Gasoline Handling Automatic Sampling Detection Device Based on Gas Chromatography

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Abstract. This article has designed a vehicle gasoline on-site sampling and rapid detection device. Automatically taking gasoline samples during gasoline handling, two-dimensional gas chromatographic method is used for the rapid quantitative detection of the unconventional additive methylal. The heavy components are separated by back-blowing to air with the non-polar capillary column while the methylal and light components are separated by a polar column to determine the methylal content. The experiment shows that linear relationship between value of peaks area and mass concentration of methylal is keep in the range of 0.020~90.0mg/mL with the correlation coefficients of 0.99, and the relative standard deviation (RSD) are less than 2%. The study shows that the limits of detection are 0.012g/L. This device can provide effective means for vehicle gasoline on-site sampling and quality control.

1. Introduction

Gasoline is one of the most used fuels at present, and the quality of oil products has attracted much attention. In recent years, due to the poor quality of vehicle gasoline, a large number of motor vehicle accidents have been caused. Among them, gasoline adulteration is one of the important causes of the poor quality of oil products. Some unscrupulous merchants add unconventional additives to gasoline, such as methylal, methanol, and benzene. These additives can not only effectively increase the octane number of gasoline to improve the anti-knocking property of gasoline, but also have a low prices and considerable economic benefits [1]. However, these unconventional additives can easily cause rubber seals to expand and vaporize, which can lead to oil circuit failures [2]. Meanwhile, the combustion exhaust gas contains a large number of carcinogens, which are very harmful to the human and environment [3]. Therefore, the accurate determination of the content of non-conventional additives such as methylal in vehicle gasoline is of great significance for driving safety and environmental protection.

According to statistics, the percent of pass of gasoline is 97.4% for quality inspection of gas stations in 2014, and the percent of pass of gasoline sampling from gas stations is 97.5% in 2016. However, the percent of pass of the corresponding production enterprises has exceeded 99% over the years [4]. It can be inferred that illegal additions or adulterations occurred in transit of the gasoline or in the gas stations, which results in lower gasoline qualification rates. Therefore, designing a device
for automatic sampling during gasoline handling and accurate determination of the contents of unconventional additives in gasoline by in-depth research on vehicle gasoline quality monitoring technology has important practical significance and application value.

In this paper, we design a gasoline automatic sampling and detection device. The device can automatically take gasoline sample and encode it during gasoline handling. At the same time, the contents of non-conventional additives such as methylal can be detected by two-dimensional gas chromatography quickly.

2. Gas Chromatography
Gas chromatography is a chromatographic separation analysis method using a gas as a mobile phase. The vaporized sample is carried by the carrier gas (mobile phase) into the column. The immobilization in the column is different from the adsorption and dissolution of the components in the sample. The elution time of the components from the column is different and the components are separated from each other. Use appropriate identification and recording systems to create chromatograms that indicate the time and response of each component as it exits the column. According to the time and sequence of the peaks shown in the chromatogram, the compounds can be qualitatively analyzed. According to the height and area of the peaks, the compounds can be quantitatively analyzed [5]. This method is proved to be simple, sensitive, selective, high analysis speed, accurate, and wide application.

The National Standard for Vehicle Gasoline GB/T 17930-2013 clearly specifies that methylal and other oxygenates cannot be added to gasoline [6]. At present, there are few reports on the detection of the contents of methylal and other oxygenates in gasoline. The US vehicle gasoline standard ASTMD4814 uses infrared spectroscopy to detect the oxygen content in gasoline, which is only suitable for the determination of higher levels of methylal [7]. Gao Zhirong [8] with other researchers use gas chromatography-mass spectrometry to detect the methylal content in gasoline, but its operation is cumbersome and the data analysis is complicated, which is not conducive to on-site detection and application promotion. Because of vehicle gasoline contains a large amount of alkanes, olefins, fenane compounds and various additives [9], it is a complex mixture of substrates. To detect the content of target compounds, other components will interfere with the measurement results [10]. It is difficult to separate the target compound completely and quickly from the complex hydrocarbon matrix using only one column. So we use two-dimensional gas chromatography technology, which has two columns with different polarities, and fast switching technology to separate methylal from other components effectively to detect the content of methylal [11].

