Establishment of analysis method for methane detection by gas chromatography

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Abstract. The study focused on the establishment of analysis method for methane determination by gas chromatography. Methane was detected by hydrogen flame ionization detector, and the quantitative relationship was determined by working curve of $y=2041.2x+2187$ with correlation coefficient of 0.9979. The relative standard deviation of 2.60-6.33% and the recovery rate of 96.36%-105.89% were obtained during the parallel determination of standard gas. This method was not quite suitable for biogas content analysis because methane content in biogas would be over the measurement range in this method.

1. Introduction

As one of the most commonly produced gases in natural biochemical process, methane widely distributes in natural environment and it is the main component of natgas, biogas, coal gas, and et al. In recent years, methane attracts intensively attentions because of its significant effects on environment, industry and daily lives. The heat value released from methane combustion reaches 50.2 kJ/kg and it is convenient to transport by pipelines, so it is widely used for energy and heat supplement in human’s lives. At atmosphere, the methane concentration is only 1.4 mg/m³ but greatly contributes to greenhouse effects [1]. The greenhouse effect from methane is considered as 25 times of that from carbon dioxide [2]. It was reported the average surface temperature increased by 0.31 °C due to the raise of methane content since the industrial revolution [3]. Basically, methane is non-toxic gas for human’s health, while it will lead to unsuitable feelings at the concentration as high as 25-30% and it is easy to explode in the concentration range of 4.9%-15% [4]. Besides, during the application of anaerobic digestion technology, the detection of methane content in biogas is increasingly significant for the estimation of the process operational performance. Therefore, it is necessary to establish a simple, rapid and accurate analysis method for methane content determination, which can be the basis for the monitoring, source analysis and early warning of the influence, production and harm of methane.

Lots of analysis methods could be applied for methane detection, such as chemical absorption, gas chromatography (GC), tunable diode laser absorption spectroscopy [5], and etc. GC has advantages on accuracy, anti-interference, visualization, adaptability, and etc. The five parts, including the carrier, injector, separator (column oven), detector, and workstation, are essential for each GC system specification. Several types of detectors are commonly used for concentration detection, which are thermal conductivity detector (TCD), electron capture detector (ECD), hydrogen flame ionization detector (FID) and flame photometric detector (FPD). Among them, the FID detector has been mostly used for carbon-containing organics analysis, and it could maintain high accuracy at the very high
dynamic range from ppm (parts per million concentrations) up to 100%. In the GC system, the component in the injected sample are separated by column, and then the quantitative analysis of the compositions in sample could be performed simultaneously and rapidly. So the GC was widely used in multi-component analysis, such as petroleum, chemical and biological engineering, environmental protection, and etc.

In this study, the methane detection method by gas chromatography was established and the chromatographic condition was determined. The working curve for methane is established and its veracity and precision are evaluated. Finally, the methane content in actual biogas produced from anaerobic digestion system was measured to verify the application of the methane detection method.

2. Materials and Methods

2.1. Preparation of standard gas
Considering the explosion limits (4.9%-15%) of methane and the biogas composition (methane content of 40-60% in common), the standard gas used in this study was comprised of 44% of methane and 56% of air in volume. For quantitative analysis of methane content by GC with FID as detector, the peak area is proportional to the methane volume injected into GC system. Based on the quantitative relationship, various volumes of standard gas injected into the GC system were equivalent to corresponding methane content in the volume of 500 μL, which was the injection volume in this method. The equivalent contents (EC) of methane gas converted from standard gas with diverse injection volumes (IV, μL) were calculated according to the equation (1), which was shown as below.

\[ EC = IV \times \frac{44\%}{500\mu L} \]  

Therefore, the EC of standard gas with the injection volumes of 100 μL, 200 μL, 300 μL, 400 μL and 500 μL were 8.8%, 17.6%, 26.4%, 35.2% and 44%, respectively. During the establishment of standard curve, 100 μL, 200 μL, 300 μL, 400 μL, 500 μL of standard gas with methane content of 44% were rapidly injected into the gas chromatograph injection port. Each condition was repeated for 3 times and the average peak area was used for quantitative analysis.

The standard gas with methane content of 44% was stepwise diluted with air for preparation of the 0.088%, 0.44%, 0.88% of methane standard gas, which were used for determination of method detection limit.

