



Gas Chromatography with Vacuum-Assisted Sampling System in the Analysis of Hydrogen-Balanced Nitrogen Gas

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Abstract A vacuum-assisted (VA) sampling system in gas chromatography (GC) with a thermal conductivity detector has been developed to analyze low-pressure hydrogen-balanced nitrogen gas (H_2/N_2) sample. The objective is to determine hydrogen-balanced nitrogen gas by GC assembled with the vacuum-assisted (VA) gas sampling system comparison to the conventional system, pressure reduced to zero (PRZ) gas sampling system. The results show that both systems were not significantly different at the 95% confidence level. The developed sampling system was applied to analyses the quality of the low-pressure-volume gas.

Keywords vacuum-assisted sampling system, pressure reduced to zero sampling system, gas chromatography

INTRODUCTION

Nitrogen is a colorless, odorless and tasteless substance. It present in the atmosphere at a concentration of 78.1%. It is used widely in commercial and technical applications. As liquid nitrogen, it is used for cooling in many industrial processes and in the food industry. As gaseous nitrogen, it is used to form an inert blanket over substances that would otherwise be oxidized by the air. It can be distributed as a cryogenic liquid or as a gas in cylinders (Greenwood, and Earnshaw, 1997, Kaganer et al.1967).

Gas chromatographic methods have been utilized for determination of many compounds present in air and gaseous mixtures (Slemer et al. 2004, Taverniers et al. 2004). In the conventional method, the GC with the pressure reduced to zero (PRZ) gas sampling system (or pressure flow sampling system) is used. This system allows the compressed gas in cylinders or containers flow into the analysis system of GC as shown in Fig. 1. Unfortunately, this method is available for the gas sample with appropriate volume and pressure. In this work, the vacuum-assisted (VA) gas sampling system in GC, as shown in Fig. 2, was developed for the analysis of low-pressure gas. Therefore, the gaseous sample was easily collected by using a gas bag and conveniently transported to the laboratory.

The present work describes a developed VA sampling system of GC for determination of low pressure - volume hydrogen-balanced nitrogen (H_2/N_2) gas. The result obtained through the use of this newly developed sampling system was statistically compared to the conventional sampling system of GC.

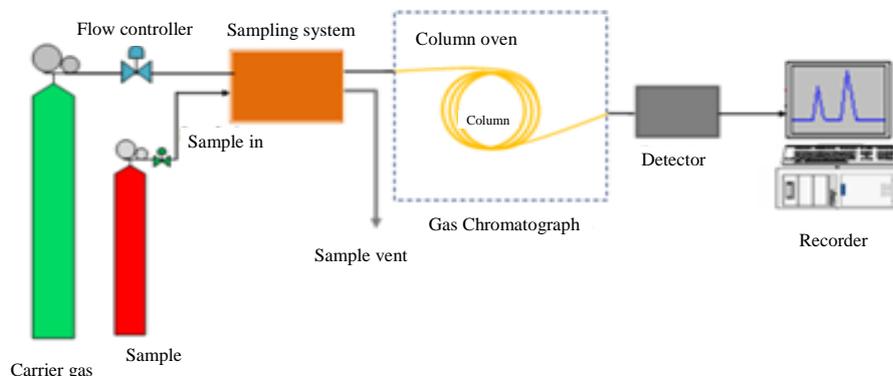


Fig. 1 Schematic diagram of the GC equipped with pressure reduced to zero gas sampling system

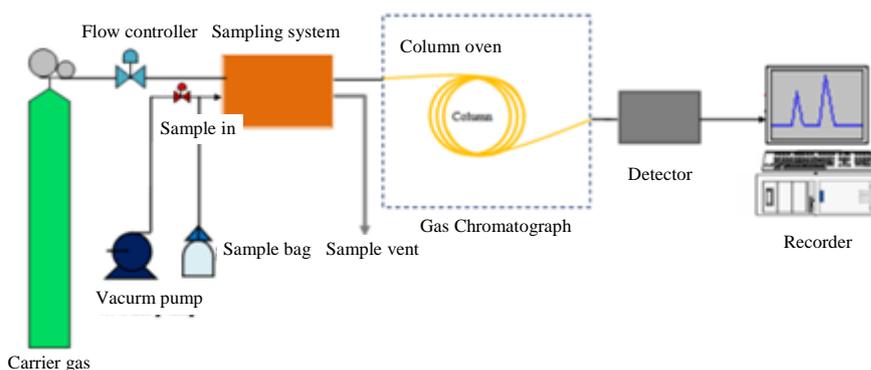


Fig. 2 Schematic diagram of the GC equipped with vacuum-assisted sampling system

OBJECTIVES

Followings are the objectives of this study.

1. To developed the vacuum-assisted sampling system in gas chromatography
2. To analyze the hydrogen-balanced nitrogen gas sample by gas chromatography equipped with the developed sampling system

METHODOLOGY

The gas chromatograph (GC) with a thermal conductivity detector (TCD) (Agilent, CA, USA) was used for quantitative analyses of the H_2/N_2 gas. Ultra high purity argon (Ar) gas cylinder with a purity of 99.99% as the carrier gas was connected to the GC. Separation was carried out in an HP-PLOT Molesieve (5\AA zeolite molecular sieve, porous layer open tubular) column ($30\text{ m} \times 0.25\text{ mm}$ i.d., and film thickness $0.25\text{ }\mu\text{m}$). The oven temperature was isothermal at $30\text{ }^\circ\text{C}$. The detector temperature was maintained at $250\text{ }^\circ\text{C}$.

The standard gas was 49.66% mol H_2/N_2 gas certificate reference material (CRM).

The working standard H_2/N_2 gases with different concentrations were individually prepared. Then the calibration gas mixture was introduced and a chromatogram was recorded. The values of peak area (y) were plotted against the concentration (x) of H_2/N_2 to obtain a calibration curve.

