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Review

Direct measurement of formaldehyde and methanol emissions from gasohol engine via pulsed discharge helium ionization detector

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ABSTRACT

Unregulated formaldehyde (HCHO), acetaldehyde (CH₃CHO) and methanol (CH₃OH) emissions from M10 blend (methanol/gasoline = 1/9 in volume) fuelled spark ignition (SI) engine were directly detected by a gas chromatography (GC) with a Gs-OxyPLOT capillary column and pulsed discharge helium ionization detector (PDHID). Chromatograms show that HCHO and CH₃OH are well separated and linearly responded on PDHID within the range of 0.8–800 μ g/L. The method is proved suitable and reliable for measuring unregulated pollutants from the engine. Experimental results show that compared with gasoline, HCHO emission from M10 is greatly larger while CH₃CHO is smaller. HCHO emission increases while CH₃OH emission decreases with engine speed and tailpipe temperature. The three-way catalytic converter (TWC) can remove over 85% of CH₃OH and CH₃CHO emissions when it is lightened off. However, an unfamiliar phenomenon of minus HCHO conversion efficiency happens when engine speed is over 3500 r/min, which infers that TWC may enhance HCHO emission rather than weaken it at high engine speeds.

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Contents

1.	Introduction	2179
2.	Experimental setup	2180
	2.1. System settings	2180
	2.2. Qualitative analysis	2180
	2.3. Calibration curve	2180
	2.4. Detection limit	2181
3.	Sampling conditions	2181
	3.1. Effects of temperature	2181
	3.2. Sample life-span	2181
4.	Results and discussion	2182
	4.1. Chromatogram analysis	2182
	4.2. Formaldehyde emission	2182
	4.3. Methanol emission	2182
	4.4. Acetaldehyde emission	2183
5.	Conclusions	2184
	Acknowledgements	2184
	References	2184

1. Introduction

Methanol is one of the most attractive alternative fuels for spark ignition engine. It can be readily made from natural gas, coal and

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biomass resources. Methanol is also a clean fuel when judged by regular emission standard, the addition of methanol in gasoline improves fuel economy and reduces the carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxides (NO_x) emissions of SI engine [1–3]. However, more formaldehyde (HCHO) and more unburnt CH₃OH is emitted as well [4–6].

Formaldehyde plays an important role in photochemistry. It is also classified as a probable human carcinogen by the US Environmental Protection Agency (EPA). The International Agency for Re-

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search on Cancer (IARC) has determined that there is "sufficient evidence" that occupational exposure to formaldehyde causes nasopharyngeal cancer in humans.

It is proved that formaldehyde is unsuitable to be detected by FID method [7]. CARB method 1004 (ASTM Method D5197, and US EPA Methods TO-11A and 8315) is commonly used to monitor aldehydes emission from engines. In this method, sample collected impregnates with 2,4-dinitrophenylhydrazine (DNPH). Aldehydes will be converted to the 2,4-dinitrophenylhydrazone derivative. After separation by column, they can be detected by high performance liquid chromatography (HPLC) with ultraviolet (UV) detector [8] or GC with FID [9]. However, excluding the sampling time, the operation of derivation, elution, extraction and detection of the DNPH hydrazone take over 1 h. The complex pretreatment of the samples is not feasible, especially when a lot of testing points are needed. Further more, this method expands a lot of money.

Over the past few years, a relatively low-cost chromatographic method, pulsed discharge helium ionization detector (PDHID), was developed, which is capable of monitoring low levels of formalde-hyde and with a simple sampling process [10–12]. PDHID utilizes a stable, low power, pulsed DC discharge in helium as the ionization source. Eluents from the column, flowing counter to the flow of helium from the discharge zone, are ionized by photons from the helium discharge above. Resulting electrons are focused toward the collector electrode by the two bias electrodes. The photon energy produced by the transition is in the range of 13.5–17.7 eV.

In this study, 2% vol of argon was doped into the discharge helium letting the detector work in selective Ar-PDHID mode. In this mode, the response of detector on HCHO and CH₃OH are improved and the selectivity is enhanced. With highly unique retention characteristics for oxygenated HCs, a type of Agilent Gs-OxyPLOT capillary column was selected to separate HCHO and CH₃OH out from the engine exhaust gas. Basing on the Gs-OxyPLOT-PDHID system, the detecting procedure and sampling conditions were optimized; a method for detecting the unregulated emission was established. The HCHO and CH₃OH emissions from a methanol/gasoline blend fueled engine were also investigated.

