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Gas chromatographic analysis and aerosol mass spectrometer measurement of diesel exhaust particles composition

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Abstract

Aerosol particles have important effects on human health, climate, regional visibility, and the deposition of acidic and toxic substances. The aerosols also have significant pharmaceutical and industrial applications. Trials of gas chromatographic analysis of extracts composition of diesel exhaust particles and aerosol mass spectrometer measurement of diesel exhaust particles composition are introduced in this paper. Usually, organic fraction of automotive exhaust particles are concentrated to 1 mL by Kuderna-Danish concentrator after extracted into dichloromethane by soxhlet extraction. Then, these extracts are analyzed by GC/MS. In the extracts from the diesel exhaust particles, there are over several thousands of components, for example paraffinic hydrocarbons, aromatics, oxygenates and other hydrocarbons.

Keywords: Gas chromatography; Diesel exhaust; Aerosol; Ultra fine particles; Fuel; Lubricant oil; Speciation; Aerosol mass spectrometer; Semi-volatile

1. Introduction

Atmospheric aerosols and particulate matter (PM) from a wide variety of emission sources are receiving increasing attention because of their influence on human health [1], visibility, acid deposition, and global climate [2]. These measurements are conventionally performed by recording PM mass. The ambient standards are written in terms of mass concentrations, and emission regulations are based on mass. However, in order to understand better the nature of the mobile source contribution to ambient PM, many research groups are currently extending their investigations to include speciation of particles in automotive exhaust.

Progress in understanding and mitigating these problems is limited by the ability of existing instruments to provide real-time, size-resolved, quantitative measurements of aerosol mass and chemical composition [3]. A number of measurement techniques possessing some of the required aerosol analysis capabilities have emerged recently. Real-time aerosol mass spectrometers aiming to provide information on chemical composition of particle ensembles or individual particles. Most of these instruments also provide information on particle size. A recent review of aerosol measurements by McMurry [3] states that "these mass spectrometers are, arguably, the most significant development in aerosol measurement in the past 20 years.

Trials of gas chromatographic analysis of extracts composition of diesel exhaust particles and aerosol mass spectrometer measurement of diesel exhaust particles composition are introduced in this paper.

2. Materials and methods

2.1. Gas chromatographic analysis

Organic fraction of automotive exhaust particles are concentrated to 1 mL by Kuderna-Danish concentrator after extracted into dichloromethane (special grade) by 24 h soxhlet extraction [4]. These extracts are analyzed by GC/MS.

GC separation was carried out using a Hewlett Packard 6890 GC System and mass detection was carried out using a Hewlett Packard 5973 MS System. Data were acquired and processed on a Hewlett Packard kayak computer using the ChemStation soft ware. DB-5MS (30 m × 0.25 mmI.D. × 0.5 μm film thickness) was used for separation column. The oven temperature was held at 40 °C for 3 min and then programmed at 20 °C min^{-1} to 100 °C, and at 8 °C min^{-1} to 300 °C, and at 2 °C min^{-1} to 320 °C

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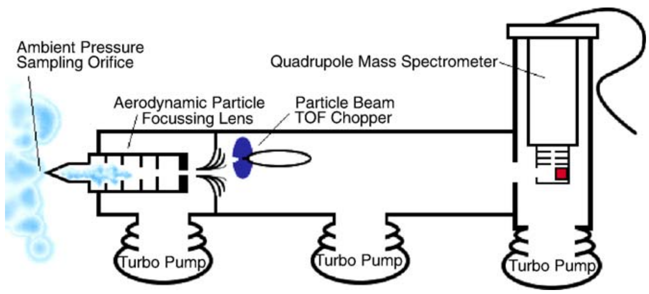

Fig. 1. Schematic of the aerodyne aerosol mass spectrometer (AMS).

and hold. Flow rate of helium was 1 mL min^{-1}, splitless injector was 320 °C and interface of MS was 280 °C.

2.2. Aerosol mass spectrometer

An aerosol mass spectrometer (AMS) developed at Aerodyne Research, which has been designed to provide real-time quantitative information on particle size-resolved mass loadings for volatile and semi-volatile chemical components present in/on ambient aerosol particles [5]. In its present configuration, the AMS cannot detect refractory aerosol components such as sea salt, soil dust, and elemental carbon. A schematic of the AMS is presented in Fig. 1.