Regression analysis for a calibration line, $y = ax + b$, was carried out by Deming's least square method (International Organization for Standardization, ISO6143:2001, 2001).

Analysis of H_2/N_2 was conducted with a GC- TCD. A vacuum-assisted gas sampling system and a pressure drop to zero gas sampling system were tested. The results obtained from the analysis of both sampling systems were compared.

RESULTS AND DISCUSSION

The response linearity of the gas analysis by GC equipped with the developed sampling system and the conventional sampling system were determined by analyzing different concentrations of the mixed standard gas containing 10-50% mol of N_2 . The response factor of the standard solutions was calculated.

For the GC equipped with VA sampling system, the peak area of N_2 gas response was plotted against the concentration of standard gas to obtain the calibration curve (Fig. 3(a)) and was found to be linear over the concentration range of 1-50% mol and the values of correlation coefficient (r^2) 0.9984. Linear regression least squares fit data are given in Table 2. Mean recovery was estimated to be 98.45%. The limit of detection (LOD), evaluated as three times the signal-to-noise ratio, was estimated to be 3.4 $\mu\text{mol/mol}$. The limit of quantification (LOQ) of the method, as the concentration that produced a signal 10 times the baseline noise, was calculated as 4.2 $\mu\text{mol/mol}$. The results of precision as relative standard deviation (RSD) of the proposed sampling system are summarized in Table 2.

For the GC equipped with PRZ sampling system, the obtained calibration curve (Fig. 3(b)) was found to be linear over the concentration range studied with the values of correlation coefficient (r^2) 0.9997. Linear regression least squares fit data are given in Table 1. The LOD was estimated to be 3.2 $\mu\text{mol/mol}$. The LOQ of the method was calculated as 5.3 $\mu\text{mol/mol}$. The results of relative standard deviation (RSD) of the PRZ sampling system are summarized in Table 2. The results indicating that there was no significant difference at 95% confidence level between the developed sampling system and conventional sampling system.

The optimum experimental conditions were used to assess applicability of GC equipped with developed and conventional sampling systems for quantitative determination of H_2/N_2 gas sample analysis. The average analytical concentrations and %recovery of the nitrogen gas samples were determined by GC. The results, as shown in Table 3, showed that the values of average analytical concentration of N_2 gas samples ($n=3$) for GC(VA) and GC(PRZ) were 9.62% mol and 9.70% mol, respectively. The percentage recovery of gas analysis determined by GC(VA) and GC(PRZ) give values in the acceptable range, $100\pm 2\%$ (AOAC Peer-Verified Methods. Nov. 1993). The analysis of the test system and vacuum sampling system is created that can use analyzing. The analysis is correct and is in an acceptable range.

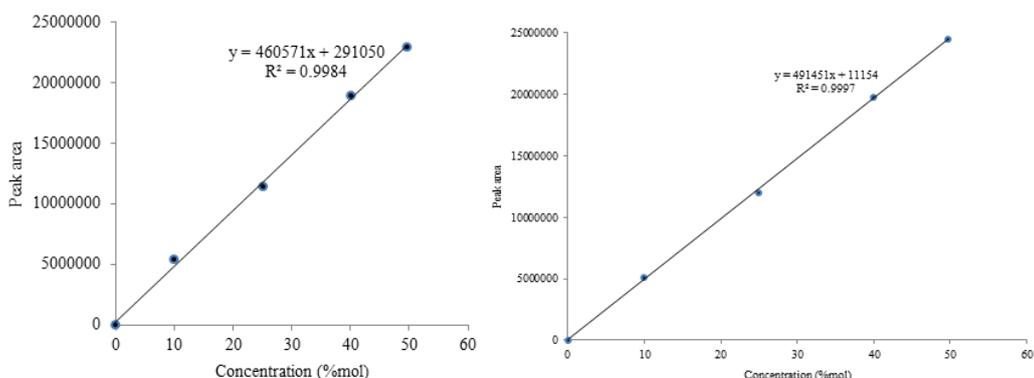


Fig. 3 Calibration curves for the standard gases with different concentrations analyzed by GC equipped with (a) vacuum-assisted (VA) and (b) pressure reduced to zero (PRZ) sampling systems

Table 1 Equations, correlation coefficients, and recovery percentage of the N₂ in the mixtures standard

Sampling system of GC	Calibration curve equation	Correlation coefficient (r ²)	Mean recovery (%)	LOD (μmol/mol)	LOQ (μmol/mol)
VA	y = 460,571x + 291,050	0.9984	98.45	3.4	4.2
PRZ	y = 491,451x + 11,154	0.9997	97.27	3.2	5.3

Table 2 Standard deviation, t-value, and percentage standard deviation of the N₂ in the mixtures standard

	VA	PDZ
SD	0.0058	0.0200
t _{cal}	-0.1632	-0.2845
t _{crit}	4.3	4.3
%RSD	0.0595	0.1050
%RSD _r	1.1880	1.1880

Table 3 Analytical concentrations and %recovery of the H₂/N₂ gas sample analyzed by GC(VA) and GC(PRZ)

Sampling system of GC	Analytical concentration (%mol)	% Recovery
GC (VA)	9.62	99.95
GC (PRZ)	9.70	99.15

Note: VA = vacuum-assisted sampling system and PRZ = pressure reduced to zero sampling system.

CONCLUSION

In this study, the vacuum-assisted sampling system for GC was developed. It was considered as an efficient sampling system for the determination of H₂/N₂ gas. The GC equipped with vacuum-assisted sampling system compared to the GC equipped with pressure reduced to zero sampling system were not significantly difference with a statistical type F-test and t-test at confidence level of 95%.

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