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Application News

GC Nexis™ GC-2030

Simple Preparation of Calibration Curves for Oxygen and Nitrogen Using Air as a Standard Gas

S. Uchiyama

User Benefits

- Simple preparation of multipoint calibration curves for the low concentration regions of O_2 and N_2 is possible without dilution of standard gases.
- Low cost analysis is possible by using air as a substitute standard gas.
- Use of an autoinjector enables high injection accuracy in measurements.

Introduction

When analyzing oxygen (O_2) and nitrogen (N_2), which exist at high concentrations in the atmosphere, the effect of contamination by air must be avoided as far as possible. Particularly when preparing calibration curves for low concentration regions, it is necessary to prepare cylinders of the standard gases and prevent contamination by air from the atmosphere during sample injection. Although a gas sampler is generally used, consumption of the standard gases is large because the sample injection lines must be purged sufficiently with the standard gas before measurements. Moreover, use of a multipoint calibration curve is desirable, but the cost of preparing multiple standard gas cylinders with different gas concentrations would be prohibitive. Although dilution of the standard gas by the analyst is possible, it is extremely difficult to avoid air leaks when preparing diluted gases.

Air contains about 21 % O_2 and 78 % N_2, and these concentrations are considered to be comparatively stable. The cost of quantitative analyses of O_2 and N_2 can be reduced if air is used as a simple standard gas. This Application News introduces the results of a study of a simple method for preparation of multipoint calibration curves for O_2 and N_2 in the low concentration region without dilution of the standard gases by using air as a substitute standard gas and varying the air injection rate.

Analysis Conditions

Table 1 shows the analysis conditions. Here, a 0.5 µL plunger-in-needle syringe (P/N: 227-35002-01) and a 10 µL Xtra Life micro syringe (P/N: 227-35400-01) were used as the autoinjector syringes.

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-Rt™-Msieve 5A (30 m × 0.32 mm I.D., 20 µm) With 2.5 m particle trap
Column Temp.	: 35 °C
Detector	: BID-2030
Detector Temp.	: 300 °C
Detector Gas.	: 50 mL/min
Injector Setting	: Pumping times 0 Pre solvent wash times 2 Sample wash times 0 Solvent water

Check for Air Leakage in Syringe Injection

To investigate the possibility of air leakage in syringe injection, the fixing knurled screw of the autoinjector plunger was loosened and the plunger holder was removed, as shown in Fig. 1, and air leakage was checked by only removal/insertion of the syringe. Fig. 2 shows the results of an air leakage test using 7 syringes to investigate the individual differences among the syringes. Although blanks were not confirmed with most of the syringes, slight air leakage was observed with one syringe. Fig. 3 shows the result for the syringe in which slight air leakage was observed in syringe injection, together with a comparison of chromatogram showing the result when 0.05 µL of air was intentionally injected. These results indicate that the amount of air leakage was extremely slight.

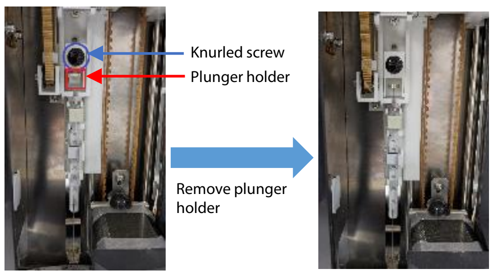

Fig. 1 Positions of Knurled Screw and Plunger Holder

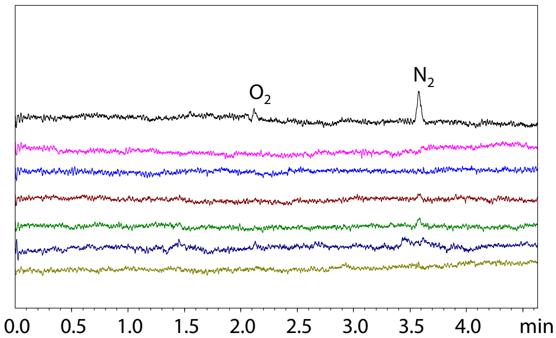

Fig. 2 Test of Air Leakage in Injection with 7 Syringes

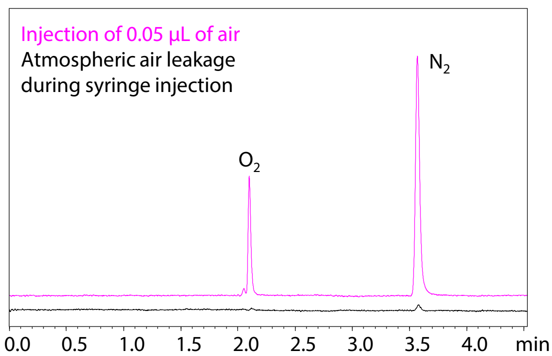

Fig. 3 Comparison of Chromatogram when Air Leakage was Observed in Injection Test of 7 Syringes and Chromatogram for Injection of 0.05 µL of Air

■ Study of Septum Purge Flow Rate

Although it is difficult to reduce air contamination during injection to zero, air leakage can be reduced by increasing the septum purge flow rate. Fig. 4 shows the results of an air leakage test for different purge flow rates. Peaks of O_2 and N_2 can be seen at the normal purge flow rate of 3 mL/min, but these peaks were reduced by increasing the septum purge flow rate.

