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NOTE

Simultaneous and sensitive analysis of inorganic and organic gaseous compounds by pulsed discharge helium ionization detector (PDHID)

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A simple gas chromatographic method has been developed for the simultaneous and sensitive analysis of inorganic (H₂, CO, and CO₂) and organic gaseous compounds (CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, *iso*-C₄H₁₀, and *n*-C₄H₁₀). The analysis of these gases generally requires multi-columns and/or multi-detectors, whereas the proposed method uses a single micropacked column and a single pulsed discharge helium ionization detector (PDHID). All of the investigated peaks (except for the N₂ and O₂ peaks, which are the major components of air) show good separation when using an oven temperature program from 40°C to 300°C. This gas chromatography–PDHID system yielded good linearity and a relative standard deviation of less than 5%. This sensitive and convenient method shows great potential in analyses of various types of gaseous compounds.

Keywords: PDHID, micropacked column, simultaneous and sensitive analysis, organic gases, inorganic gases

INTRODUCTION

The pulsed discharge helium ionization detector (PDHID) is a sensitive and universal detector used for the detection of permanent gases, volatile inorganics, and all classes of organic compounds (Wentworth *et al.*, 1992, 1994). In general, organic and inorganic volatiles are analyzed using a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively, although the PDHID can perform the same analyses as TCD and FID with similar or better sensitivity (Hunter *et al.*, 1998; Woo *et al.*, 1996). However, few studies have examined the simultaneous analysis of organic and inorganic volatiles (Etiope, 1997). The PDHID has been used in many analyses of certain gases that cannot be detected with FID, and its sensitivity makes it a better choice than TCD (Janse van Rensburg *et al.*, 2007; Roberge *et al.*, 2004). The PDHID has also been used to measure the composition of natural gas, although only in terms of light hydrocarbons (Kim *et al.*, 1999).

Given the universal detection capability of the PDHID, the simultaneous analysis of organic and inorganic volatiles requires a high degree of separation, sufficient to quantify each compound. For measurements of samples containing air, special care must be taken for to separate the major components of air (O₂, N₂, and moisture). In the present study, a simple and convenient system, comprising a single column and a single detector of the PDHID, is designed for simultaneous analyses of organic and inorganic volatiles. We also evaluate the performance of this gas chromatography (GC)–PDHID system.

MATERIAL AND METHODS

Sample preparation

Pure and mixed standard gases in disposable cans were purchased from GL Sciences (Tokyo, Japan). The degree of purity of each pure gas (CH₄, C₂H₆, C₃H₈, H₂, CO, and CO₂) is more than 99.5%. The concentrations of each component in mixed gases (C₂H₄, C₂H₆, C₃H₆, C₃H₈, *i*-C₄H₁₀, and *n*-C₄H₁₀) are *ca.* 1%. To prepare mixtures of the standard gases, their concentrations were adjusted by introducing them into a 200 ml glass canister. The solvent gas in the standards was air. The end of the canister was capped with a silicon septum, and the gas samples were collected through the septum with a gastight syringe.

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The gas mixtures were used within the same day. Small gas cylinder containing CH_4 , C_2H_6 , C_3H_8 , and CO_2 (each *ca.* 500 ppmv) in a helium base was obtained from Japan Fine Products (Kanagawa, Japan). The cylinder was directly connected to the 6-port valve inlet, and gas samples were introduced into the GC column.

For analysis, samples of borehole cuttings were collected from coal-bearing formations in the Ishikari Group, as obtained from depths greater than 3000 m in the Numanohata SK-10D well, Yufutsu oil-gas field, Hokkaido, Japan.

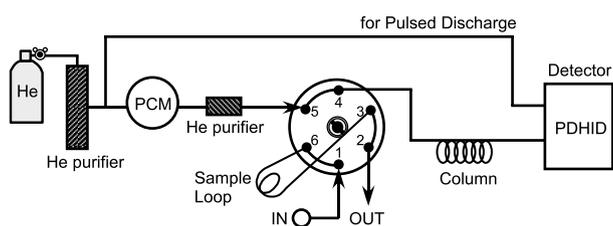


Fig. 1. Schematic of the GC-PDHID configuration in the sample loading position. PCM: Pressure control module.

