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Effect of Combustion Residues of Typical Rubber Products on GC-MS Identification of Gasoline

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Abstract. There is a certain interference between the combustion of rubber products and the combustion improver such as gasoline. In this paper, rubber products with three different combustion degrees of unburned, burned and completely burned are prepared. Gas chromatography-mass spectrometry (GC-MS) is used to analyze the spectral characteristics of rubber product residues with different combustion degrees. The results show that the composition of the rubber combustion residue was similar to that of gasoline combustion residue, and the fused aromatic hydrocarbon component and the polycyclic aromatic hydrocarbon component are relatively stable, which has great interference to the gasoline identification. Different from the combustion residues of gasoline, the alkanes in the combustion residues of rubber products are mainly concentrated above C₁₀ and the matching degree of aromatic hydrocarbons is low. Benzothiazole and dimethyl phthalate can be detected almost in the combustion of rubber products. The test results can provide reference for the detection of gasoline in the identification of fire evidence.

1. Introduction

The arson case is a global problem that causes serious harm to people's lives and property, and to a certain extent, causes people's psychological panic and becomes an insecure factor affecting social stability [1]. At present, the most commonly used method for the analysis of combustion improver residues is gas chromatography-mass spectrometry (GC-MS), which uses solid phase microextraction for the sampling and preconcentration of fire residue. This method is mainly used for comparative analysis of alkane, aromatics and polycyclic aromatics in combustion promoter and combustion residues [2-3]. The fire situation is complex and there are many kinds of combustion residues, usually containing some interference compounds [4]. Rubber products are one of the main combustible materials, which are composed of macromolecular hydrocarbon compounds, similar to the composition of gasoline, which will interfere with the detection of gasoline in the actual identification process.

Domestic and foreign scholars have carried out a large number of studies on the influence of combustion residues of interferents on the detection of accelerant. Clodfelter and Hueske [5-7] analyzed gc-ms of 10 kinds of substrates, including carpet products, wood and roof materials, and compared them with the characteristic components of accelerant. Bertsch also studied the formation of cracking products from the burning of carpet products and detected the presence of aromatic compounds such as styrene, methylstyrene, naphthalene and methylnaphthalene [7-8]. As a commodity of common polymer materials, rubber products are widely used [9]. There are few studies on the interference of rubber products to accelerant. Therefore, this paper analyzes the characteristics of



combustion residue spectra of typical rubber products under different combustion degrees in daily life, so as to study its influence on gasoline identification.

2. Experience Set-up

2.1. Experimental Materials and Instruments

Experiment material: The gasoline used throughout the study was Ordinary 92# gasoline purchased from a local gas station; Acid and alkali resistant latex gloves (Leping Nanjian Rubber & Plastic Factory, Sanshui District, Foshan City); Labor insurance gloves (Linyi Fuan Special Labor Insurance Co., Ltd.); Blue rubber gloves (Mei Baobao Latex Products Factory); Single-use medical nitrile test gloves (Azov (Shanghai) Trading Co., Ltd.); Labor insurance rubber shoes (Henan Jiaozuo City Yuntaishan Rubber Co., Ltd.); High boots (Shanghai Huili Shoes Co., Ltd.); Blue poncho (Henan Qiuqiu Yulong Rain Gear Factory); Green Raincoat (Wuxi Qi'an Industry and Trade Co., Ltd.); Bicycle inner tube (Jiangsu Feiyue Rubber Co., Ltd.); Bicycle tires (Zunkun Tire Wholesale Trade Co., Ltd.); Tire (Shandong Chengshan Tire Co., Ltd.).

Instruments: ultrasonic cleaning instrument; gas chromatography-mass spectrometry (Agilent 7890B/5977B); HP-5MS column (30m×250μm×0.25μm); solid phase micro-extraction-large volume headspace sampler (Beijing Octagon technology Ltd.) extraction handle (100μm); ultrasonic cleaning instrument (Kunshan Ultrasonic Instrument Co., Ltd.); beaker; measuring cylinder; sample bottle; igniter.

2.2. Method

The following parameters were selected: Column: HP-5MS (30m×0.25mm, 0.25μm film thickness); carrier gas: helium at 1.0mL/min constant flow; inlet temperature: 250°C; split ratio:5:1; The GC oven temperature program used was: 50°C isotherm for 3 min, increased by 5°C to 250°C and then increased by 10°C to 300°C (held for 15 min); mass spectrometer ionization source at 230°C; mass quadrupole analyzer at 150°C in scan mode.

