NOTE

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

HIROYUKI SAITO,1* NORIYUKI SUZUKI1,2 and KOJI U. TAKAHASHI2

1 Research Division of JAPEX Earth Energy Frontier, Creative Research Institution (CRIS), Hokkaido University, N21, W10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan
2 Department of Natural History, Faculty of Science, Hokkaido University, N10, W8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

(Received April 14, 2011; Accepted March 12, 2012)

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, i-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 (Etope, 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–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, C3H6, C3H8, C4H10, 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. At the end of the canister was capped with a silicon septum, and the gas samples were collected through the septum with a gastight syringe.
The gas mixtures were used within the same day. Small gas cylinder containing CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and CO\textsubscript{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.

**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 × 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. 1. Schematic of the GC–PDHID configuration in the sample loading position. PCM: Pressure control module.](image)

**Fig. 1. 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.

Table 1. Repeatability of standard gas analyses

<table>
<thead>
<tr>
<th>Component</th>
<th>Repeatability (%RSD)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2.51</td>
</tr>
<tr>
<td>CO</td>
<td>1.18</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.59</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.47</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>1.63</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1.94</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>3.27</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1.91</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>2.73</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>4.96</td>
</tr>
</tbody>
</table>

*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.

Simultaneous analysis of inorganic and organic gaseous compounds by PDHID 257
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 influence 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.

Acknowledgments—We thank JAPEX (Japan Petroleum Exploration Co., Ltd.) for financial support and for providing the samples used in this study. This research was supported by a Grant-in-Aid for Scientific Research (No. 21540466 to N.S.) from the Ministry of Education, Culture, Sports, Science, andTechnology of Japan. We are grateful to anonymous reviewers for constructive comments, which greatly improved the manuscript.

REFERENCES


