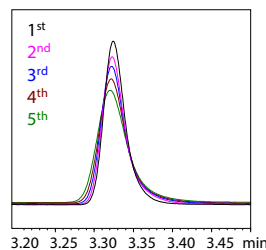


Fig. 3 Chromatogram of N₂ in Continuous Measurement of Acetone

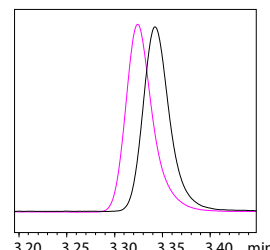


Fig. 4 Chromatogram of N₂ in Measurement of Acetone After Conditioning

■ Countermeasures for Decrease of Oxygen Peak

Although the SH-Rt-Msieve 5A column used in this experiment has an extremely strong retention ability, solvents with comparatively low boiling points can be eliminated from the column by conditioning at 300 °C. However, in some cases, the oxygen peak decreases as a result of conditioning (depending on the condition of the column). Fig. 5 shows a comparison of the chromatogram when 0.05 μL of air was injected immediately after conditioning at 300 °C for 30 min, and the chromatogram when the same 0.05 μL of air was injected after first injecting 0.5 μL of air 5 times. Although the peak of O₂ decreased after conditioning at 300 °C for 30 min, the oxygen peak improved after injecting 0.5 μL of air 5 times. Thus, in cases where this kind of decrease in the oxygen peak after conditioning at 300 °C is observed, trace amounts of O₂ can be detected if air is injected after conditioning.

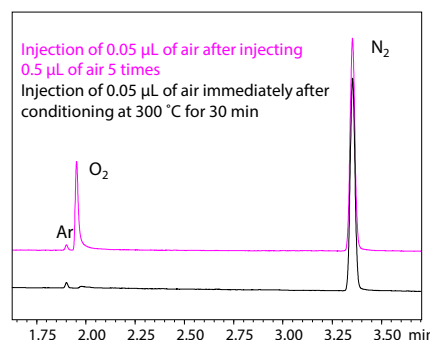


Fig. 5 Comparison of Chromatograms for Injection of 0.05 μL of Air

■ Conclusion

A quantitative analysis of argon, oxygen, and nitrogen in various solutions was conducted using a BID detector. The processes from preparation of the calibration curves to measurement and quantitation of the solutions are possible by using a 0.5 μL plunger-in-needle syringe. The area value of the water sample was small in comparison with that of the organic solvents, indicating poor repeatability for water. Therefore, accurate measurement of water samples is considered to be difficult.