2.3. Extraction Preparation

Take 100g of rubber products and place them in a beaker to ignite with a lighter. They are extinguished at half of the burning, completely burned to natural extinction. After half an hour, they are placed in a sealed bag and kept for later use. The bulk headspace sampler was heated to 200°C for 4-8 hours to remove volatile compounds. When the temperature of the sampler is constant at 70°C, the samples with different combustion degrees are respectively placed in the 100μm extraction handle of the large volume headspace sampler for adsorption, and the sample is manually injected after 30 minutes, and the desorption time is 3 min. Under the same conditions, 0.5μL of the gasoline standard sample was placed in a large volume headspace sampler and extracted.

3. Results and Discussion

3.1. GC-MS Flow Chart Analysis of Burning Residues in Rubber Shoes

Taking rubber shoes as an example, the total ion chromatogram of the complete combustion residue is shown in Figure 1. The combustion analysis of other typical rubber products is similar, and some of the components are shown in Table 1. Since the identification criteria for gasoline combustion residues are clearly given in GB/T18294.5, the spectrum of gasoline combustion residues is no longer analyzed separately. Analysis of Figure 1 by standard mass spectrometry library search reveals: The peak of the combustion residue of the rubberized shoes is mainly concentrated at 10 to 25 minutes. Among them, the alkane peak detected after 15 minutes is mainly C₁₂ and above. The characteristic components of gasoline specified in GB/T18294.5, such as alkanes, olefins, polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, etc., can be detected. Therefore, there is some interference in the identification of gasoline. The peaks of 6, 9, and 10 correspond to 3-ethyl-1-methylbenzene, 1,2,3-trimethylbenzene, and 4-ethyl-1-methylbenzene, respectively, the retention time is 9.901~13.541min. There are two kinds of C₄ benzene, which are 1, 2, 4, 5-tetramethylbenzene and 1,

2, 3, 4-tetramethylbenzene, and the corresponding peaks are 12 and 13, and the retention time is 13.743min and 15.112min. The rubber shoes completely burned C_3 , C_4 benzene has a greater interference to gasoline.

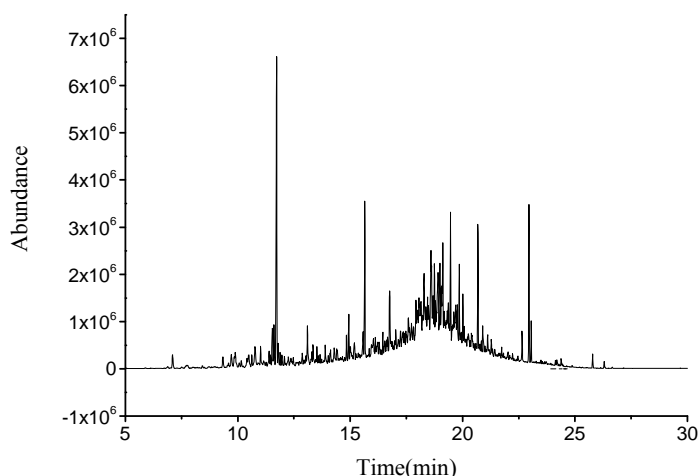


Figure 1. Total ion chromatogram of the complete combustion residue of rubber shoes

3.2. Analysis of Aromatic Hydrocarbon Components

As shown in figure 2 (a) and (b), the chromatograms of the gasoline standard sample and the rubber shoe complete combustion sample extracted from $M/Z=91, 105, 119$ are respectively. Analysis of toluene, xylene, trimethylbenzene and tetramethylbenzene in aromatic hydrocarbons. The results shows that aromatic hydrocarbons were detected in the complete combustion residue of the rubber shoes. There is one kind of C_1 benzene in the complete burning residue of rubber shoes, which is toluene, and the retention time is 4.523min, corresponding to peak 1, which is very similar to gasoline. There are three kinds of C_2 benzene which are ethylbenzene, p-xylene and m-xylene, the corresponding peaks are 2, 3, 4, and the retention time is 6.877~9.114min. The retention time of ethylbenzene and p-xylene is very similar to that of gasoline standard, which has great interference to gasoline detection. The retention time of m-xylene and gasoline standard is large, which can be used as a basis for differentiation. There are 3 kinds of C_3 benzene, which are 10~25 min respectively. Among them, the alkane peak detected after 15min is mainly C_{12} and above. However, the characteristic components of gasoline specified in GB/T18294.5, such as alkanes, olefin, polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, etc., can be detected, so there is some interference in the identification of gasoline. Peaks 6, 9, and 10 correspond to 3-ethyl-1-methylbenzene, 1, 2, 3-trimethylbenzene, and 4-ethyl-1-methylbenzene, respectively, and the retention time is 9.901-13.541min. There are two kinds of C_4 benzene, which are 1, 2, 4, 5-tetramethylbenzene and 1,2,3,4-tetramethylbenzene. The corresponding peaks are 12 and 13, and the retention time is 13.743min and 15.112min. In conclusion, the interference of C_3 and C_4 benzene in the samples of complete combustion of rubber shoes on the detection of gasoline is greater.

