Characterization of functional groups of airborne particulate matter

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Abstract. Particulate matter of organic combustibles burning consists of various hydrocarbons and radicals, which may cause harmful impact to human health. In this study solid particulate matter were collected on the filters from burning of various combustibles in a burning chamber and from atmosphere of city of Riga by dichotomous impactor. FTIR spectra were obtained before and after samples’ treatment. Absorptions associated with aliphatic and aromatic hydrocarbons and alcohol functional groups were observed in the FTIR spectra. Free radicals of particulate matter were detected by electron paramagnetic resonance (EPR).

1. Introduction

When organic combustibles such as candle, kerosene, gasoline or diesel are burning, combustible breaks up and forms other substances by thermal decomposition process. The precursor of formation of black carbon is the formation of first aromatic ring, which molecular weight growth with the formation of polycyclic aromatic hydrocarbons. When the fine particles are formed, they grow up by surface reactions and by agglomeration [1]. Particles of black carbon are not solid and compact, but look like a spongy, which is formed from very fine particles. Airborne particulate matter from atmosphere of city and particles from candles burning are agglomerates of Aitken (1nm - 0.1 μm) and accumulation (0.1 - 2 μm) mode particles [2]. Particulate matter of candles burning consists of about 27% weight carbon and 73% weight of oxygen [3]. Ambient particulate matter may contain sulfate, ammonium, silicate, inorganic nitrate and organic compounds, which functional groups are hydroxyl, aliphatic carbon and carbonyl [4; 5]. It has been suggested that the nervous system may be more susceptible to attack by organic particles, which appear to have a greater tendency to cross into the olfactory nerve and may pass into the olfactory bulb than inorganic species [6]. Burning of organic combustibles also produces active products of thermo destruction – radicals (CH; CH₂; CH₃; CHO; Č₂; CHCH and other) [7], which increase harmful impact to the human health. The chemical characterization of particulate matter to which humans are exposed to provides information important to the understanding of our chemical environment and associated health risks. The aim of current studies is to characterize functional groups of airborne particulate matter by Fourier-transform infrared (FTIR) spectroscopy and electron paramagnetic resonance (EPR).

2. Experimental

Airborne particulate matter was collected on the glass fiber filters from burning of various combustibles in a burning chamber and from atmosphere of city of Riga by dichotomous impactor. The dichotomous impactor was placed in Riga, on Kr. Valdemara 48 (~8 m above ground level and ~1 m from building wall). Dichotomous impactor fractionated aerosol particles by size: coarse (2.5-10 μm, which designate
PM\textsubscript{10} and fine (≤2.5 μm, which designate PM\textsubscript{2.5}). Particulate matter from atmosphere of city was sampled in February and March, 2013. Candles were used for the burning to obtain fine particulate matter. Kerosene was used in the burning experiment for the larger particles formation. The closed system for different candles and kerosene combustion was laboratory built (Figure 1). Candle or kerosene (1) was burning in the closed burning chamber (2). A flow of purified air (3) was controlled by reductor and rotameter (4). The pressure in the chamber was controlled by manometer (5). Particulate matter from candles and kerosene combustion was collected on filters, using the particle sampler which consists of filter holder (6), pump (7), rotameter (8) and flowmeter (9).

![Figure 1. The burning system for the obtaining particulate matter from combustion process (1 – candle, 2 – burning chamber, 3 - bottled air, 4 and 8 – rotameter, 5 – manometer, 6 – filter holder, 7 – pump, 9 – flowmeter)](image)

The functional groups of particulate matter were determined by Fourier-transform infrared spectroscopy (FTIR). The top layer of collected particulate matter was scraped from glass fiber filters. A thin tablet was formed from particulate matter and KBr powder. FTIR spectra were measured using Spectrum Two IR spectrometer (PerkinElmer, USA) with computer program PerkinElmer Spectrum v.10.03.07. The spectral signal was measured from 4000 to 400 cm\(^{-1}\) wave lengths. Each spectrum was taken by averaging 6 scans at a resolution of 4 cm\(^{-1}\).

All samples for electron paramagnetic resonance (EPR) analysis were placed in flat dismountable cell WG 806-B-Q. EPR spectra were recorded using an EMX-plus EPR spectrometer (Bruker, Germany). Reference marker ER 4119HS-2100 (g-factor 1.9800, radical concentration 1.15·10\(^{-3}\) %) was used for quantitative EPR. The EPR instrumental settings for field scan were as follows: field sweep, 200G; microwave frequency, 9.78 GHz; microwave power, 0.2 mW; modulation amplitude, 5 G; conversation time 163 ms; time constant, 327 ms; sweep time 167 s; receiver gain, 1·10\(^3\); resolution, 1024 points, 5 scan. The concentration of free radicals in the samples was calculated using the double integration method of the first derivative signal and comparison with the marker (using Bruker’s WINEPR program). All treatments of blank filter (without particulate matter) were done parallel with treatments of samples of particulate matter. The spectrum of blank filter was subtracted from obtained EPR spectrum of sample. So, in this paper showed EPR spectra pertain only to particulate matter.

The FTIR spectra of airborne particulate matter were obtained before and after treatment. Samples were dried over phosphorus pentoxide 2 weeks. Tar products were removed by acetone and benzene extraction. Samples of particulate matter were carbonized in nitrogen (N\textsubscript{2}) flow at 450° C to remove volatile compounds and compounds, which evaporate at this temperature. Presence of carbonyl group was checked by reduction by sodium borohydride.

