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Research on the accurate sampling position of non-regulated emissions

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Abstract. This paper selected several test vehicle, and collected the samples at constant volume sampler (CVS) tunnel, sampling bag, and exit of the gas pump respectively, and analysed the carbonyls using high performance liquid chromatography (HPLC). The result shows that the gas at the sampling bag is uniform and stable in concentration, compared with that at the tunnel and the gas pump exit; it is the right site to collect the non-regulated emissions to reduce the test error and improve the precision.

1. Foreword

The non-regulated emissions from vehicles include the carbonyls and the aromatic compounds in gaseous HC, and the microelement and the soluble organic fractions (SOFs) in PM[1-2]. They mainly include formaldehyde, acetaldehyde, butadiene, benzene and polycyclic aromatic hydrocarbons (PAHs). They are considered to have mutagenicity and carcinogenicity, and are extremely harmful to the body.

With the advancement of medical and analytical sciences, the dangers and harmfulness of some emissions have been discovered. This leads to a more stringent emission regulation to control them. However, as the non-regulated emissions in the exhaust is far less than the regulated emissions, using the method provided in the emission standard [3] to analyze the non-regulated emissions may lead to a large error, which is mainly affected by the sampling method of the non-regulated emissions.

This paper introduces and studies the sampling method of non-regulated emissions, collected data at different sampling sites in the vehicles, and analyses the carbonyls using HPLC. The method to improve the precision of measuring emissions is proposed.

2. The sampling method of non-regulated emissions

As the formation of carbonyls and VOCs is affected by the temperature of the exhaust pipe and the retention time in the pipe, the sampling method is critical to the accurate measure of the non-regulated emissions[4-5]. In this research, three applicable sites namely A, B and C as shown in Figure 1 are selected, representing the CVS tunnel, the sampling bag and the gas pump exit. The exhaust flows into the CVS tunnel (A site) with the fresh air propelled by dilution fans, and flows through B site, which collects a minor part of the exhaust in to the gas bag. The remaining part of the exhaust continues flowing at the tunnel and flows to the outlet (C site) propelled by the pump. This research studies the gasoline vehicles and follows the procedure of Type I Test provided in the emission regulation. The carbonyls are collected at the three sites and then analyzed. The test is repeated twice to reduce the error. The CVS tunnel and the sampling gas bag are purged, and the analyzer is calibrated before each



test. The three tests are driven by the same driver, and the sampling and pre-conditioning are done by the same operator.

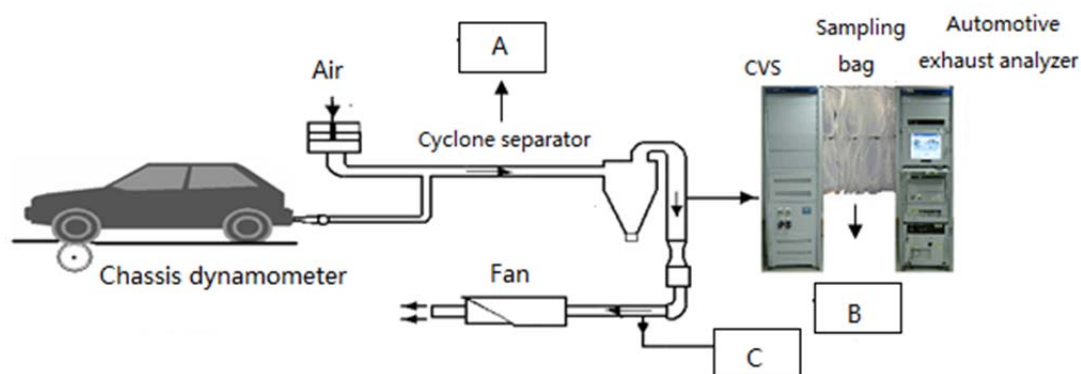


Figure 1. Different sampling positions.

3. The analysis of the non-regulated emissions

The solid phase extraction (SPE)[6-8] is a method of chromatographic fractionation. It follows a similar process to the HPLC. The 2,4-DNPH sampling tube is placed in the solid phase extractor (Agilent), and the sealed caps are opened. The test tube is placed in the extractor corresponding to the sampling tube. An amount of 3mL acetonitrile is injected into the tube to elute the sample. The eluted liquid is placed in the test tube and is filtered using a 0.45 micrometer porous filter. The filtered liquid is placed in a 5mL measuring flask, and mixed with acetonitrile to 5mL line. It is further disposed in ultrasonic machine to eliminate the bubble, and finally placed in the sampling bottle which is labelled for further analysis.

