

# Identification of Organic Compounds Released from Low-Metallic Automotive Model Brake Pad and its Non-Airborne Wear Particles

Daniela Plachá, Pavlina Peikertova, and Jana Kukutschova  
Nanotechnology Centre, VSB-TU

Poh Wah Lee  
Southern Illinois University

Kristina Čabanová and Jiří Karas  
Nanotechnology Centre, VSB-TU

Jana Kuchařová  
ENET Centre, VSB-TU

Peter Filip  
Southern Illinois University

## ABSTRACT

The brake wear contribution to the environmental pollution has been extensively discussed, with major focus on asbestos and heavy metals released to the environment. Only limited attention was paid to released organic compounds generated during friction processes, although the organic and carbonaceous components are not the minor part in brake lining formulations.

Friction processes in brakes are associated with relatively high temperatures and high pressures on the friction surfaces which relates to the thermal decomposition of the organic components in friction materials and to brake lining thermal fade. Thus, this study focuses on the identification of organic compounds released from a model low metallic brake material. Several methods were used for the analysis: GC/MS screening of brake pad samples, brake wear debris and carbonaceous raw materials used in formulations of model pads; GC/MS screening of brake pad samples pyrolyzed at 300, 750, and 1000°C, respectively, and FTIR analysis of brake pads and their wear debris.

Higher quantity of organic compounds was identified in extract of the milled brake pad composite compared to the wear debris. More than 80 organic compounds were identified to be potentially released during braking. The major constituents were phenols, aliphatic and aromatic hydrocarbons, and their derivatives. Some of the identified compounds are known to have adverse effects even with mutagenic and carcinogenic potency to humans.

**CITATION:** Plachá, D., Peikertova, P., Kukutschova, J., Lee, P. et al., "Identification of Organic Compounds Released from Low-Metallic Automotive Model Brake Pad and its Non-Airborne Wear Particles," *SAE Int. J. Mater. Manf.* 9(1):2016, doi:10.4271/2015-01-2662.

## INTRODUCTION

Road transport is one of the main anthropogenic activities which has a considerable impact on the modern society with a significant contribution to urban air and soil pollution [1,2]. Gaseous and particulate emissions from automobile exhausts have been widely discussed in many research works for several decades. Simultaneously, numerous studies have reported pollutant emissions from non-combustion automotive processes including wear of tire and brakes, lubricant oil leakages, and corrosion products released

from vehicle components [2, 3, 4, 5, 6]. Important part of the environmental pollution is also ascribed to road pavement material release, particularly resuspension of wearing asphalt to soil [7,8].

It is well known that heavy metals and polycyclic aromatic hydrocarbons (PAHs) represent the main hazardous substances released to the environment from combustion processes in automobiles. Their compounds are mainly associated with the airborne particulate matter (PM) that was identified to have different

shapes, sizes, and complex chemical composition. Different research groups addressed road dust samples, atmospheric samples of settled dust, particles, gaseous phases, and runoff water from roads and highway surfaces collected in retention ponds [9, 10, 11].

The metal emissions found within the fine PM fraction are typically correlated with a high volume of metallic components applied in the automotive industry. Metals such as Fe, V, Cr, Ni, Zn, and Cu are the most frequently used and detected. However, they are also released due to impurities present in fuel additives, and are present in tire and brake wear. The coarse fractions of ambient PM typically contain significant amount of elemental carbon (EC) sometimes referred to as black carbon (BC), and organic carbon (OC) [9]. Both these carbon types originate predominantly from combustion processes, but they were also discussed in conjunction with the carbonaceous aerosols from biological sources like pollens, viruses, and plant debris [9]. The organic carbon fraction adsorbs the volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and non-volatile organic compounds (NVOCs). It also interacts with the secondary organic aerosol formed from natural and anthropogenic hydrocarbon emissions. More than 200 organic species such as alkanes, alkenes, aromatics, aldehydes, ketones, carboxylic acids, amino- and nitro-compounds, PAHs, and their derivatives were identified in PM particles. The main attention was paid to PAHs which originate mostly from the exhaust gases, and wear of road pavement materials, including asphalt, tires and oil lubricants [1,7,9,10,12].

Contribution of friction processes to the environmental pollution was discussed in numerous research works [5,6,13]. However, these studies were aimed especially on release of inorganic materials during braking. A characteristic brake lining pad is a multicomponent composite formed of more than 10 constituents and polymer matrix which acts as binder [13]. Several of the afore mentioned materials such as antimony trisulphide, copper, lead, iron, tin, hexavalent chromium, cadmium, potassium titanate, and barite could have potentially negative environmental impact and are often discussed in several research works [14].

