Mass Spectrometric Analysis of PM$_{2.5}$ Aerosol Samples

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At the present time mass-spectrometric analysis widely used in atmospheric researches. Mass spectrometry provides with high probability to observe the content of many organic compounds in atmospheric aerosol samples. Due to anthropogenic pollution, the particulate matters are one of the major and dangerous air components. Detrimental effect on human health as a consequence of the presence in their composition carcinogens and mutagens. This study includes the analysis of chemical composition of atmospheric aerosol in the range of 2.5 pm and less. HRMS ESI method was used for the samples, collected throughout all year round. EPA US separated 16 polycyclic aromatic hydrocarbons from others to show potentially high risk of carcinogenic activity. The main goal of this work was to focus our research in search of these compounds in urban air of St. Petersburg city of Russia.

Keywords: Atmospheric aerosol, PM$_{2.5}$, Polycyclic aromatic hydrocarbons, Mass spectrometric analysis.

INTRODUCTION

Identification of priority polycyclic aromatic hydrocarbons (PAHs) in the composition of atmospheric aerosol particles collected on filters at different time periods, was the main goal of this research. Aerosols particles less than 2.5 pm, invisible by human eye, thinner than human hair mix up in turbulent air and as a consequence-long time of sedimentation. These particles are inhaled into lungs where it can remains. The upper respiratory defenses like nose hairs and mucous cannot remove them. The Environmental Protection Agency (EPA) standard identifies human health effects such as cardiovascular effects, heart attacks and premature death, effect of aerosol particles on the reduction of lung function [1]. The following size modes are known: ultrafine particles (smaller than 0.1 μm), fine particles (between 0.1 and 2.5), and coarse particles (larger than 2.5 μm). Lifetime of fine particles range from a few days to weeks and transfer distance is about 1000 km [1].

Carbonaceous aerosols with an aerodynamic diameter 2.5 μm (PM$_{2.5}$ and less) represent about 40 % of PM$_{2.5}$ mass in cities worldwide [2,3]. Diseases of the respiratory system, cardiovascular diseases may occur due to the presence of particles in the blood stream and lungs [4]. Ecosystem can be exposed to effects of these aerosols [5]. Ultrafine fraction (PM$_{0.1}$) contains black carbon [6]. Particles PM$_{0.1}$ can penetrate through the respiratory tract and membranes of lungs and then into the bloodstream they can move to other organs. Black carbon is recognized as substance that can cause cancer [6]. Recent researches

defined there is clear evidence that long-term exposure to particles affects to increased levels of cardiovascular diseases [7].

PM$_{2.5}$ are emitted directly into the atmosphere by pollution source. PM$_{2.5}$ fraction contain volatile organic compounds, along with elemental and organic carbon [1]. The main traffic sources include exhaust emissions from diesel engines. The situation is exacerbated by the fact that particles produced from anthropogenic source as combustion (coal, oil, gasoline, diesel, wood) can contain heavy metals (Pb, V, Ni, Cd, Zn, Mn, Fe, Cu, *etc*.). Elemental and organic carbon can be found with the range from 0.002 to 1 μm in a fine-mode, respectively [8]. Essential fraction of fine aerosol mass contains organic carbon, ranking from ~10 % in the rural areas to ~30 % in the urban air [9]. Relatively non-polar compounds, which were being extracted by organic solvent detected only for 10-30 % of organic carbon mass. Contrarily, water-soluble organic compounds can be the main fraction of organic carbon (in rural areas) [9]. It was shown that condensed aromatic formulae are inherent to urban aerosols. Meanwhile, aromatic nitrogen species are intrinsic for biomass burning aerosols [10]. Ratio between black carbon, water soluble organic carbon) and pyridine soluble organic carbon $6.5 \pm 0.7/33.6 \pm 2.6/66 \pm 20$ for biomass burning aerosol and $3.4 \pm 3.2/40.8 \pm 5.5/44 \pm 6$ for urban aerosol, respectively [10].