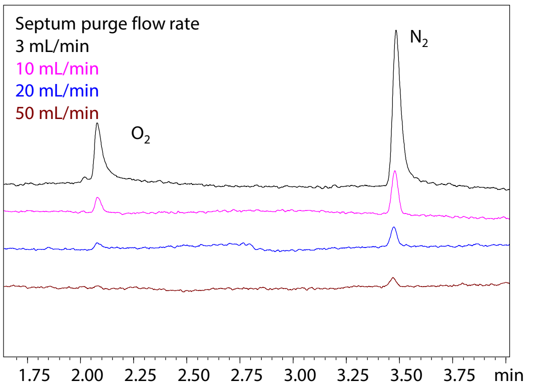

Fig. 4 Relationship of Septum Purge Flow Rate and Air Leakage in Injection

■ Study of Autoinjector Conditions

There is a possibility that the airtightness of the micro syringe used in liquid injection can be increased by water washing, and this syringe can then be used as a simple gastight syringe. Therefore, washing before sample injection was carried out with an autoinjector wash bottle filled with water and an empty bottle. An empty vial was set in the sample bottle, and linearity was confirmed by changing the air injection volume. Fig. 5 compares the change of RF (response factor; area per unit amount) with and without water washing. Here, the RF of O_2 with injection of 0.5 µL of air after washing the syringe with water is defined as 1. When the syringes were washed with water, there were no large changes in RF with injection of 0.05 µL or more, but RF did not become constant in the syringes without water washing. Therefore, it is thought that the passage of gases (in this case, air) can be prevented by forming a layer of water on the outer side of the plunger by water washing prior to sample injection, and as a result, injection of an accurate volume of air is possible. Even though the water on the syringe tip is introduced into the injection port, this did not affect the calibration curve because the amount of air contained in the water was negligible.

In preparation of calibration curves for O_2 and N_2 using air as a substitute standard gas, the injection volumes of 0.05 µL and more were satisfactory when water washing was carried out before sample injection.

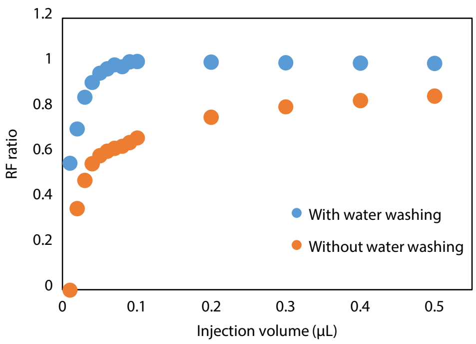

Fig. 5 Relationship of Injection Volume and RF of O_2

■ Preparation of Calibration Curves

Calibration curves were prepared with various injection volumes using syringe ①: 0.5 µL plunger-in-needle syringe and ②: 10 µL Xtra Life micro syringe. Fig. 6 shows the results of the calibration curves for O_2 and N_2. Good linearity was obtained in the calibration curves prepared using both syringes. Table 2 shows the area values and area ratios for injection volumes from 0.1 to 0.5 µL when using syringes ① and ②. Although the area values are lower with syringe ② owing to its smaller volume, it was possible to obtain almost the same values when the results were compared at 0.5 µL. Based on this, it is considered possible to prepare accurate calibration curves in the range from 0.05 µL to 8 µL.

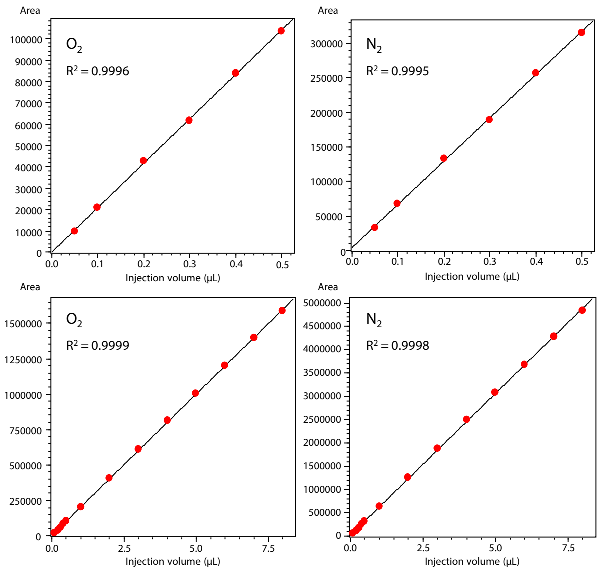

Fig. 6 Calibration Curves of O_2 and N_2
(Top: Syringe ①, Bottom: Syringe ②)

Table 2 Comparison of Areas with Same Volume in Syringes with Different Capacities

	Injection volume (µL)	0.1	0.2	0.3	0.4	0.5
O_2	Syringe①	20791	42709	64830	85844	107281
	Syringe②	19329	40101	61558	83675	103579
	①/②	1.076	1.065	1.053	1.026	1.036
N_2	Syringe①	67242	133069	198763	264945	329871
	Syringe②	59641	126356	189493	256188	315789
	①/②	1.127	1.053	1.049	1.034	1.045

■ Conclusion

Calibration curves for O_2 and N_2 were prepared by using air as a substitute standard sample and varying the injection volume. Good linearity was obtained in the range from 0.05 µL to 8 µL. Satisfactory linearity could also be obtained when injecting small volumes by washing the syringe with water prior to sample injection to form a water layer on the outer side of the plunger.

It is thought that this calibration curve preparation technique can be used in analyses of gases and analyses of dissolved gases in liquid samples.

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Analytical & Measuring Instruments Division
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