3. Device Design
This paper uses two-dimensional gas chromatography to achieve the determination of methylal in gasoline. Firstly, we inject the sample to be tested into the capillary inlet from the autosampler, the sample to be tested first enters a non-polar capillary column, and the components are separated according to the boiling point from low to high. Secondly, when the light components flow out of the non-polar capillary column, the valve is switched to the back flushing state to let them enter the strongly polar column for achieving the separation of hydrocarbon components and methylal, while the heavy components are back flush out the non-polar capillary column vent. The target component (methylal) is cut from the background of the non-target components. Finally, the amount of methylal in gasoline can be quantitative analyzed by a flame ionization detector (FID) and an external standard method. The detection process is shown in Figure 1.
Figure 1. Methylal detection flow chart.

The detection device mainly includes a sampling module and a detection module. The sampling module consists of electronic control system, pipeline system, and sample labels. The detection module consists of columns, a six-way valve, and flame ionization detector (FID).

3.1. Sampling Module Design
The device sampling module is mainly composed of sample barrel, electronic control system, pipeline system, sample label and other components. Its structure is shown in Figure 2.

Figure 2. Sample module structure.
1-sample barrel, 2-Sampling line, 3-discharge line, 4-solenoid valve of sampling line, 5-solenoid valve of discharge line, 6-inlet line main valve, 7-Total outlet main valve

(1) Electronic Control System
The electronic control system mainly realizes automatic sampling, coding, control, result storage and display, including PLC controller, radio frequency reader, and solenoid valve and so on. PLC controller selects CPU 226 of S7-200, which possesses very strong control ability with 40 I/O points and 6 high-speed pulse counters. The PLC controller controls the solenoid valve to open the sampling barrel and encodes the electronic tags of the sample through a radio frequency reader. Each sampling barrel is provided with an independent solenoid valve to ensure that the sampling does not interfere with each other to improve the sampling accuracy.
(2) Piping System

It’s set a variety of pipelines to work with the sampling module. In order to allow the oil to enter the sampling drums while gasoline handling, configuring the sampling lines to connect the sampling pump and insert it into the oil tanks directly. The gasoline is automatically sampled. For the gasoline samples that do not have quality problems in a certain period of time, discharge lines are automatically discharged to the oil tanks for repeated use to avoid the waste of resources. According to the safety requirements, the exhaust lines are configured to discharge the mixed gas in the pipeline, which can avoid exploding.

3.2. Detection Module Design

The detection module consists of columns, a six-way valve, and a flame ionization detector (FID).

(1) Column

Non-polar capillary column use 100% methyl polysiloxane (colloidal) bonded SE-30 capillary column to efficiently separate heavy components with higher boiling points than methylal. The polar capillary column is packed with TCEP. The carrier gas is pure N2, the column temperature is 60°C, the injection port temperature is 200°C, and the injection volume is 1.0μL. Methylal is effectively separated from light components which have a lower boiling point than methylal.

(2) Flame Ionization Detector

The flame ionization detector (FID) is a standard detector for gas chromatography which can detect a variety of organic components. The peak area can be used to detect the content of methylal effectively. The schematic diagram is shown in Figure 3.

![Figure 3. FID Schematic.](image)

The FID includes a H₂/air flame and a current collector plate. When the organics flowing from the column pass through the flame, the organics ionize in the flame. Then, the generated ions are collected on the polarized collector to generate an electrical signal. The chemical reactions in the flame are as follows:

\[
\text{CH} + \text{O} \rightarrow \text{CHO}^+ + \text{e}^- \quad (1)
\]

\[
\text{CHO}^+ + 4\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})n\text{H}^+ \quad (2)
\]

\text{CHO}^+ will be deprived of a proton by the surrounding H₂O and form (H₂O)nH⁺ by burning. Thus, the number of ions is detected [12].
4. Experiments and Results

4.1. Determination of Valve Switching Time
The valve switching time plays an important role in the accurate quantitative detection of methylal. The valve switching time for detecting the methylal content is determined based on the retention time of methylal on the column. The retention times of different substances on SE-30 non-polar capillary column are shown in Table 1. The peak of methylal is before the hexane, so when hexane enters the polar column, the valve is switched to the back flushing state. By trial and error, according to the difference in the retention time to change the valve switching time, the time when the peak area of hexane is very small (hexane just completely emptys), and the error of the methylal peak area is within 5% while observing the changes in the peak area of each component is the valve switching time for determining the methylal content. Finally, the valve switching time is determined to be 36~54s. It excludes the interference of hydrocarbon compounds on the detection of methylal maximally.