Polycyclic aromatic hydrocarbons (PAHs) mixtures can provoke lung, skin, gastrointestinal, bladder and scrotal cancers. There is ample evidence that some carcinogenic polycyclic aromatic hydrocarbons (cPAHs) can induce different types of

cancer in laboratory animals (*e.g.*, oral contact with benzo[*a*]-pyrene or dibenzo[*a,l*]pyrene mainly leads to gastrointestinal cancer or lung cancer, respectively) [11]. Relying on evidence of carcinogenicity on researches, which were carried out on experimental animals, 15 PAHs are presumably assumed to be human carcinogens [12]. Polycyclic aromatic hydrocarbons caused tumors in mice at several different tissue sites: malignant lung tumors (adenoma or adenocarcinoma), liver cancer (hepatocelluar carcinoma), skin tumors, urinary-bladder cancer (carcinoma), lung cancer, malignant tumors of forestomach [12]. It has been observed in human lung cells that parental PAHs must be metabolically activated to electrophilic intermediates (radical cations and *o*-quinones) to behave as lung carcinogens [13].

Scientific group from Kozani (Greece) detected and quantified 16 PAHs with a molecular mass from 152 to 278 [14]. It was revealed that the most frequently encountered PAHs in all samples were fluoranthene, pyrene, benzo[*a*]anthracene and benzo[*b*]fluoranthene. Seasonal variability in airborne particulate PAHs concentration was also noted. Usually, the concentration of PAH in air decreased with increasing temperature. The decrease of particulate PAH concentrations in warm periods is presumably associated with the temperature dependence of the vapor pressure, which controls the equilibrium in the gas/particle system [14]. Recent researches in Hunan and Catonese provinces of China showed that typical PAHs from cooking are pyren, phenanthrene, anthracene, fluoranthene, totally 23 PAHs were detected [15].

EXPERIMENTAL

The ambient aerosols were collected on a monitoring station of Voeikov Main Geophysical Observatory, situated close to the street with intensive traffic. For collecting the aerosol samples aspirator Derenda LS was used. $PM_{2.5}$ aerosols samples were collected on quartz filters GF 10 (Whatman^{TM}) at a flow rate of 38 L/min. Prolonged sampling of aerosol (72 h) was preferable owing to the need to accumulate the required number of aerosol for further analysis. After sampling, quartz filters with aerosol samples were delivered to our laboratory in sealed plastic bags. Prior to the analysis, samples were stored in the refrigerator at -20 ºC. Extraction of samples was carried out using a Soxhlet system with dichloromethane as solvent. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF 10223 spectrometer using electrospray ionization (ESI). Experimental parameters for HRMS-ESI were meticulously optimized to increase the signal intensity by using a standard PAH solution, with sixteen pollutants in methanol:methylene chloride (1:1) (EPA 610 polynuclear aromatic hydrocarbons mixture, lot 4S8743), which was purchased from Sigma-Aldrich.

RESULTS AND DISCUSSION

In the present work, high-resolution electrospray ionization mass spectrometry (HRMS ESI) has been used for the analysis of $PM_{2.5}$ aerosol samples. Fig. 1 shows a positive ion HRMS ESI spectrum of PAHs from ambient aerosols extract. Initially, 16 EPA's priority polycyclic aromatic hydrocarbons (PAHs) pollutants in ambient aerosols were studied in this work. Before the start of the investigation, all 16 PAHs were fixed in the ESI HRMS spectra of standard samples. It should be noted that some