The AMS consists of three main parts: an aerosol inlet [6,7], a particle sizing chamber, and a particle composition detection section. The different sections are separated by small apertures and differentially pumped. A computational fluid dynamics simulation of the AMS inlet system shows nearly 100% transmission efficiency to the detector for particles in the aerodynamic diameter range 70–500 nm, and shows substantial transmission for particles in the 20–70 and 500–2.5 mm ranges for spherical particles. Irregularly shaped particles may have lower transmission efficiencies [5]. Size-dependent particle velocities created by expansion into vacuum are used to determine particle size through a particle time-of-flight measurement. The focused particle beam is modulated by a rotating wheel chopper operating at about 100 Hz. Time-resolved particle detection after a known flight distance gives the particle velocity from which the particle aerodynamic diameter is obtained. Detection is performed by directing the particle beam onto a resistively heated, roughened surface under high vacuum. On this surface, the volatile and semi-volatile components in/on the particles flash vaporize. The vaporization source is integrally coupled to an electron impact ionizer at the entrance of a quadrupole mass spectrometer. When the quadrupole is tuned to a representative *m*/*z*, bursts of ions are produced that are averaged to produce a size-resolved mass distribution.

3. Result and discussion

3.1. Gas chromatographic analysis

Fig. 2 shows typical two types of total ion chromatogram (TIC)s of the extracts from diesel exhaust particulate matter. Fig. 3 shows typical TIC of boiled diesel fuel (diesel fuel

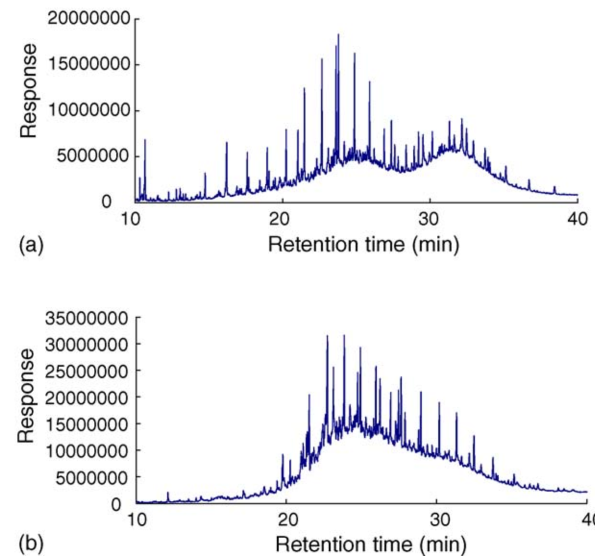

Fig. 2. Typical TIC examples of diesel exhaust particle extract: (a) one of the typical TIC of diesel exhaust particle extract (type 1); (b) one of the typical TIC of diesel exhaust particle extract (type 2).

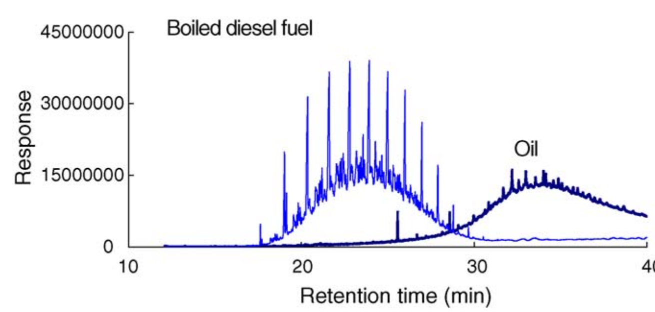

Fig. 3. Typical TIC of boiled diesel fuel and lubricant oil.

removed of low boiling point hydrocarbons) and lubricant oil. Composition of the extract shown in Fig. 2(a) is mixture of boiled fuel and lubricant oil, and composition resulted in Fig. 2(b) seems to mainly composed of boiled fuel and small amount of lubricant oil is exist in this extract. It is thought that this difference depends on type of engine and driving cycle. Extract resulted in Fig. 2(a) and (b) are named type 1 and type 2. There are many peaks on these chromatograms. Fig. 4 shows mass chromatogram of $m/z = 99$ in the type 1 extracts that shows the presence of compounds including $C_7H_{15}^+$ hydrocarbons. This mass chromatogram of $m/z = 99$ shows almost paraffin

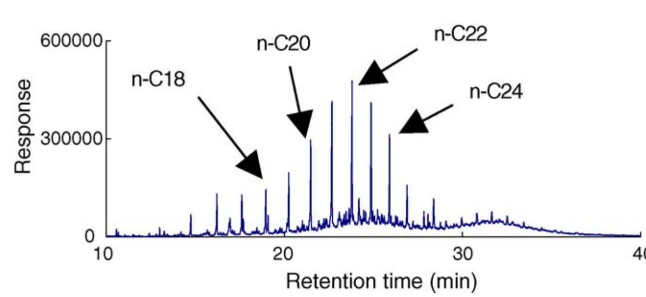

Fig. 4. Typical mass chromatogram ($m/z = 99$:$C_7H_{15}^+$) of diesel exhaust particle extract.