4. The influence of sampling method on the measurement of emissions

The results in the three sampling sites of carbonyls are listed in Table 1. 1, 2 and 3 represents the results in the repeated tests. The pentanal, toluyaldehyde, cyclohexanone and hexanal are not detected, and thus not listed. It is shown that the results in the sampling bag (B site) are the most stable, while in the rest two sites are much less stable.

The standard deviation and RSD are listed in Table 2 based on the data originated from the three tests.

It is shown that the deviation in B site is the least. Compared with the result in A site, the standard deviation and RSD of formaldehyde in B site are 80% and 85% less respectively; compared to the result in C site, they reduced by 94%.

The formaldehyde is an important intermediate product in the oxidation of HC. The formaldehyde from the engine is originated from the intermediate oxidation of HC minus the oxidation of formaldehyde itself. The oxidation of HC mainly happens in the exhaust pipe, and is influenced by the gaseous temperature and reaction time, and thus the formation of formaldehyde is affected by exhaust temperature and engine speed. As the test cycles are the same, the vehicle speed at the same elapsed time is similar, and thus the formaldehyde in the exhaust pipe is majorly influenced by the site temperature and the retention time[9-11].

Table 1. Results of aldehydes and ketones under different sampling methods.

Emission factor mg/km	A			B			C		
	1	2	3	1	2	3	1	2	3
Formaldehyde	0.519	0.632	0.876	0.900	0.964	0.963	1.612	0.407	0.813
Acetaldehyde	0.078	0.179	0.327	0.320	0.473	0.441	0.124	0.424	0.261
Acrolein + acetone	0.237	0.146	0.227	0.240	0.208	0.091	0.101	0.442	0.177
Propionaldehyde	0.140	0.034	0.065	0.111	0.102	0.075	0.166	0.416	0.057
Crotonaldehyde	--	--	--	0.046	0.053	--	--	--	--
Butanone	--	--	--	0.372	0.411	0.402	--	--	--
Methacrolein	--	0.048	--	--	--	--	--	--	0.066
Butyraldehyde	1.375	--	--	--	--	--	0.308	--	--
Benzaldehyde	--	--	0.089	--	--	0.279	--	--	0.036

(Note: The "--" in all the table data of this study indicates that the substance was not detected)

Table 2. Standard deviation and relative standard deviation of the same sampling method.

Aldehyde and ketone pollutants	Standard deviation S (mg/km)			Relative standard deviation RSD (%)		
	A	B	C	A	B	C
formaldehyde	0.182	0.037	0.613	27	4	65
Acetaldehyde	0.126	0.081	0.150	65	20	56
Acrolein + acetone	0.050	0.078	0.179	24	43	74
Propionaldehyde	0.055	0.019	0.184	69	20	86
Crotonaldehyde	--	0.029	--	--	87	--
Butanone	--	0.020	--	--	5	--
Methacrolein	0.028	0.161	0.038	173	--	173
Butyraldehyde	0.794	--	0.178	173	--	173
Benzaldehyde	0.051	--	0.021	173	173	173

The data in the CVS tunnel or the pump exit is inaccurate, as the exhaust varies significantly, which is not helpful to adsorb unregulated emissions whose concentration is low. For the CVS tunnel, as the exhaust from the vehicle directly enters into the tunnel without enough mixture with the air and the temperature is high, the mixed exhaust is uneven and thus not suitable for the sampling. The pump exit is the end of the system, while the mixture is enough and the temperature is moderate, the

retention time is too long to represent the accurate condition in the exhaust. Meanwhile, the pump flow is much less than the CVS tunnel flow, and thus not suitable for the sampling. For the sampling bag, the gas is diluted by the fresh air, and thus the concentration and temperature are stable, and are not affected by the surroundings. Therefore, it is better to sample at the sampling bag.

5. Conclusions

This paper concludes the best sampling position by analyzing carbonyls at different sampling sites. Compared with the CVS tunnel and the pump exit, the concentration in the sampling bag is stable and thus is suitable for sampling low concentration fraction such as non-regulated emissions. It is helpful to reduce the error and improve the precision.

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