3. Results and discussion

Figure 2 show FTIR spectra of airborne particulate matter, collected from burning of various combustibles. Functional groups associated with infrared absorption were identified by previously published FTIR analyses of ambient particulate matter [4; 5; 8] and by guidelines of functional groups identification [9]. Absorptions associated with hydroxyl (3430 cm\(^{-1}\)), aromatic C-H (3055 cm\(^{-1}\)), ammonium ion (3242 cm\(^{-1}\)), aliphatic C-H (2925 and 2857 cm\(^{-1}\)), C=C (1631 cm\(^{-1}\)), C-H (1435 cm\(^{-1}\)) and
C-O (1055 cm\(^{-1}\)) functional groups are indicated in figure 2. The sharp peak of aliphatic carbon C-H group at 2925 cm\(^{-1}\) was chosen as internal standard, because it has presence in all obtained spectra and it has the same intensity of absorption in all spectra. A baseline was drawn from 4000 cm\(^{-1}\) to 500 cm\(^{-1}\). The intensity of peaks was measured from baseline. Ratio of peak intensity to intensity of internal standard was calculated.

**Figure 2.** FTIR spectra of particulate matter from burning of various combustibles (1 - kerosene, 2 – from atmosphere of city, 3 – paraffin candle, 4 - stearin candle). The dotted lines represent (from left to right) C-OH (3430 cm\(^{-1}\)), NH\(_4^+\) (3242 cm\(^{-1}\)), aromatic C-H (3055 cm\(^{-1}\)), aliphatic C-H (2925 and 2857 cm\(^{-1}\)), aromatic C=CH (1631 cm\(^{-1}\)), C-H (1435 cm\(^{-1}\)) and C-O (1055 cm\(^{-1}\)).

Figure 3 show FTIR spectra of particulate matter from kerosene combustion before (solid line) and after (dotted line) treatment (A – drying over P\(_2\)O\(_5\), B – extraction, C – reduction, D – carbonization).

Figure 3 show FTIR spectra of particulate matter from kerosene combustion depend of treatment. After particulate matter drying over phosphorus pentoxide, peak intensity of C-OH group (3430 cm\(^{-1}\)) was decreased, but not got lost (Figure 3, A). Water, which was produced in the burning process, was removed after drying over P\(_2\)O\(_5\). Remained signal at this region indicated about -OH group, which is chemically connected. The peak of ammonium vibrations at 3242 cm\(^{-1}\) was uncovered after drying. After extraction by acetone intensity of the peaks of C-H bending (1435 cm\(^{-1}\)) and aromatic C=C (1631 cm\(^{-1}\)) were decreased (Figure 3, B). That is products of tar were successfully removed. Intensity of C-H bending
(1435 cm\(^{-1}\)) and C-O stretching (1055 cm\(^{-1}\)) was increased after treatment by sodium borohydride, but intensity at region from 1640 to 1850 cm\(^{-1}\) was not changed (Figure 3, C). That means, analyzed particulate matter did not contain carbonyl group, in despite of literature data [4; 5; 8]. After carbonization (Figure 3, D) only intensity of peak of C-O group (1055 cm\(^{-1}\)) was changed (it was increased). For the most part in the obtained FTIR spectra intensity of C-O stretching (1055 cm\(^{-1}\)) is higher than an intensity of O-H stretching (3430 cm\(^{-1}\)). It was assumed that the residuary intensity of C-O stretching may be from radicals, which are formed in the burning process. The same differences of functional groups absorptions were obtained in FTIR spectra of particulate matter from candles burning and from atmosphere of city.

Obtained EPR spectra (Figure 4) show, that all samples of particulate matter from various sources contain organic radicals. In Figure 4 can see a tendency - the smaller particles the higher is concentration of radicals. Particulate matter with diameter ≤2.5 μm (PM\(_{2.5}\)) contained more radicals than particulate matter with diameter 2.5-10 μm (PM\(_{10}\)). Perhaps the reason of smaller quantity of radicals of coarse particles is an agglomeration of particles by radical mechanism.

Figure 4. EPR spectra of airborne particulate matter (1 and 3 - PM\(_{10}\) and PM\(_{2.5}\) from atmosphere of city respectively, 2 – from kerosene combustion, 4 – from paraffin candle burning)

EPR spectra of particulate matter from kerosene combustion after treatment are shown in Figure 5. After acetone and benzene extraction quantity of radicals was a little bit decreased (from 1.1\(\times\)10\(^{-5}\) % to 0.6\(\times\)10\(^{-5}\) %). Products of tar contain ed very low quantity of organic radicals. Extraction and carbonization in N\(_2\) flow removed tar products and volatile compounds from particulate matter. In the EPR spectra we can see, that quantity of radicals is highly increased after carbonization (from 0.6\(\times\)10\(^{-5}\) % to 2.5\(\times\)10\(^{-4}\) %), which concurs with increase of intensity at 1055 cm\(^{-1}\) in the FTIR spectra (Figure 3, D).

4. Conclusions
Particulate matter obtained from candles and kerosene burnt in the closed chamber and from atmosphere of city consists of organic compounds with aromatic, aliphatic and hydroxyl functional groups. Particulate matter from paraffin candle burning and from atmosphere of city also contains ammonium ions. Particulate matter of various sources contains about 1\(\times\)10\(^{-4}\) % organic radicals, which are not identified for the time being. The smaller is particles the higher concentration of radicals was observed.
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