of them are structural isomers, so their signals will overlap. All the PAH ion signals are in the form protonated molecular ions ([M + H]$^+$), which makes their identification fairly simple. In the mass spectrum, there are peaks with m/z = 129.0504, 153.1390, 167.0834, 279.1556 ions are [M + H]$^+$ that belong to naphthalene (nap), acenaphthylene (acy), fluorene (flo) and dibenzo[*a,h*]anthracene (dbA), respectively [16]. A number of the overlapping signals was also observed, *e.g.* m/z = 179.0736 corresponds to the overlapping [M + H]$^+$ signals of phenanthrene (phe) and anthracene (ant); m/z = 203.0764 identified as the overlapping [M + H]$^+$ signals of pyrene (pyr) and fluoranthene (flu); m/z = 229.1136 refers to the overlapping signals of chrysene (chry) and benzo[*a*]anthracene (BaA); m/z = 277.1214. we define as the overlapping [M + H]$^+$ signals of benzo-[*g,h,i*]-perylene (BgP) and indeno[1,2,3-*cd*]pyrene (InP). Also note that m/z for [M + H]$^+$ such structural isomers as benzofluoranthene (BbF), benzo[*k*]fluoranthene (BkF) and benzo[*a*]-pyrene (BaP) is 253.1337. When using the analytical standard, peak m/z = 275.1235 was identified as indeno[1,2,3-*cd*]pyrene together with structural isomers. We did not observe in the mass spectrum the signal of acenaphthene (ace), probably because of the extremely low concentration of this compound in the ambient aerosols extract. When using standard samples of other hydrocarbons, we were able to identify in the ambient aerosols extract pentamethylbenzene (Me5Bzn) (m/z = 149.0275, [M + H]$^+$), dimethylnaphthalene (Me2Nap) (m/z = 157.0639, [M +H]$^+$), hexamethylbenzene (Me6Bzn) (m/z = 163.1193, [M + H]$^+$), methylphenanthrene (MePhe) (m/z = 193.1008, [M + H]$^+$) and coronene (m/z = 301.1419, [M + H]$^+$ (Fig. 2).

The mass spectra of aerosol extracts in the range m/z 400-700 contain sequence of major signals with an interval of 44 Da, as well as sequences of minor signals that have the same interval of 44 Da; the interval between the major and minor signals is 26 Da (Fig. 3). The difference in molecular weight between the PAHs corresponding to the major and minor peaks can be explained by the successive addition of C2 moiety as ethylene bridge. The difference in molecular weight of 44 Da (for major and minor peaks) is probably due to the detachment of $C_2H_4O^+$ fragment from the organic components present in the aerosol extract. The presence of an interval of 26 Da between ionic peaks suggests that PAHs growth is mainly due to the gradual addition of two carbon atoms to the aromatic system as a result of the reaction with acetylene (or ethylene) [17]. At the same time, 12 Da intervals between the peaks indicate the growth of PAHs through the introduction of a methylene bridge (-CH_2-) into a bay-region of angular polyaromatic system, as a result of which a cyclopenta-fused ring is formed [18,19] (Fig. 4).

