

# Component Analysis of Deposits in Selective Catalytic Reduction System for Automotive Diesel Engine

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**Abstract.** In this paper, deposits in exhaust pipes for automotive diesel engines were studied by various chemical analysis methods and a kind of analysis process to determine the compositions of organic matter was proposed. Firstly, the elements of the deposits were determined through the element analysis method. Then using characteristic absorption properties of organic functional groups to the infrared spectrum, the functional groups in the deposits were determined. Finally, by GC-MS (gas chromatography - mass spectrometry) test, the content of each main component was determined quantitatively. Element analysis results indicated that the deposits adsorbed metal impurities from fuel oil, lubricating oil, mechanical wear and urea water solution. The result of GC-MS test showed that the area percentage of cyanuric acid was the biggest (about 85%), the second was urea (about 4%), and the content of biuret and biurea was scarce.

## 1 Introduction

Diesel engines are widely used in heavy vehicles because of its superior performance on the economy and reliability. Selective catalytic reduction (SCR) which uses urea water solution (UWS) as the reductant is widely regarded as one of the most promising technology to reduce NO<sub>x</sub> emissions of diesel engine and to meet increasingly stringent emission regulation standards [1-4]. As for SCR system in practical engineering application, however, there are still many problems to be solved, especially the deposit problem, which has brought serious challenges for the application of the SCR system.

In the ideal situation, UWS generates reductant NH<sub>3</sub> after evaporation, pyrolysis and hydrolysis [5-7]. Schaber, etc. [8] studied the thermal decomposition process of urea by thermo-gravimetric analysis method in the lab. The results showed that the urea pyrolysis and the generation of related by-products are related to the temperature. When the temperature was above 152 °C, urea started to break down, and at the same time biuret would form. When the temperature was above 190 °C, a lot of cyanuric acid generated. Thagard [9] dealt with the chemical analysis of the by-products formed by urea decomposition at about 150 °C - 200 °C in a dielectric barrier discharge (DBD). Recent researches [10-14] showed that we could get hydrogen by urea pyrolysis reaction, which was considered as a potential source of hydrogen/fuel cell power. In addition, other researchers [15-17] found urea related deposits formed at different places in vehicles with SCR system, such as the exhaust pipe wall, the surface of catalyst entrance, the inside of urea nozzle and urea pump. We also observed a large

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number of deposits existing on the exhaust pipe wall through road test for a certain type of commercial vehicle. The exhaust pipe was serious congestion, which affected the performance of diesel engine seriously. What's more, the deposits formed in diesel engine exhaust pipes after continuous injection of urea aqueous solution for 5 h caused exhaust back pressure increased by 1.4 kPa and  $\text{NO}_x$  conversion efficiency reduced by 3%.

In terms of SCR system for automotive diesel engine, the operation condition of the given engine and exhaust flow field is very complex, the formation of deposits is an extremely complicated physical chemistry process. In order to avoid or reduce the formation of deposits, it is necessary to study its composition. In this paper, the deposits from a vehicle diesel engine exhaust pipe wall were analyzed by various chemical analysis methods. Not only its compositions were determined, but also the content of each component in the deposits was analyzed quantitatively.