Gas chromatographic system

All analyses were performed with a Hewlett Packard 7890 instrument equipped with a Valco PDHID system (PDD3i-HP, VICI) and a micropacked column packed with a Shincarbon ST (MICROPACKED ST, 2 m \times 1.0 mm i.d.; Shinwa Chemical Industries, Kyoto, Japan). This column can be connected to a GC in the same way as a widebore capillary column, and large volumes of samples can be injected into the column. It also has good heat resistance, with a maximum working temperature of 330°C. The gas samples were introduced into the GC column by the 6-port valve with a 250- μl sampling loop to inject a constant amount of sample. UHP helium (99.9999%) was used as both the carrier gas and discharge gas, and was further purified by passing through two heated helium purifiers (HP2 and HPM, VICI) to remove impurities in the UHP helium and to obtain a stable baseline. The flow rate of carrier gas was 4.5 ml/min, which was limited by the purification capabilities of the purifiers. The flow rate of discharge gas is 30 ml/min. Typical background signal is *ca.* 1000. The oven temperature program was set from 40°C (3 min) to 300°C (held 15 min) at 15°C/min. The detector was set at 300°C. A schematic of the GC-PDHID system used in this study is shown in Fig. 1.

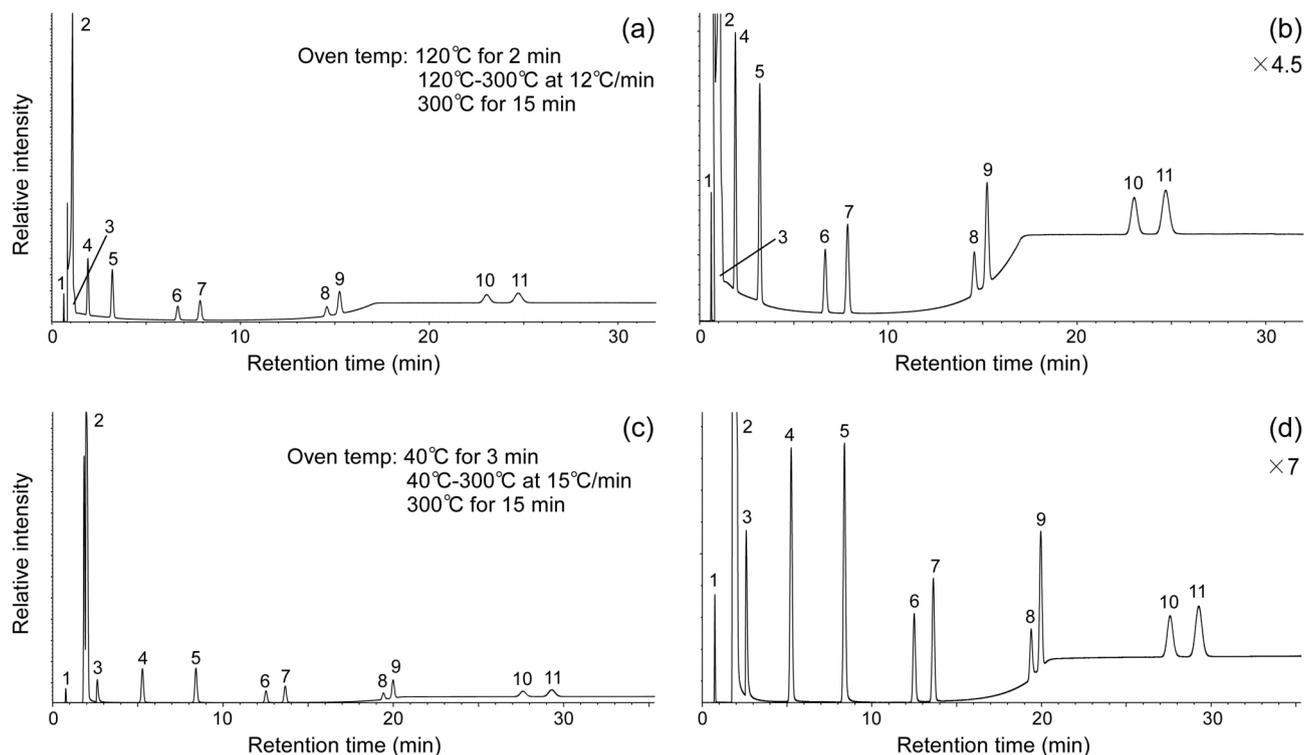