Using a standard C_{60} sample, we identified in the aerosol extract a fullerene C_{60} peak (m/z 720.5063) (Fig. 5). This result confirmed the data that fullerene can be formed in very small quantities during the combustion of fuel and subsequently enter into the composition of aerosol particles. Previously, it was reported about the identification of fullerenes in an atmospheric carbon-containing aerosol [20,21]. Fullerene soot can get into the atmosphere as a result of combustion processes of natural gas [22], fuel (including aviation fuel) [23-26], coal [20] and biomass [27]. Earlier, it was reported that polycyclic aromatic hydrocarbons in the combustion process can turn into soot containing fullerenes [28]. Some fullerenes contained in aerosols may
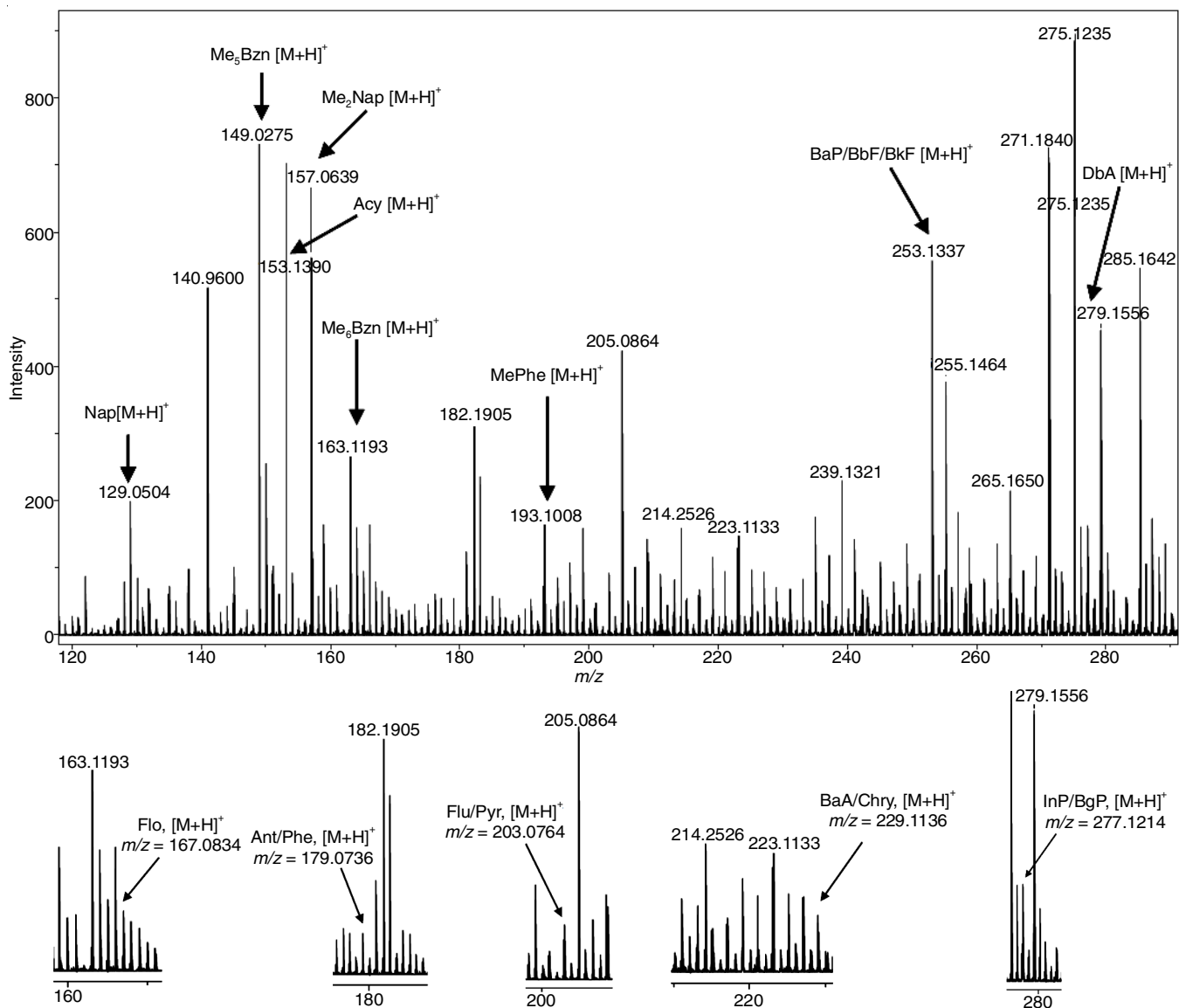
Fig. 1. A typical HRMS ESI spectrum of ambient aerosol extract. Only signals priority PAH pollutants were marked
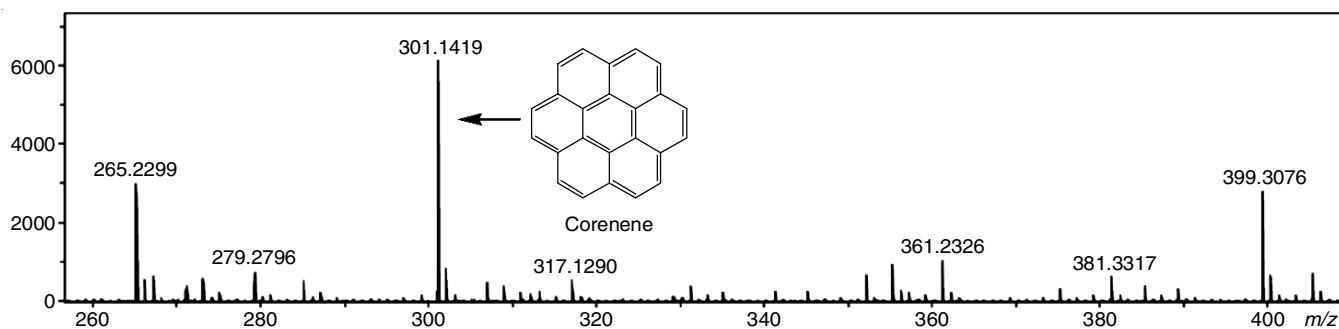