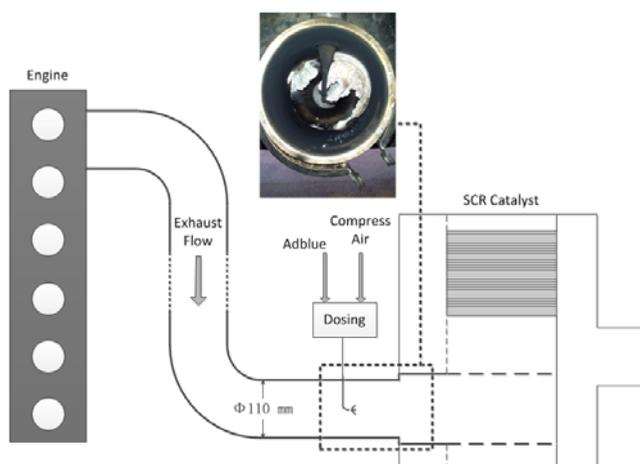
## 2 Experimental

### 2.1 Reagents

A road test was conducted using a certain type of commercial vehicle with SCR system. Technical parameters of the engine and the test vehicle are shown in Table 1. After 1000 km of road test, a large amount of deposits were found on the exhaust pipe wall, as shown in Figure 1. The vehicle driving route included suburban road, plain expressway and mountain road. The collected deposits weighted 131.67g, which was the sample for the following chemical analysis.

**Table 1.** Technical Parameters.

Parameter Name		Parameter Value
Vehicle	The Maximum Allowable Total Mass	31000 kg
	Unladen Mass	10200 kg
Engine	Displacement	11.12 L
	Quantity of cylinders	6
	Air Admission Mode	Supercharged Inter-cooling
	Fuel System	High Pressure Common Rail
	Rated Rotate Speed	1900 r/min
	Rated Power	257 kW



**Figure 1.** The deposits on the exhaust pipe wall.

## 2.2 Apparatus

Based on the chemical and physical properties of deposits, its components were researched by chromatographic analysis, spectral analysis, spectrum analysis and thermal analysis. Chemical analysis apparatus are shown in **Table 2**.

**Table 2.** Test apparatus.

Apparatus name	Specifications	Manufacturer
X-ray Fluorescence Spectrometer	AXIOS	PANalytical.B.V
Plasma Emission Spectrometer	Optima4300DV	PerkinElmer
CHNS/O elemental analyzer	Vario EL cube	Elementar
Fourier transform infrared spectrometer	NEXUS	Thermo Nicolet
GC-MS	Agilent 7890/ 5975	Agilent

## 2.3 Procedures

Firstly, the elements of the deposits were determined through the element analysis method. According to JY/T 016-1996 type of general principle of wavelength dispersion X-ray fluorescence spectrometer method, the contents of inorganic elements in the sample were determined using Axios advanced X-ray fluorescence spectrometer. In order to study the sources of the inorganic elements in the deposits, the inorganic elements contents of UWS and deposits were compared and analyzed by Optima4300DV plasma emission spectrometer. In addition, the UWS for SCR system used in the test process was provided by KeLanSu Environmental Protection Technology Co., Ltd. The deposits sample was dissolved by aqua regia and diluted with hydrochloric acid of 10% concentration. What's more, carbon, hydrogen, nitrogen, oxygen and etc. are the common elements in the organic matter. In this paper, organic elements in the sample were determined by Vario EL cube model CHNSO element analyzer manufactured by Elementar in German.

Then the deposits were analyzed using potassium bromide (KBr) pressed-disk technique by Fourier transform infrared spectrum and the functional groups in the deposits were determined as the characteristic absorption properties of organic functional groups to the infrared spectrum.

Gas chromatography-mass spectrometry (GC-MS) technology has high detection sensitivity and good separation effect, which has become one of the most effective means to analyze complex unknown material. In this paper, the deposits were dissolved using methanol as solvent and the supernatant was collected to be analyzed by GC-MS. As a result, the content of each main component was determined quantitatively.

## 3 Results and Discussion

### 3.1 Elemental analysis

The results of x-ray fluorescence spectrum test are shown in **Table 3**. The loss on ignition of the sample was as high as 99.8% after burning under the high temperature of 1000 °C for 2 h, which indicated that the main ingredients in the sample were organic matters.

**Table 3.** Results of x-ray fluorescence spectrum test.

Elements	Si	Al	S	Mo	Zr	Ba	Pb	Br	Loss on ignition
Contents (%) <sup>b</sup>	0.042	0.033	0.007	0.015	0.003	0.016	0.046	0.038	99.8

b. Calculated by oxide content.