Fig. 2. Gas chromatograms of standard gases with different oven-temperature programs. The chromatogram in (a) and (c) is expanded in (b) and (d), respectively. 1. hydrogen, 2. oxygen and nitrogen, 3. carbon monoxide, 4. methane, 5. carbon dioxide, 6. ethylene, 7. ethane, 8. propylene, 9. propane, 10. isobutene, 11. butane.

RESULTS AND DISCUSSION

Separation

A gas mixture containing H₂, CO, CO₂, CH₄ (each 500 ppm), C₂H₄, C₂H₆, C₃H₆, C₃H₈, *i*-C₄H₁₀, and *n*-C₄H₁₀ (each 100 ppm) in an air base was used as a representative sample to determine the appropriate separation conditions. In the measurement using a MICROPACKED ST micropacked column, the oven temperature required for the detection of propane and butane was more than 150°C and 200°C, respectively. It was necessary to increase the oven temperature to 300°C to reduce the analysis time. Figure 2 shows gas chromatograms of standard gas mixtures for different oven-temperature programs. The peak areas of unsaturated and branched hydrocarbons (e.g., ethylene, propylene, and isobutene) are smaller than those of *n*-alkanes with the same carbon number. In particular, the area of propylene is less than half that of propane,

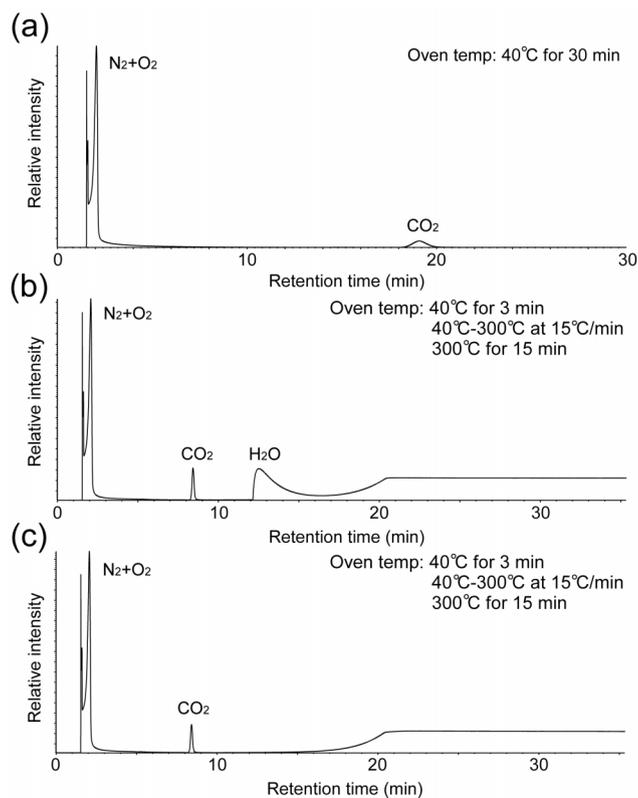


Fig. 3. Gas chromatograms of air samples with different oven-temperature programs. (a) Analysis at an isothermal oven temperature (40°C). (b) Subsequent analysis with an oven temperature program (15°C to 300°C at 15°C/min) after three-times repeated analyses of (a). (c) Subsequent analysis of (b) with the same oven-temperature program as that used for (b).