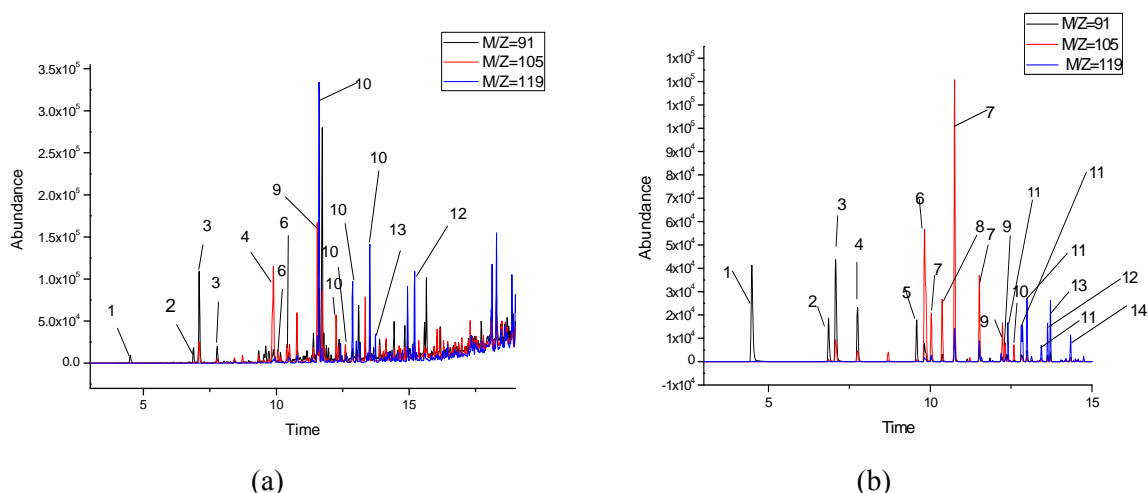


Figure 2. (a) (b) shows the extracted ion chromatogram of complete combustion of gasoline and rubber shoes

3.3 Analysis of Naphthalene and Methylnaphthalene in Fused Aromatic Hydrocarbons

Analysis of naphthalene and methylnaphthalene in polycyclic aromatic hydrocarbons. The results shows that naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and other polycyclic aromatic hydrocarbons are detected in the burning residues of rubber, corresponding peaks are 1, 2, 3. It coincides with the characteristic components of the condensed aromatic hydrocarbons identified by gasoline in the category, which has a great interference to the identification of gasoline.

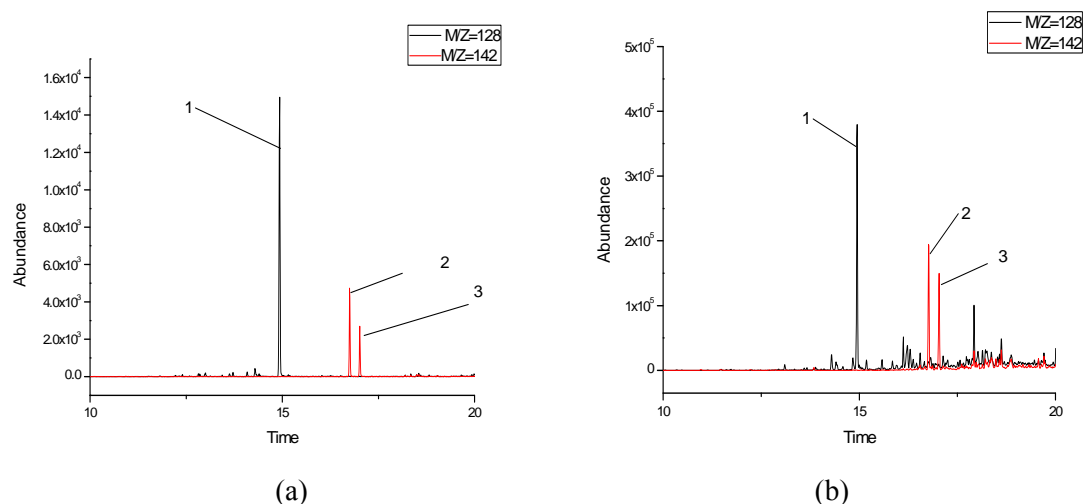


Figure 3. (a) (b) shows the extracted ion chromatogram of complete combustion of gasoline and rubber shoes

3.4 Indans Component Analysis

As shown in Figure 4 (a) and (b), the mass chromatograms of gasoline standard samples and complete combustion residues of rubber shoes with mass to charge ratio $M/Z=117$ are extracted respectively. The analysis of indans components in polycyclic aromatic hydrocarbons shows that the above characteristic components could be detected in both combustion residues, with retention time between 10~15min, and the peak height is higher, which have great interference to gasoline identification.