In order to study the sources of the inorganic elements in the deposits, the results of plasma emission spectrum test are shown in **Table 4**. It is observed that the mass fraction of metal elements

detected in the samples are higher than that in the UWS. Hence, we can infer that the deposits have absorbed metal impurities from fuel oil, lubricating oil, mechanical wear and urea water solution.

**Table 4.** Results of plasma emission spectrum test.

Elements	Wave length /nm	Urea water solution /10 <sup>-6</sup>	Deposits/10 <sup>-6</sup>
Al	396.153	69	110
Cr	267.716	3	10
Fe	238.204	2	50
Mg	285.213	0	50
Mn	257.610	1	10
Pb	220.353	0	10
Zn	206.200	0	100
K	766.490	8	70
Na	589.592	63	120
Ca	317.933	0	850
Si	251.611	0	20

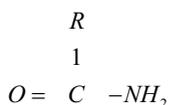
The results of organic elemental analysis are shown in **Table 5**. At the same time, **Table 5** lists the theoretical value of the content of each element in urea and related by-products. It indicates that the sample is composed of a variety of organic compounds by comparing the organic elements in the sample, urea and by-products.

**Table 5.** Results of organic elemental analysis.

Elements	C (%)	H (%)	N (%)	O (%)
<b>Deposits</b>	27.26	2.74	36.33	32.1
<b>Urea</b>	20	6.67	46.67	26.67
<b>Biuret</b>	23.3	4.85	40.78	31.07
<b>Cyanuric acid</b>	27.91	2.33	32.56	37.21

### 3.2 Qualitative analysis

Figure 2 shows the Fourier infrared spectra of deposits. As the characteristic absorption peaks shown in Figure 2, two absorption peaks at 3466 and 3334 cm<sup>-1</sup> respectively are the absorption bands of antisymmetric stretching vibration  $\nu(\text{NH}_2, \text{as})$  and symmetric stretching vibration  $\nu(\text{NH}_2, \text{s})$ . Strong absorption peaks at 1778, 1752 and 1721 cm<sup>-1</sup> are the absorption bands of stretching vibration  $\nu(\text{C}=\text{O})$ . Absorption peak at 1605 cm<sup>-1</sup> is the absorption band of deformation vibration  $\delta(\text{NH}_2)$ . Strong absorption peak at 1053 cm<sup>-1</sup> is the absorption band of stretching vibration  $\nu(\text{C}-\text{N})$ . Absorption peaks across 900 ~ 700 cm<sup>-1</sup>, whose peak type is wide and strong, is the characteristic absorption bands of wagging vibration  $\omega(\text{NH}_2)$ . These characteristic absorption peaks appeared at the same time, which showed that the composition of the sample contained aliphatic amide. Its structure formula is



Strong absorption peak at 3334 cm<sup>-1</sup> is the absorption band of stretching vibration  $\nu(\text{N}-\text{H})$  with hydrogen-bonding association. Strong absorption peaks at 1778, 1752 and 1721 cm<sup>-1</sup> are the absorption bands of stretching vibration  $\nu(\text{C}=\text{O})$ . Absorption peak at 1461 cm<sup>-1</sup> is the absorption band of deformation vibration  $\delta(\text{N}-\text{H})$ . Strong absorption peak at 1053 cm<sup>-1</sup> is the absorption band of stretching vibration  $\nu(\text{C}-\text{N})$ . These characteristic absorption peaks appeared at the same time, which

showed that the composition of the sample contained aliphatic secondary amide. Its structure formula