Fig. 2. Fragment of HRMS ESI spectrum of an extract of atmospheric aerosol (*m/z* 301.1449 – coronene)

undergo oxidation to form various oxygen-containing compounds [29].

Conclusion

The determination of PAHs in St.-Petersburg city of Russia ambient aerosol using a HRMS ESI mass spectrometry is reported. In aerosol extract were identified polycyclic aromatic hydro-carbons from the US EPA priority pollutant list and some other aromatic hydrocarbons. The investigation of mass spectra of aerosol extracts provided information on the basis of which assumptions were made about the structural transformations occurring in the process of PAHs growth under fuel combustion conditions. The interval of 26 Da between ionic peaks of the same PAH sequence suggests that PAHs growth is mainly due
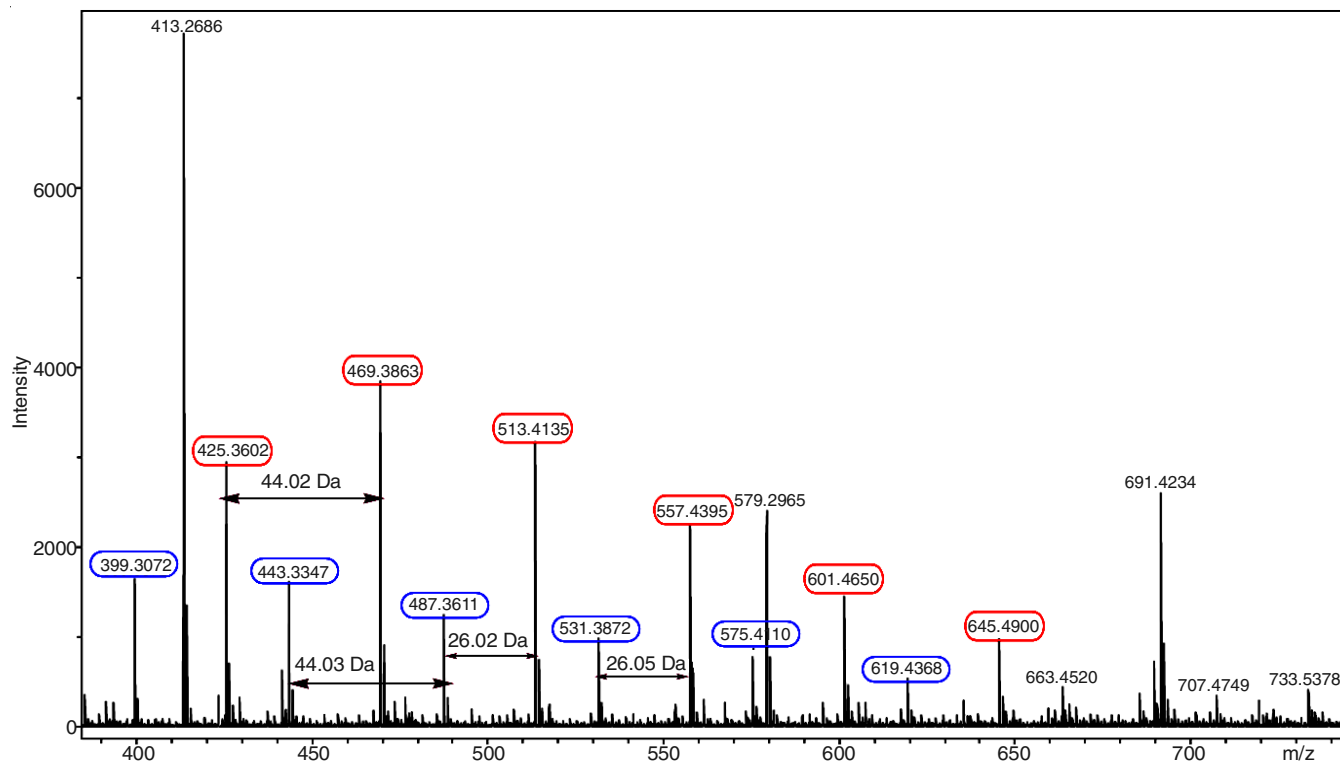
Fig. 3. Mass spectra of aerosol extracts in the range *m/z* 400-700
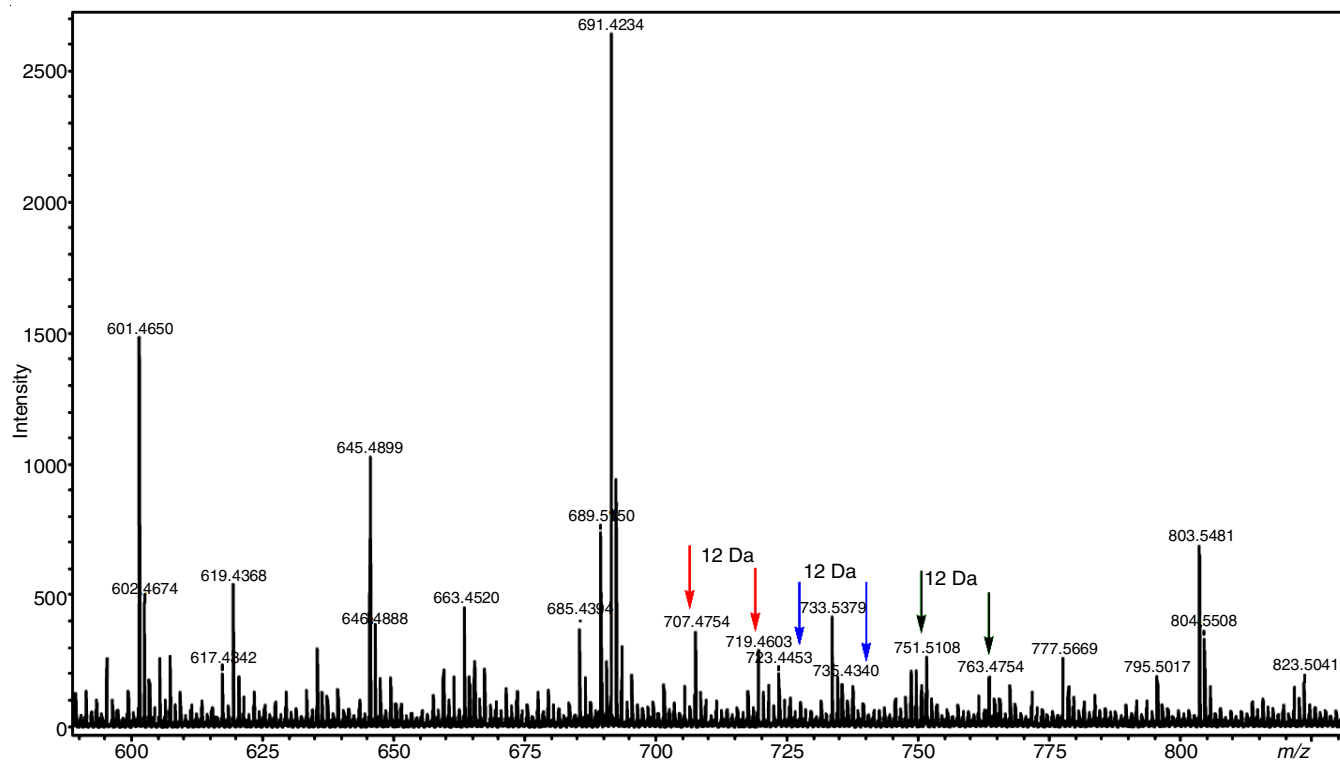
Fig. 4. Mass spectra of aerosol extracts in the range *m/z* 600-900

to the gradual addition of two carbon atoms to aromatic system as a result of the reaction with acetylene (or ethylene). The presence of an interval of 12 Da between the ion peaks indicate the growth of PAHs by another mechanism through the introduction of a methylene bridge (-CH$_2$-) into a bay-region of angular polyaromatic system.