2. Experimental setup

2.1. System settings

Methanol and aldehydes, formaldehyde and acetaldehyde, were detected by a gas chromatography (GC-2010, Shimadzu, Japan). The system consists of a Gs-OxyPLOT capillary column and a pulsed discharge ionization detector (PDHID, Model D4-I-SH-17R, VICI (Valco instrument Co. Inc.)). The carrier gas is helium (99.999%) and the discharge gas helium doped with 2% Ar (both 99.999%). The discharge flow was 30 mL/min (at 6 psi) maintained by a calibrated restrictor (TGA-R-30F60P, Valco, Switzerland). Since a stringent purity of gases are required in the system, the high purity carrier gas helium and discharge gas were both "cleaned" by gas purifiers (HP2, Valco, Switzerland). The purifiers contain a non-evaporable gettering alloy, consisting of zirconium, vanadium and iron. Once activated by heating at 400 °C, the surface is free from passivating oxide layers and therefore available for sorption. The working temperature of the purifier is 240 °C.

The pollutants HCHO, CH_3CHO and CH_3OH were detected by PDHID in Ar-PDHID mode to improve the response and selectivity on HCHO and CH_3OH by eliminating the response of water and permanent gases [12]. Exhaust gas collected in the sample bag was drawn through the stainless steel quantitative loop (volume 100 µL) on six-way switch at the speed of about 200 mL/min via a vacuum pump. During the injection, the six-way switch turned the gas path from solid line to dashed line, thus, sample in the loop



Fig. 1. Chromatogram of formalin solution.

was transmitted to the column (Gs-OxyPLOT, 10 m \times 0.53 mm \times 10 µm, Agilent technologies) by helium carrier gas (100 cm/s). The split ratio was set as 5. To obtain the best resolution and shortest analysis time, a programmed column temperature was developed as: 90 °C for 1 min, up to 170 °C at 20 °C/min. The total analysis time is 5 min.

2.2. Qualitative analysis

Chemically pure formalin solution, acetaldehyde solution and methanol were used for qualitative analysis. As shown in Fig. 1, PDHID has good responses to HCHO, CH₃CHO and CH₃OH, especially on HCHO. These compounds have retention time of 1.028 min, 3.056 min and 4.723 min, respectively. It takes only 5 min for a single analysis.

2.3. Calibration curve

Chromatographically pure formaldehyde (40%, Guangfu Chem., Tianjin, China), acetaldehyde (40%) and chemically pure methanol $(\geq 99.5\%)$ were chosen as the sources of calibration. The mixture of HCHO, CH₃CHO and CH₃OH solution was prepared at the ratio of 2:2:1 in volume. Here, methanol also serves as the inhibitor to prevent formaldehyde from polymerization. The standard gases were made by vaporizing the mixture balanced with pure nitrogen in fluorinated ethylene propylene (FEP) refractory plastic bag. For example, a FEP bag was filled with pure N_2 and 12.5 µL mixture solutions, the volume of FEP bag was quantitated to be 5.145 L at 80 °C. So, the concentration of HCHO, CH₃CHO and CH₃OH are 428, 378 and 412 μ g/L, respectively. In this way, six standard gases with different concentrations of HCHO were prepared. The concentrations are from 0.8 to 800 µg/L. Each concentration was measured for three times independently. The regression equations, absolute errors (σ) and relative errors (CV) are listed as follows:

HCHO: $Y_1 = 47055X_1$, $R^2 = 0.9994$, $\sigma = 12.6 \ \mu g/L$ (at 856 $\mu g/L$), CV = 1.48%

CH₃CHO: Y₂ = 18009X₂, R^2 = 0.9989, σ = 23.2 µg/L (at 756 µg/L), CV = 3.07%

 $\begin{array}{ll} {\rm CH_3OH}:Y_3=10903X_3, \quad {\it R}^2=0.9973, \sigma=28.7~\mu g/L~({\rm at}~824~\mu g/L),\\ {\rm CV}=3.48\% \end{array}$

where *X* is concentration, μ g/L, and *Y* is the peak area, V s. The intercepts on *x*-axis of the three compounds are merely 0.035, 0.099 and 0.072 μ g/L, respectively. Thus, the effects of the intercepts on measurements are neglected.



