CHEMICAL AND PHASE ANALYSIS OF ROAD DUST

Kristina ČABANOVÁ, Daniela PLACHÁ, Jana KUKUTSCHOVÁ, Radmila KUČEROVÁ

VSB – Technical University of Ostrava, Ostrava, Czech Republic, EU, kristina.cabanova@vsb.cz

Abstract:
Increasing number of automobiles on roads is related to growing emissions from road traffic. Every use of brake is connected to release of wear particles into the environment, which may contribute to air, soil, and water pollution. Settled micro- and nano-sized particles derived from both, combustion and non-combustion processes, therefore settled fraction of dust near a busy road was analyzed. Samples for the study were obtained from real conditions: 1) dust sample near a crosswalk of a busy road, and 2) dust sample from a road near a parking place. These samples were characterized by a combination of analytical and microscopic techniques. Elemental composition was analyzed by scanning electron microscopy with energy dispersive spectroscopy. Amount of total organic carbon was analyzed using total carbon analyzer. Phase composition of the dust samples was determined by using Raman microspectroscopy and Fourier transform infrared spectroscopy (FTIR). Organic compounds detected by FTIR were compared with experimental data of organic compounds analysis in organic extract performed by gas chromatography with mass spectrometry results. Raman microspectroscopy detected various metallic compounds and also elemental carbon. Organic and inorganic compounds from road dust were detected by these methods; some of them may be assigned to traffic pollution.

Keywords:
chemical and phase composition, Raman microspectroscopy, infrared spectroscopy, gas chromatography with mass spectrometry

1. INTRODUCTION
Road dust consists of soil minerals, organic matter (derivable from plant matter) and potentially toxic pollutants [1]. These pollutants come from anthropogenic sources such as petrol and oil products, brake wear debris, tire debris and metals from exhaust [2]. The automotive brake wear debris contains particles with sizes between 10 nm and 20 µm [3]. Emissions from combustion processes, especially from diesel engines, contain high number concentration of nano-sized particles based mainly on elemental amorphous carbon [4]. These particles may settle on road surface and become a part of the road dust where they are mixed together from particles released from all the sources and thus a multicomponent mixture originates [1,2]. There is an increasing concern about these nano- and micro-sized particles because of their possible adverse effects on the environment and human health [4]. The aim of the study was to evaluate differences in chemical and phase composition between two samples collected from a busy road and a parking place using a combination of several analytical and microscopic techniques.

2. EXPERIMENTAL

2.1. Road dust samples
Samples of the settled particle fraction of road dust were collected in Ostrava City which represents an industrial area of the Czech Republic. Samples A was obtained from a border of a busy road near a crosswalk. The second sample B was collected from a parking place. Both samples were obtained by
sweeping the surface of the selected area. The samples were milled using a ball-mill to achieve size fraction below 60 µm. These samples were used for further evaluation using a combination of selected techniques.

2.2 Characterization of road dust samples

The X-ray diffraction (XRD) data of the road dust particles samples were recorded under CoKα irradiation (\(\lambda = 1.789\) nm) using the Bruker D8 Advance diffractometer equipped with the fast position sensitive detector VANTEC 1. The measurements were carried out in the reflection mode. Phase composition was evaluated using the PDF-2 Release of the 2004 database (International Centre for Diffraction Data).

Raman spectra of the road dust samples were measured using a Smart Raman Microscopy System XploRA TM (HORIBA Jobin Yvon, France). Raman spectra were acquired with 532 nm excitation laser source, 100x objective and using 1200 gr./mm grating in the range from 80 to 2000 cm\(^{-1}\). Experimental data were processed with LabSpec software. Mid-infrared spectra were obtained using an ATR technique with diamond crystal on Fourier transform infrared spectrometer (FTIR) Nicolet 6700 FT-IR (Thermo Nicolet, USA) in spectral range between 400-4000 cm\(^{-1}\) with resolution of 4 cm\(^{-1}\) and 32 scans. The experimental data were processed by using Omnic software.

Scanning electron microscopy (SEM) was used for characterization of morphology and size of the road dust particles. Quanta FEG 450 (FEI) with EDS analysis APOLO X (EDX) was utilized to obtain images of the sample structure and information on elemental composition achieved by point analysis.

Phase composition of road dust particles was determined using X-ray fluorescence spectroscopy SPECTRO XEPOS (SPECTRO Analytical Instruments, Germany) equipped with 50 W Pd X-ray tube. Total organic carbon analysis was carried out using Multi N/C 3100 TOC analyzer with HT 1300 Solids module (Analytik Jena).

Screening and identification of organic compounds was performed by gas chromatography with mass spectrometry detection (GC/MS) Agilent Technologies 7890/5975C. Before GC/MS analysis, both samples were extracted with acetone: hexane (1:1) in Speed Extractor Büchi E-916.