Table 1. Repeatability of standard gas analyses

Component	Repeatability (%RSD)*
H ₂	2.51
CO	1.18
CH ₄	1.59
CO ₂	1.47
C ₂ H ₄	1.63
C ₂ H ₆	1.94
C ₃ H ₆	3.27
C ₃ H ₈	1.91
<i>i</i> -C ₄ H ₁₀	2.73
<i>n</i> -C ₄ H ₁₀	4.96

*Calculated from the results of three runs within a day (at concentrations of 100 or 500 ppmv).

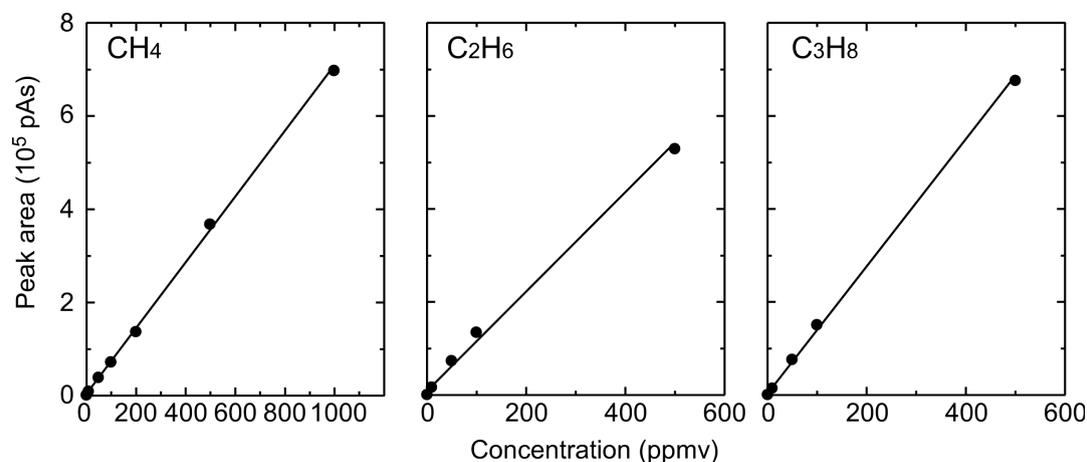


Fig. 4. Calibration curves for methane, ethane, and propane.

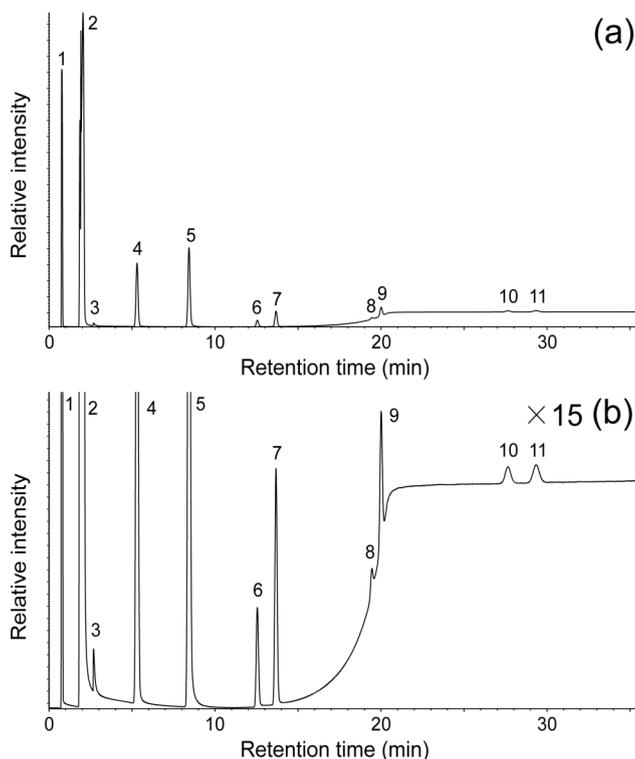


Fig. 5. Gas chromatograms of gas released from a pulverized cutting sample over a period of 60 min. The chromatogram in (a) is expanded 15 times in (b). Numbers next to peaks correspond to the compounds listed in Fig. 2. Absolute concentrations of compounds are as follows: 1. 119.9 ng, 3. 14.0 ng, 4. 64.6 ng, 5. 320.3 ng, 6. 16.5 ng, 7. 21.8 ng, 8. 5.2 ng, 9. 10.5 ng, 10. 11.4 ng, 11. 10.8 ng.