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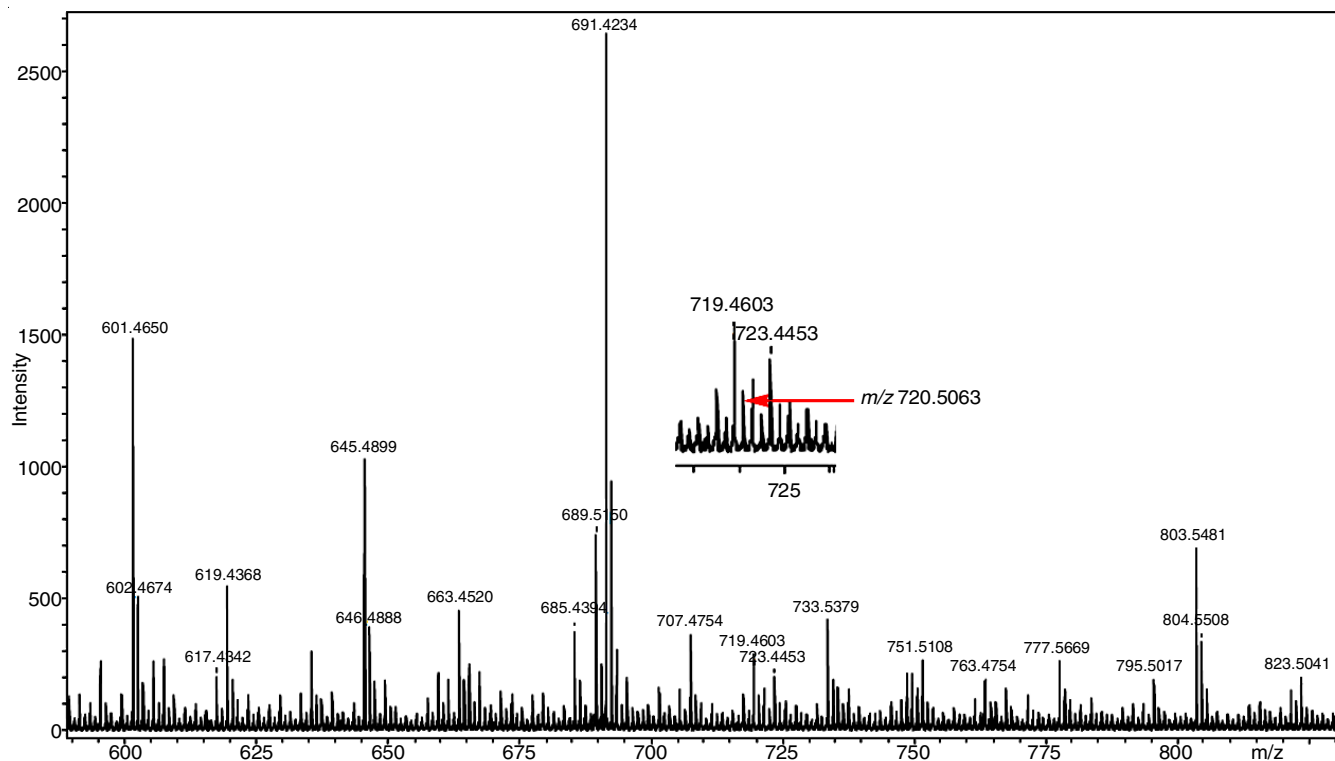
Fig. 5. Fragment of HRMS-ESI spectrum of an extract of atmospheric aerosol (m/z 720.5063 – fullerene C_{60})

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