2.2. Experiment methods for GC analysis
The GC served in this study was produced from PerkinElmer Collaboration (Clarus 680, USA) equipped with FID detector and capillary column (Elite-5, 30m*0.25mm*0.25μm). The workstation was Totalchrom Navigator used for data processing. The temperature for column chamber, inlet chamber and detector were 150 °C, 200 °C and 250 °C, respectively. High purity nitrogen was used for carrier gas in this study, and the flow rate for nitrogen was 2.0 ml/min. The split ratio of gas sample in inlet chamber was 20:1, which is used to control the amount of biogas flew into column, and prevent the unconventional peak, such as flat peak, trailing peak. The flow rate was 450mL/min for air produced by automatic air source (BCHP, SPB-300, China) and 45mL/min for hydrogen produced by hydrogen generator (BCHP, SPH-300, China)

2.3. Experiment methods for food waste digestion
The biogas sample was collected from mesophilic anaerobic digestion reactor (37°C±1°C) with food waste as substrate. The total solid and volatile solid of food waste were 10.5 g/L and 10.0 g/L, respectively. The inoculum was the digested sludge treating sewage sludge derived from Tianjin Jingu wastewater treatment plant. The reactor has the total volume of 300 ml with working volume of 150 ml. The methane content in biogas produced during the fermentation process was detected by the analysis method established in this study.
3. Results and discussion

3.1. Qualitative analysis
The chromatogram of the standard gas is shown in figure 1. As illustrated, the only peak appeared in each chromatogram was the response of methane, because the other component in standard gas was air, which was non-detectable by FID detector. The retention time of methane peak was 0.233 min at the column temperature of 150 °C.

![Figure 1. The chromatogram of the standard gas.](image)

3.2. Quantitative analysis
The standard curve indicating the relationship between the methane equivalent content in standard gas and the peak area, as shown in figure 2. The working curve was obtained by linear fitting, which was y=2041.2x+2187, and correlation coefficient (R²) was 0.9979 (>0.995).

![Figure 2. The working curve for methane content determination.](image)
3.3. Accuracy and recycle rate
In order to estimate the accuracy of the methane detection method, the standard gas with methane concentration of 8.80%, 17.6%, 26.4%, 35.2% and 44% are performed for 5 parallel determinations. And the relative standard deviation (RSD) was calculated to verify the precision of this method. Besides, the recycle rate that was the ratio of measured content and standard content was calculated to evaluate the accuracy of this method. Results of RSD and recycle rate are shown in Table 1, which were in the range of 2.60-6.33% and 96.36-105.89%, respectively.

The quantitative analysis was assured and controlled by precision and accuracy of this method, but more works should be done during the sampling. Firstly, the R² of the working curve should be higher than 0.995. Secondly, the intermediate methane content in working curve should be verified every 20 times measurement of samples, and the relative deviation should be lower than 10%, otherwise it must re-make the working curve. Finally, parallel determination of 10% of samples should be done and the relative deviation should be lower than 10% [6].

| Standard content (%) | Measured content (%) | RSD (%) | Recycle rate (%) |
|----------------------|----------------------|---------|------------------|
| 8.80                 | 8.48                 | 6.33    | 96.36            |
| 17.6                 | 18.05                | 4.34    | 102.56           |
| 26.4                 | 25.72                | 3.78    | 97.42            |
| 35.2                 | 36.72                | 2.60    | 104.32           |
| 44.0                 | 46.59                | 2.96    | 105.89           |

3.4. Method detection limit
The methane standard gas with near zero concentrations of 0.088%, 0.44%, 0.88% were measured for 5 repeat parallel determination, and the standard deviation for each concentration point were record. And then the curve with gas concentration as abscissa and the standard deviation as ordinate was made and the linear regression equation is y=0.6654x+0.0651 (R²=0.9734) was obtained. The standard deviation of zero concentration was obtained by extrapolation and recognized as S₀, and the method detection limit is defined as 3S₀ [7]. Results are shown in Table 2.

| Gas concentration (%) | standard deviations | S₀    | 3S₀  |
|-----------------------|---------------------|-------|------|
| 0.088                 | 0.1516              |       |      |
| 0.44                  | 0.3076              | 0.0651| 0.1953|
| 0.88                  | 0.673               |       |      |

3.5. Gas samples
The external standard method was using for determination of methane content during food waste digestion, and the variation of methane content with fermentation hours in the batch experiment are illustrated in figure 3. The chromatogram of biogas also had only one peak, which could be speculated to be methane according to the retention time in qualitative analysis. As shown in figure 3, the methane content in fermentation reactor slightly increased form 0% to 12.75% in the initial fermentation phase, while sharply increased to 63.03% from 300 h to 453.7 h with the highest increase rate of 0.78% per hour, and then maintained for 53.9 h and finally dropped to 50.76%. However, it should be noticed that the range of working curve was 0-44%, which was lower than the highest methane content in food waste digestion process, so this method was not suitable for methane content determination in biogas.
4. Conclusion
The study set up methane detection method by GC, the percentage of methane concentration and the chromatographic peak area has a good linear relationship, parallel test results also showed high accuracy and precision and also good recycle rate and repeatability. This method was applied for methane content during food waste digestion but the methane in biogas was out of scope of this methane.

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