The available data addressing organic compounds being released from brake lining materials are still limited, although the carbonaceous components are not the minor part in their formulations [10,11]. Friction processes in brakes are associated with relatively high temperatures and high pressure conditions on the friction surfaces. It is well known that thermal decomposition of the organic components in friction materials is often related to thermal fade [14, 15, 16]. Thermal gravimetry (TG) and differential scanning calorimetry (DSC) studies of brake materials demonstrated that loss of organic matter is related to formation of the VOCs [5,17,18]. Thus the studies addressing the formation of various organic compounds released from brakes with potentially negative environmental impact seem to be a relevant topic.

The aim of this study was to qualitatively determine the organic compounds which are present in the non-airborne wear debris of a model low-metallic friction composite and can represent potential hazard to the environment. The received brake pad sample and selected carbonaceous constituents used as raw materials in this brake

pad composite were also analyzed. When analyzing the capacity to release organic compounds from these three different sample types i) the milled pad, ii) its wear debris and iii) carbonaceous raw materials, several analyses were performed: screening GC/MS analysis of dichloromethane extracts of all three sample types, screening GC/MS of pyrolyzed milled pad, heated to 300°, 750°, and 1000 °C, respectively, and FTIR analysis of the milled pad and wear debris. Total carbon content was determined to estimate quantities of carbonaceous compounds in the milled pad and its wear debris.

The milled brake pad samples were used for pyrolysis chromatography in order to predict the release of organic compounds which can be potentially generated during braking. The pyrolysis temperature programs were chosen on the basis of previous studies, which indicated temperatures occurring during friction process tests. It was found that the mass losses determined by TG and DSC start above 300 °C; graphite and coke oxidation occurs in 500-800 °C and localized temperatures of the friction surface can easily reach up to 1000 °C [6,14,18].

## EXPERIMENTAL

### Material

Three types of samples were analyzed to identify organic compounds which can be released from a model low metallic brake friction composite to the environment: i) ball milled brake material, ii) non-airborne wear debris generated during a full-scale brake dynamometer AO4D test, and iii) selected individual components used for brake formulation: coke, synthetic graphite, and resilient graphitic carbon [5,19].

### Friction Composite Preparation

The formulation of the model brake material is presented in Table 1. Total mass of one brake lining pad is 113g and two pads are used in one dynamometer test. The brake linings were manufactured in the Center for Advanced Friction Studies (CAFS) at Southern Illinois University Carbondale, IL USA laboratories by mixing ingredients in a Littleford W-10 vertical batch mixer (30 minutes), molding, and hot pressing (180°C/45,000 N/15 minutes) followed by post curing in air at 180°C for 4 hours. Ford Crown Victoria 1999 set-up with corresponding original equipment cast iron disc and caliper were used in this experiment (note that the brake pad is not the OEM Ford formulation and the mold type was used for convenience only).

### Methods of Characterization

Total carbon content (TC) was determined in the milled pad sample and the non-airborne wear debris utilizing the Multi N/C 3100 analyzer with HT 1300 Solids module (Analytik Jena, Germany). The screening analyses of dichloromethane extracts of the ball milled brake pad, its wear debris, and three carbonaceous raw materials were performed by using gas chromatography method in connection with mass spectrometry detector (GC/MS, 7890N/5975C, Agilent Technologies USA). The solid samples of ball milled brake pad and its wear debris were also analyzed by infrared spectrometry (FTIR, Nicolet 6700, Thermo USA). In addition, the milled brake pad

sample was subjected to pyrolysis gas chromatography in connection with mass spectrometry (Py/GC/MS, Analytical Inc. Pyroprobe 5200 in connection with 7890N/5975C, Agilent Technologies USA).

Table 1. Formulation of the studied model brake pad composite

| Inorganic constituent          | Weight % | Carbon containing constituent  | Weight % |
|--------------------------------|----------|--------------------------------|----------|
| Steel Fiber                    | 10       | Phenolic Resin                 | 24       |
| Iron Powder                    | 3        | Coke                           | 15       |
| Vermiculite                    | 5        | Synthetic Graphite             | 5        |
| ZrSiO <sub>4</sub>             | 2        | Resilient Graphitic Carbon-RGC | 5        |
| BaSO <sub>4</sub>              | 9        | Nitrile Rubber                 | 5        |
| Copper                         | 4        | Twaron                         | 2        |
| MgO                            | 3        |                                |          |
| Sb <sub>2</sub> S <sub>3</sub> | 3        |                                |          |
| Tin                            | 3        |                                |          |
| MoS <sub>2</sub>               | 1        |                                |          |
| Al <sub>2</sub> O <sub>3</sub> | 1        |                                |          |