Fig. 2. Typical PDHID baseline.

2.4. Detection limit

The calibration curve is set up by means of peak area method, it can also be determined in the way of peak height method. Since the minimum detection limit (MDL) is defined as the concentration when the signal to noise ratio (*S*/*N*) equals 2, the relationship between peak height and concentration must be solved for MDL determination. The correction factor is $f'_m = C_i/H_i$, where C_i is the concentration of compound *i*, $\mu g/L$; H_i is the corresponding peak height, μV . The correction factors of HCHO, CH₃OH and CH₃CHO are as followings:

$$\begin{split} f'_{m(\text{HCH0})} &= \frac{C_{(\text{HCH0})}}{H_{(\text{HCH0})}} = 21286.93 \ \mu\text{V}/(\mu\text{g}\cdot\text{L}^{-1}) \\ f'_{m(\text{CH}_3\text{CH0})} &= \frac{C_{(\text{CH}_3\text{CH0})}}{H_{(\text{CH}_3\text{CH0})}} = 12953.21 \ \mu\text{V}/(\mu\text{g}\cdot\text{L}^{-1}) \\ f'_{m(\text{CH}_3\text{CH0})} &= \frac{C_{(\text{CH}_3\text{CH0})}}{H_{(\text{CH}_3\text{CH0})}} = 6717.44 \ \mu\text{V}/(\mu\text{g}\cdot\text{L}^{-1}) \end{split}$$

The typical baseline in Fig. 2 shows that the noise level of the PDHID is 200 μ V. Here the MDL is estimated with *S*/*N* = 3, where the minimum peak height is 600 μ V, thus, the MDL of the three compounds are:

$$\begin{split} \text{MDL}_{\text{HCHO}} &= 600 / f_{m(\text{HCHO})}' = 28.2 \times 10^{-9} \text{ g/L} \\ \text{MDL}_{\text{CH}_3\text{CHO}} &= 600 / f_{m(\text{CH}_3\text{CHO})}' = 46.3 \times 10^{-9} \text{ g/L} \\ \text{MDL}_{\text{CH}_3\text{OH}} &= 600 / f_{m(\text{CH}_3\text{OH})}' = 89.3 \times 10^{-9} \text{ g/L} \end{split}$$

3. Sampling conditions

As the targets are those trace components of the engine exhausts, the fluctuation of exhaust pressure may result in significant errors if directly sample from the exhaust pipe. In this study, the exhaust gas was collected under stable operating condition with FEP bag. In this case, the detected value was an averaged one. Because the exhaust gas contains a lot of water, it will condense and absorb HCHO and CH₃OH at the room temperature. So the sample bag was kept in a thermostat at 80 °C before detection. The effects of temperatures and time on concentrations were investigated.

3.1. Effects of temperature

Fig. 3 shows the effect of the bag temperature on HCHO and CH_3OH concentrations. Their concentrations in "dry" gas (similar to standard gas) are less affected by the heating temperature (Fig. 4a). The concentrations of HCHO and CH_3OH in the sampled exhaust depend on the heating temperature obviously. As can be seen from Fig. 4b, methanol concentration is not stable until the



Fig. 3. Relationship between sample heating temperature and measured concentrations.



Fig. 4. Life-span of samples in different storage conditions.

temperature reaches 80 °C, so 80 °C is chosen as the standard temperature for the samples to be kept.

3.2. Sample life-span

Two bags were prepared to investigate the validation of the samples. One was kept in thermostat at 80 °C; the other was kept at room-temperature. As can be seen from Fig. 4, the room-temperature sample will keep constant even after 11 days (260 h) (Fig. 4b). However, when heated continuously, formaldehyde concentration will go down after 24 h (Fig. 4a). That is because the trace formaldehyde in the condensed water stays in the form of methylene glycol (CH₂O·H₂O, CH(OH)₂), this compound is rather stable [13]. Obviously, methanol has almost no change.