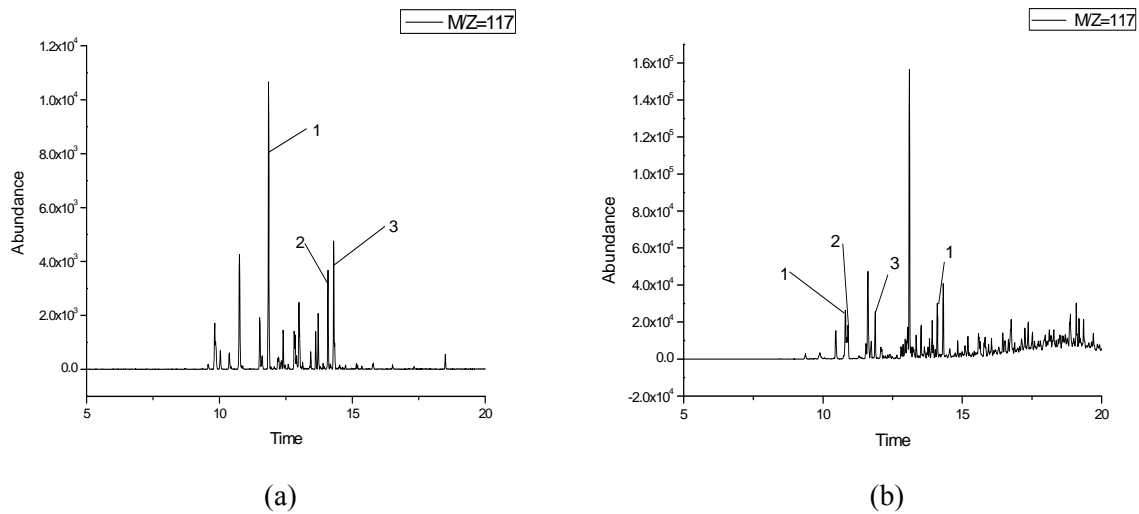


Figure 4. (a) (b) shows the extracted ion chromatogram of complete combustion of gasoline and rubber shoes

4. Conclusion

According to the experimental analysis in table 1, it can be concluded that :the detected substances of several rubber combustion residues are mainly concentrated at the peak at 5~25min, and alkanes, olefin, polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons can be detected, which are similar to the composition of gasoline combustion residues; From the characteristics of components, unlike gasoline combustion residue, rubber burning residue mainly concentrated in the more than C_{10} , alkane component in aromatic hydrocarbons matching degree is low, can distinguish in the identification, but rubber polycyclic aromatic hydrocarbons in the combustion residue composition and indan components is relatively stable, the bigger disturbance identification for gasoline; Benzothiazole and p-phthalate dimethyl ester could be detected in the burning residues of rubber, and the retention time is around 15.66min and 18.96min respectively. The substance is not detected in the gasoline combustion residues, and is the key component to distinguish rubber from gasoline.

Table 1. Analysis of the composition of some rubber products

Sample	Blue rubber gloves			High boots		
Compound	Ontology	Burning half	Complete combustion	Ontology	Burning half	Complete combustion
Toluene	+	+	+	+	+	+
Ethylbenzene	—	—	+	—	+	+
M-xylene	—	—	+	—	+	+
P-xylene	—	—	+	—	—	+
o-xylene	—	—	—	—	—	+
propyl benzene	—	—	—	—	—	+
3-ethyl-1-methylbenzene	+	+	—	+	—	+
4-ethyl-1-methylbenzene	+	+	—	+	—	+
1,3,5-trimethyl-benzene	+	—	—	+	—	+
2-ethyl-1-methylbenzene	+	—	—	+	—	+
1,2,4-trimethyl-benzene	+	—	—	+	—	+
1,2,3-trimethyl-benzene	+	+	—	+	+	+
C ₄ alkyl-benzene	+	+	+	+	+	+
1,2,4,5-tetramethyl-benzene	—	+	+	+	+	+
1,2,3,5-tetramethyl-benzene	—	+	+	+	+	+
indane	—	+	+	+	+	+
5-methyl indane	+	—	+	+	+	+
4-methyl indane	—	—	+	+	+	—
Naphthalene	+	+	+	+	+	—
2-methyl-naphthalene	+	+	+	+	+	—
1-methyl-naphthalene	+	+	+	+	+	—

5. Acknowledgments

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