| Substance | Methanol | Ethanol | Hexane | Methylal | N-hexane |
|-----------|----------|---------|--------|----------|----------|
| t/s       | 18.12    | 20.94   | 31.26  | 32.46    | 36.96    |

4.2. Standard Curve Drawing and Detection Limit Determination
A standard sample of a certain amount of methylal is weighed and placed in a 100 ml volumetric flask. In order to eliminate the interference of other components, the solvent is diluted to a mark with a petroleum ether solution to obtain a standard stock solution. We take the appropriate standard stock solution in a volumetric flask and dilute with petroleum ether to obtain 6 sets of standard solutions of methylal in different concentrations \( \rho \) (mg/mL). The concentration of each standard solution is shown in Table 2.

| Numble | Scheme 1 | Scheme 2 | Scheme 3 | Scheme 4 | Scheme 5 |
|--------|----------|----------|----------|----------|----------|
| 1      | 456      | 456      | 123      | 123      | 123      |
| 2      | 789      | 213      | 644      | 644      | 644      |
| 3      | 213      | 654      | 649      | 649      | 649      |

Methylal standard solution is detected according to the chromatographic conditions. The standard curve is plot with the mass concentration of methylal and its corresponding peak area, as shown in Fig.4. The mass concentration of methylal (\( x \)) is the abscissa, and the corresponding peak area (\( y \)) is the ordinate. We can obtain the linear regression equation \( y=ax+b \) and the correlation coefficient \( R \). There is a good linear relationship between the mass concentrations of methylal in the range of 0.020 to 90.0mg/mL. The linear regression equation is \( y=0.32x-9.32 \) with the correlation coefficients of 0.9999 which can meet the needs of quantitative analysis when measuring actual samples. The detection limit is determined with the lowest concentration response in the standard methylal solution configured. The detection limit of methylal is calculated to be 0.012g/L using the 3 times signal to noise ratio (3S/N), which can meet the detection requirements.
Figure 4. Standard working curve of methylal in gasoline.

4.3. Determination of Precision

The precision of this method is determined using 5 sets of different concentrations of methylal solution configured with non-methylal gasoline. The results are shown in Table 3. The relative standard deviation (RSD) of each group of n=6 tests results can be obtained by:

\[
\text{RSD} = \frac{S}{\bar{x}} \times 100\% \tag{3}
\]

\[
S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}} \tag{4}
\]

\(\bar{x}\) is the average value of n=6 tests results. From Table 3, the relative standard deviation (RSD) of each group of n=6 results are all less than 2%. Thus the quantitative results are accurate and reliable.

| Number | Frequency | 1   | 2   | 3   | 4   | 5   | 6   | RSD%  |
|--------|-----------|-----|-----|-----|-----|-----|-----|-------|
| 1      | 89.435    | 89.347 | 89.834 | 89.984 | 88.431 | 88.593 | 0.7125 |
| 2      | 70.119    | 70.023 | 70.084 | 69.436 | 69.644 | 69.899 | 0.3901 |
| 3      | 49.856    | 49.785 | 49.239 | 49.497 | 49.682 | 49.216 | 0.5544 |
| 4      | 29.384    | 29.591 | 29.832 | 29.183 | 29.498 | 29.275 | 0.7941 |
| 5      | 9.638     | 9.598  | 9.587  | 9.743  | 9.855  | 9.689  | 1.0495 |

5. Conclusion

Gasoline handling automatic sampling detection device can take gasoline sample during gasoline handling automatically, and detect non-conventional additives in the sample quickly, such as methylal. On-site sampling and content detection are performed at the same time. The sampling process is free from human interference, which improving the authenticity of the sample. Two-dimensional gas chromatography is used to detect the methylal content of gasoline samples without pretreatment of the
samples and is easy to handle. The single-component cutting is achieved using the valve switching and back-blowing techniques which eliminate the interference between the components and improve the accuracy of chromatographic analysis. Its relative standard deviation (RSD) is less than 2%, and it has a good linear relationship in the range of 0.020 to 90.0mg/mL. The detection limit is 0.012g/L, which meets the requirements for the detection of gasoline in vehicles. The quantitative data is reliable and has broad application prospects.

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