4. Results and discussion

Applications of the method were carried out on a type of threecylinder in line, electronic controlled, Euro II (equipped with Bosch M1.5.4P multi-point injection system), JL368Q₃ spark ignition (SI) engine. Its bore and stroke are 68 mm and 72 mm, so the total displacement is 0.796 L. The unregulated exhaust emissions were measured and compared when the engine fueled with M10 (methanol/gasoline = 1/9 in volume) and gasoline respectively. The fuels used in the experiment were commercial 93# gasoline and chemically pure methanol (\geq 99.5%). The conversion efficiencies of a standard three-way catalytic converter (TWC) were investigated as well. The tailpipe temperature was measured at 20 cm downside from the exhaust port, and TWC temperature was measured at the inlet of TWC (100 cm downside from the exhaust port) with type K thermocouples.

4.1. Chromatogram analysis

When doping 2% of argon in discharge helium gas, the detector functions as a selective Ar-PHHID mode. This reduces the photon energy from the range of 17.7-13.5 eV to the range of 11.8-9.8 eV [14], therefore, the response to H₂O (with ionization potential of 12.6 eV) will be avoided [12,14,15]. Fig. 5 gives a chromatogram of exhaust gas from an M10 operating condition. HCHO has good resolution and excellent response to samples from both before and after three-way catalytic converter (BTWC, ATWC). Most of the low carbon number HC are eluted out of the ultra-strong polarity Gs-OxyPLOT column before HCHO, they have no interference on aldehydes and alcohols [16]. However, CH₃CHO peak is prone to be flooded by the following water peak, and CH₃OH sits on the tail of an unknown peak. So, the repeatability of the two compounds is limited, their relative errors are both around 10% while HCHO less than 5%, as can be seen in Table 1. Fortunately, the interference of the peak on CH₃OH quantification is negligible when the concentration of CH_3OH is over 10 µg/L. Thus, the combination of Gs-OxyPLOT capillary column and Ar-PDHID detector



Fig. 5. Chromatogram of exhaust gas from M10 engine operating at 2000 r/min, 20 N m.

Table 1				
Repeatability of three	compounds	from	M10	engine.

on GC is a good method to analyze unregulated emissions from methanol/gasoline blends fueled engine.

4.2. Formaldehyde emission

Formaldehyde (HCHO) is an important intermediate product of HC and methanol oxidation, gas temperature and the residence time determine the oxidation process. With the increase of engine speed, the tailpipe temperature is increased, while the residence time of exhaust gas in the cylinder and tailpipe is shortened. More HC and methanol are oxidized to HCHO, but less time is left for HCHO consumption, as can be seen in Fig. 6a, M10 engine-out HCHO emission rises with engine speed.

Fig. 6b shows the effects of TWC on HCHO. The conversion efficiency rises with the TWC temperature at the lightening-off stage. However, not like the removal on the other HC, the conversion efficiency on HCHO varies much when the TWC is lightened off, especially at high engine speed and TWC temperature, minus conversion efficiency occurs, the abnormal phenomenon means that the formation effect of HCHO from HC and methanol oxidation is stronger than its consumption effect.

Abian et al. [17] proved that the present of ethanol shift the oxidation regime of acetylene to higher temperatures, acetylene oxidized slowly until ethanol was consumed up. That means ethanol has the priority to oxidize, and it restrains acetylene oxidation until it is used up. Methanol may have the similar effects on HC oxidation. Moreover, literatures [18,19] implied that a majority of the HC consumption occurs at temperatures higher than 1500 K, while the methanol oxidation starts at 1000 K [20]. Thus, the HCHO is mainly formed from methanol oxidation if there exists methanol in exhaust, while from other HC with the absence of methanol. And due to the different temperature threshold of oxidation between methanol and HC, the increase of in-cylinder and exhaust temperature between the thresholds will help the consumption of residual gasoline engine-out HCHO, while help methanol oxidize to HCHO, thus, although gasoline engine-out HCHO also increases with the increase of engine speed, see as in Fig. 7, it tends to decrease while M10 engine-out one increases with increase of engine torque. Moreover, due to the simplicity of methanol oxidizing to HCHO and high HCHO concentration in the oxidation process [21], the addition of methanol in gasoline caused the increase of HCHO emission at middle and high engine torque.