suggesting that the ionization efficiency of propylene is lower than that reported by Wentworth *et al.* (1994). The major components of air (oxygen, nitrogen, and moisture) can interfere with separation detected with the PDHID (Roberge *et al.*, 2004). In both chromatograms, the N_2 and O_2 peaks were not separated because of their high concentrations in the samples. Although the elution of moisture can be restricted in measurements for which the oven temperature is maintained above 100°C , the CO peak is completely overlapped by the N_2 peak. To overcome this problem, the oven temperature program was started at a lower temperature (40°C). Consequently, all the peaks (except for N_2 and O_2) showed sufficient separation to quantify each compound (see Fig. 2).

To examine the influence of air moisture on separation in the low- and high-temperature measurements, the same air sample was measured with different oven-temperature programs (Fig. 3). In the isothermal measurement at 40°C , the moisture-derived peak was detected as a minor swelling of the baseline, but this did not influ-

ence the identification and quantification of other components. In the measurement in which the oven temperature was raised from 40°C to 300°C after three analyses of air at 40°C , a large moisture-derived peak was detected. Subsequent measurements in the same program showed no moisture-derived peak. These results indicate that the moisture in air does not affect subsequent measurements as long as the final oven temperature reaches 300°C in each analysis.

Linearity and reproducibility

The calibration curves for methane, ethane, and propane were obtained by measuring five or seven different concentrations in the range from 1 to 1000 ppmv (Fig. 4). Because the solvent gas was air, the amount of methane present in air was reduced from the measured amount of methane. The correlation coefficients of the calibration curves from the origin are between 0.9967 and 0.9996. The lower detection limits for methane, ethane, and propane are 0.7, 0.3, and 0.3 ppmv, respectively (determined by the standard deviation of the response).

To investigate the precision of the analysis, relative standard deviations (RSDs) were calculated from the results of three runs performed on the same day. The resulting RSDs are between 1.18% and 4.96% (Table 1). Although the CO peak is located on the trailing edge of the N_2 peak (Fig. 2), the RSD of carbon monoxide is the smallest of the components analyzed in this study. Reproducibility for peak areas of 500 ppmv CH_4 , C_2H_6 , C_3H_8 , and CO_2 is less than 5% RSD over a 7-month period. Therefore, the GC-PDHID system is able to simultaneously analyze inorganic and organic gaseous compounds with an RSD of less than 5%.

Application to an environmental sample

To evaluate the GC-PDHID system in terms of an environmental sample, we analyzed the gas released from pulverized borehole cuttings over a period of 60 min. The resulting gas chromatograms show good separation except for the O_2 and N_2 peaks (Fig. 5). The concentrations of the components in the sample were quantified using a single point calibration curve (0–500 ppmv). Volatile light hydrocarbons and inorganic compounds, except for hydrogen, were detected in the range from 17 to 652 ppmv. The concentration of hydrogen is very high (*ca.* 0.5%). Previous study has reported the generation of hydrogen during grinding in a ball mill (e.g., Kameda *et al.*, 2004). It is known that hydrogen is generated by the reaction between water molecules and the surface mechanoradicals created by grinding. The high concentration of hydrogen measured in the present study could be attributed to a mechanochemical reaction that occurred during pulverization in the stainless-steel ball mill.

CONCLUSIONS

The performance of a GC system with a single micropacked column and a single detector of PDHID was evaluated to assess its capability for sensitive and convenient measurements of inorganic and organic gaseous compounds. The system yielded good linearity above 1 ppmv and an RSD of less than 5%. The simultaneous analysis of inorganic and organic gaseous compounds by GC with PDHID is sensitive and convenient compared with analysis by multi-column and/or multi-detector methods. Further improvement of the flow rate would increase analytical precision, leading to make this system more suitable for analyses of these gases.

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