3. RESULTS AND DISCUSSION

The experimental techniques utilized for the characterization of the studied samples revealed the following differences. Phase composition of crystalline compounds is according to the XRD patterns of both samples. Fig. 1 shows an example of the XRD pattern achieved. Major compounds in both samples were quartz (SiO\(_2\) - Q) and calcium (sodium) aluminium silicate (AlSi), titanium dioxide (rutile - R) and crystalline carbon. The only difference was in the presence of corundum (Al\(_2\)O\(_3\) - Cor) in the sample A (see the Fig.1). This finding was confirmed by XRFS which detected the following components: quartz, calcium aluminium silicate and titanium dioxide (Tab.1). Furthermore, it showed presence of the following elements: Fe, Mg, S, and Ca (Tab.1). The difference in elemental composition of the samples A and B was not significant. Presence of silicates and quartz in both samples was confirmed also by FTIR (Fig. 2) according to the presence of the bands about 1000 cm\(^{-1}\) and doublet below 800 cm\(^{-1}\), respectively. The bands about 3400 cm\(^{-1}\) characteristic for O-H bonds, the bands between 2900 -2800 cm\(^{-1}\) and 1450-1475 cm\(^{-1}\) proved the presence of CH\(_2\) and CH\(_3\) groups in the sample A (busy road) [5] (Fig.2).
Fig. 1: Example of the XRD pattern of the sample A

Fig. 2: Mid-FTIR spectra of both samples

SEM-EDX revealed particles of various morphology, size and elemental composition in both samples. Particles with sharp edges as well as round particles were found. Examples of elemental composition of elements detected see in Figures 3b and 4b. These results are in accordance with XRD and XRFS results.

Fig. 3: Example of SEM image (a) of the sample A with corresponding EDX pattern (b) of the point marked with arrow

Fig. 4: Example of SEM image (a) of the sample B with corresponding EDX pattern (b) of the point marked with arrow
\textbf{Tab. 1:} XRFS experimental results

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Content in solid sample (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>Sample A</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.180</td>
</tr>
<tr>
<td>CaO</td>
<td>6.053</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.589</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>68.240</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.514</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.751</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.442</td>
</tr>
<tr>
<td>MgO</td>
<td>1.977</td>
</tr>
</tbody>
</table>

\textbf{Tab. 2:} Total carbon content (TOC)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample A (parking place)</th>
<th>Sample B (road dust)</th>
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<tbody>
<tr>
<td>TOC (g/kg)</td>
<td>38.24</td>
<td>9.40</td>
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Raman spectra in the figure 5a display characteristic bands of quartz [6], on the figure 5b shows band of calcium carbonate [7], on the figure 5c representative band of titanium dioxide (anatas) [8] and spectra of the figure 5d are typical for graphite [9]. These figures (5a – 5d) were identified in sample A. Only representative spectrum for amorphous carbon [10], was in sample B see in figure 5e.

\textbf{Fig. 5:} Raman microspectroscopy of the sample A and B

In sample A (busy road) was found quartz, these finding was confirms the XRD data (Fig.1), FTIR data (Fig.2) and also Raman spectra (Fig.5a). Present calcium carbonate in the sample A (busy road) was documentary into the SEM (Fig.3) and in Raman spectra (Fig.5b). Iron was detected in both samples (Tab.1), but particles having high content of Fe were found much more often in the sample A, i.e. from area near the busy road (Fig.3). The difference between iron content may be given be wear of brakes and cast.

In sample A (busy road) was found quartz, these finding was confirms the XRD data (Fig.1), FTIR data (Fig.2) and also Raman spectra (Fig.5a). Present calcium carbonate in the sample A (busy road) was documentary into the SEM (Fig.3) and in Raman spectra (Fig.5b). Iron was detected in both samples (Tab.1), but particles having high content of Fe were found much more often in the sample A, i.e. from area near the busy road (Fig.3). The difference between iron content may be given be wear of brakes and cast.
iron discs due to braking of automobiles near a crosswalk [3]. Quartz and calcium aluminium silicates come from soils around the road [11]. Titanium dioxide and calcium carbonate detected can be released from road surface marking [12]. Amorphous carbon may arise from degradation of resin as a major component of brake lining and from particulate emissions from diesel engines. Further synthetic graphite is component which also added to friction composites [13] together with calcium carbonate, which is added to friction composites as a filler [14].

Analysis of organic carbon (TOC) confirmed higher content of organic and elemental carbon in the sample A. Screening analysis of both extracts by GC/MS confirmed presence of benzene, toluene, ethylbenzene, xylene, alkylated benzenes, polycyclic aromatic hydrocarbons and their methylated derivatives, benzo thiophenes and their derivatives. Aliphatic hydrocarbons including those with branched chains were also identified. Occurrence of those compounds in road dust samples is connected especially with traffic. Hydrocarbons from natural sources such as squalene, Z-14-Nonacosane and triterpenes were also detected. There were some differences between both samples, sample A was characterized with higher presence of aliphatic hydrocarbons, while aromatic and polyaromatic compounds together with hydrocarbons from plant material were prevailing in the sample B. These compounds in the sample B may be connected with presence of shrubs and trees around the parking place.

4. CONCLUSION

Differences in chemical and phase composition between studied samples from various sites were not considerable. The experimental techniques utilized revealed the following differences. Major compounds in both samples were quartz and calcium (sodium) aluminium silicate, titanium dioxide (rutile) and crystalline carbon. The only difference was in the presence of corundum in the sample A. Furthermore, it showed presence of the following elements: Fe, Mg, S, and Ca. The difference in elemental composition of the samples A and B was not significant. Presence of silicates, quartz and organic compounds in both samples were confirmed by FTIR. Screening analysis of both organic extracts by GC/MS confirmed presence of benzene, toluene, ethylbenzene, xylene, alkylated benzenes, polycyclic aromatic hydrocarbons and their methylated derivatives, benzo thiophenes and their derivatives. Aliphatic hydrocarbons including those with branched chains were also identified.

This study represents a pilot study of chemical and phase composition of road dust and further evaluation is needed for more comprehensive characterization of this material.

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LITERATURE