4.3. Methanol emission

No methanol (CH₃OH) emission is detected from the gasoline fueled engine; the CH₃OH emission from M10 engine is produced from the unburnt fuel methanol. Fig. 8 gives the CH₃OH emission characteristics of M10 engine. CH₃OH emission decreases with the engine speed and tailpipe temperature; it is not detectable when the engine speed is over 3500 r/min, as can be seen in Fig. 8a. With the increasing engine speed, the quantity of unburnt methanol from the crevice storage of the fuel–air charge and release is reduced, and with the help of increasing cylinder and tailpipe temperature, the reduced unburnt methanol is further oxidized, thus CH₃OH emission decreased. No detectable CH₃OH

Compound	Measured	Measured value (µg/L)					Mean value (µg/L)	σ	CV (%)
НСНО	32.81	31.52	30.11	33.23	34.18	34.24	32.68	1.61	4.93
CH ₃ CHO	14.13	12.26	13.37	16.33	14.46	15.55	14.35	1.47	10.2
CH ₃ OH (L)	8.99	8.02	9.28	7.81	9.13	7.54	8.46	0.76	8.95
CH ₃ OH (H) ^a	20.33	19.96	20.91	19.57	21.74	21.23	20.62	0.82	3.96

^a Measured at 2000 r/min, 8 N m, else at 20 N m.



Fig. 6. Formaldehyde emission characteristics from M10 engine.



Fig. 7. Comparison of formaldehyde emission from M10 and gasoline engine.

is emitted into atmosphere when TWC is lightened off at around 270 °C (Fig. 8b).

4.4. Acetaldehyde emission

Acetaldehyde (CH₃CHO) is also an intermediate product of HC oxidation [22], it has two effects of formation and consumption as well. With the increase of engine torque, tailpipe temperature increases, and it helps the formation of CH₃CHO, see as in Fig. 9, CH₃CHO emission from both gasoline and M10 engine firstly increases with engine torque, however, the consumption effect takes the dominant role when temperature is over a critical point, thus CH₃CHO emission slightly decreases at 2000 r/min, high engine load. Nevertheless, the slight decrease does not occur due to the enrichment of fuel/air mixture at 3000 r/min, wide open throttle condition.

Not like HCHO, the HC oxidizing to CH₃CHO must contain more than one carbon atom in molecule. Methanol has only one carbon atom, its oxidation does not help acetaldehyde formation [22,23].



Fig. 8. Methanol emission characteristics from M10 engine.



Fig. 9. Comparison of acetaldehyde emission from M10 and gasoline engine.

In M10 fuel blend, 10% of long carbon chains are replaced by C–O bonds, the formation source is reduced. As a result, acetaldehyde emission from M10 is obviously lower than from gasoline. The TWC performs well in removing acetaldehyde; over 85% of acetaldehyde from M10 engine is removed when TWC is lightened off. Unfortunately, the acetaldehyde peaks from gasoline engine were flooded by the following water peak; further studies must be done for improvement.

5. Conclusions

A direct gas chromatographic method for the analysis of engine exhaust formaldehyde has been described. Estimated detection limits of 28×10^{-9} g/L for formaldehyde, 46×10^{-9} g/L for acetal-dehyde and 89×10^{-9} g/L for methanol were achieved with a 100 µL sample at flow velocity of 100 cm/s and split ratio as 5. The system was automated to take continuous measurements of engine exhaust formaldehyde every 5 min. The samples can be kept for over 11 d at room temperature, but only one day when continuously heated at 80 °C. Some conclusions from the study are as follows:

- (1) Oxygenated low molecule number HC emission, especially formaldehyde, from methanol/gasoline blends fueled engine can be detected by gas chromatography with Gs-OxyPLOT capillary column and pulsed helium ionization detector (PDHID) working at argon mode.
- (2) The addition of methanol in gasoline gives methanol emission and reduces CH₃CHO emission while greatly enhances HCHO emission.
- (3) The HCHO emission rises while CH₃OH decreases with engine speed and tailpipe temperature.
- (4) TWC performs well in removing CH₃OH and CH₃CHO. However, it "produces" HCHO at high engine speeds.

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