### Sample Preparation for Chemical Analysis

The “milled brake pad samples” were ball milled for 10 min using a laboratory vibrating mill VM4 (MOBIKO, Czech Republic) with stainless steel beads and subsequently sieved through a 200 µm sieve. The analyzed sieved fraction contained the majority of particles with size varying between 5 and 200 µm as determined by the particle size distribution measurement (Mastersizer 2000, Malvern Instruments UK). The nonairborne wear debris sample was used in as-produced conditions: collected as the settled fraction from the bottom of the dynamometer chamber by sweeping a surface during A04D test. Thus a representative sample of settled fraction was obtained. The individual carbonaceous raw materials (coke, graphite, RGC - see Table 1) were analyzed in as received state.

### Extraction of Organics

Dichloromethane extractions of investigated organic components were performed by pressurized solvent extraction using Speed Extractor E-916 (Büchi Labortechnik AG, Switzerland). Five 3.00 ± 0.01 g samples were extracted in dichloromethane of HPLC grade (Sigma Aldrich) in 3 cycles at 110°C and 100 bar. The crude extracts were placed into a vacuum evaporator and concentrated to a volume of approximately 5 ml under nitrogen flow at 40°C. The resulted extracts were cleaned through a silica gel column chromatography, evaporated to the final volume of 1 ml under nitrogen atmosphere, and immediately analyzed by GC/MS.

### GC/MS Screening

A quadrupole mass spectrometer (Agilent Technologies MSD5975C) in connection with a gas chromatograph (Agilent Technologies 7890N) equipped with capillary column DB-XLB (30 m × 0.25 mm × 0.25 µm) were used for screening analysis. The GC/MS operating

conditions were: the ion source operated in 230°C, the injection port maintained at 290°C, and the samples injected in splitless mode followed by 1.5 min purge after the injection. The program column temperature started at 40° C for 2 min, then increased by 5°C/min to 300°C, and was held for 10 min at 300°C. The scan mode was employed after additional 6 minutes of delay time. The experimental data were measured in the range of 50-550 amu.

Obtained data were subsequently evaluated by using mass spectra library NIST011, and confirmed by Willey Registry of Mass Spectral Data, 9<sup>th</sup> Edition. Tentative identifications reflect the most reasonable match in named mass spectral libraries. Only compounds with high or moderately high confidence in structure were identified. This means an excellent (RSI > 900) or good (RSI = 800-900) match between mass spectrum and that of electron ionization mass spectra library, where RSI is one of the factors describing the accuracy of that match to the identified spectrum [20].

### FTIR

Mid-IR spectra were obtained for samples in solid original state by a Fourier transform infrared spectrometer Nicolet 6700, using the single reflection ATR technique on a diamond crystal. Measurements were performed with a resolution of 4 cm<sup>-1</sup> and 32 scans. Achieved data were interpreted using the OMNIC software.

### Py/GC/MS

Milled brake composite (0.0500 ± 0.0010 g) was analyzed by GC/MS (Agilent Technologies, 7890N/MSD 5975C) in connection with the CDS (Analytical Inc. Pyroprobe 5200) pyrolysis unit. The material was inserted into the quartz chamber of the pyrolysis unit and then heated resistively in a nitrogen environment under the following program: the initial temperature of pyrolysis was set at 250°C for 30s, after that, temperature ramp of 5°C/min up to one of the final temperature of 300°C, 750°C or 1000°C was programmed. The interface temperature between pyrolysis unit and GC/MS was set to be 285 °C.

Gaseous products of pyrolysis were swept directly into the GC/MS equipped with capillary column HP-5ms (60m × 0.25 mm × 0.25 µm). The GC/MS operating conditions were: the ion source operated at 280°C; the injection port maintained at 290°C and the samples were injected in split mode (1:50). The column temperature program started at 40° C for 4 min, then temperature increased by 20°C/min to 220°C (held for 10 min), and consequently by 33°C/min to 320°C with a hold for 10 min. The scan mode was employed after 6 min of delay time holding. The experimental data were measured by scan mode in the range of 50-550 amu. The mass spectra evaluations were performed in the identical way as described in part “GC/MS screening”.

## RESULTS AND DISCUSSION

### TC Analyses

The total carbon (TC) analyses of the brake pad sample and wear debris revealed a significant difference in carbon content. The milled brake pad sample contains 494 g kg<sup>-1</sup> of carbon, which is in good accord with brake composition, listed in Table 1, where carbonaceous constituents