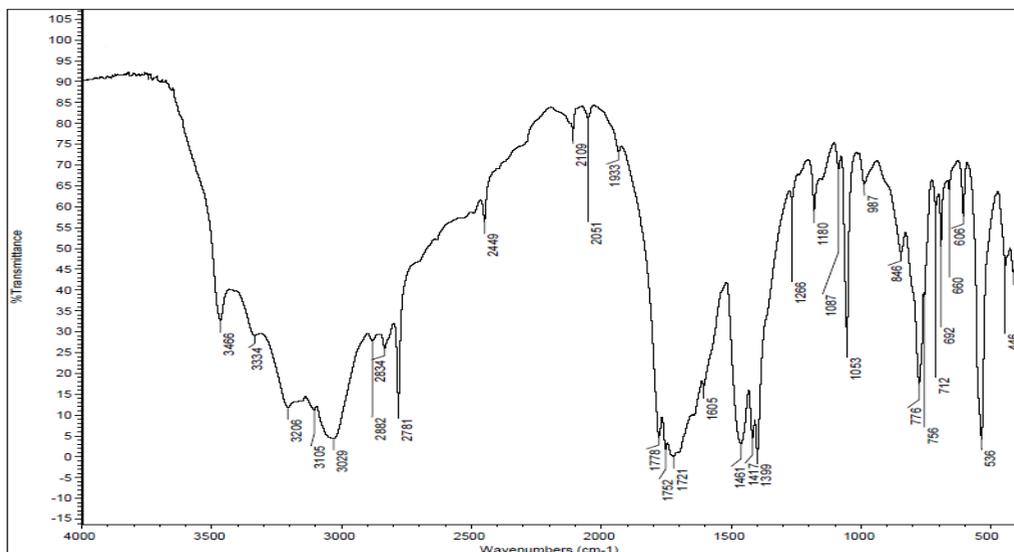
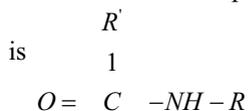


Figure 2. Fourier infrared spectra of deposits.

The infrared spectrograms of the deposits, biuret and cyanuric acid are compared in Figure 3. The results show that the matching degree of deposits and cyanuric acid is as high as 70% above, so we can primarily infer that the main ingredient in deposits is cyanuric acid.

### 3.3 Quantitative analysis

Figure 4 shows the chromatograms of deposits dissolved in methanol. Mass spectrometry results show that, the deposits contain biuret, urea and cyanuric acid. What's more, biurea, which haven't been observed in deposits ever, is also detected here. Hence, the reaction related biurea should be taken into account on the research of deposits in the future.

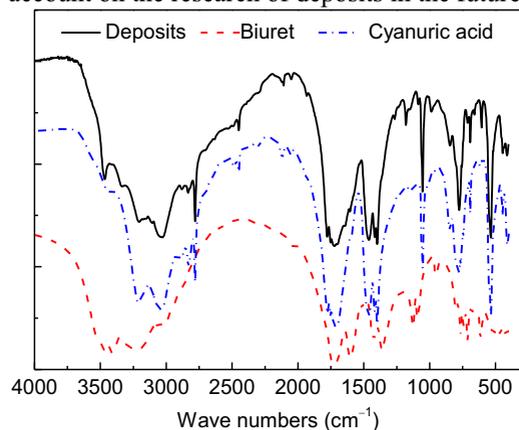


Figure 3. Infrared spectrum comparison results.

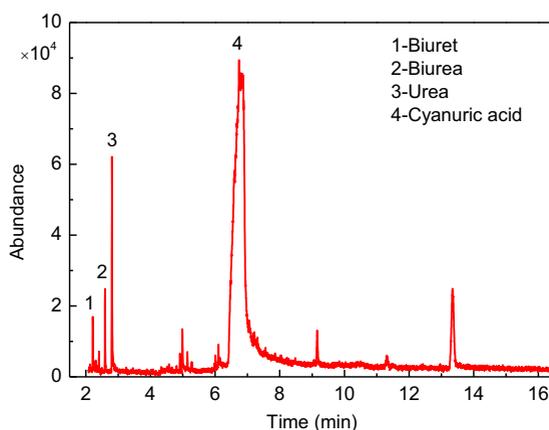


Figure 4. Chromatograms of the deposits.

According to the results of the area percentage, cyanuric acid has the largest peak area (about 85%), followed by urea (about 4% peak area), and the content of biuret and biurea is scarce. Similarly,

