

Challenges at characterization of particulate matter – a case study

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Nowadays, the particulate matter (PM) has been recognized as one of the major air pollutants with established scientific evidences on risks to human health [1–4]. Major interdisciplinary and multilayer research efforts have to be done to improve scientific understanding of airborne PM and its effects on human health. This new information will help to reduce uncertainties in the framework for assessing the public health risks from emissions of airborne particles and their gaseous precursors. The aim of our project is to investigate PM samples collected in Sofia, to identify global and regional particle sources in order to develop tools needed to formulate effective control strategies. This study reports an example of the challenges ahead for Particulate Matter physicochemical characterization. In this regard several different approaches have been utilized including techniques of powder XRD, elemental analysis, FTIR, SEM microscopy, XPS and Mössbauer spectroscopy. The main focus of the study were the smallest magnetic grains (<10 µm) as the most dangerous ones for the human health [1–5]. On the other hand, the mixture of multiple phases presented in PM and also their small size makes difficulties in their identification [3–5]. Therefore the preparation of standard procedures and methodology for investigation and control of PM is both challenge and priority [6].

Keywords: particulate matter (PM), physicochemical characterization, PM collected in Sofia, global and regional particle sources.

INTRODUCTION

Atmospheric aerosol particulate matter (PM) is one of the most challenging issues in environmental research [1–5]. Airborne PM vary greatly in size, composition, and origin. PM includes all solid and liquid particles that are suspended in the atmosphere as non-gaseous phases such as smoke, dust and droplets of liquids [1–3]. Airborne PM has a great impact on the environment and earth's climate, on precipitation levels and can have substantial negative health effects on humans or other living organisms [3]. PM can be directly emitted into the air (primary PM) or to be formed in the atmosphere [4]. Primary particles undergo chemical and physical transformations that result in a continuous change of their chemical composition and particle size distribution. Secondary particles are formed

in the atmosphere by chemical reactions between gaseous phase reagents as SO₂, NO₂, hydrocarbons, etc. The interaction between primary and secondary particles led to coagulation processes [4]. Both natural and anthropogenic particulate material can occur from either primary or secondary processes [1–5]. The smaller and lighter particles travel further and stay longer in the air in comparison to bigger and heavier particles, as well as they may be inhaled easier [1–5]. Particulates are the deadliest form of air pollution because of their ability to penetrate deeply into the lungs and blood streams unfiltered [2–3]. Therefore, the PM is a complex and heterogeneous mixture that changes in its lifetime. Great variations of PM chemical composition and physical characteristics could be regarded to multiple sources, seasonal variations and interaction with other co-pollutants. Instead of multiple investigations, the problem of precise quantification of regional PM emissions from different sources or of individual PM components is still not resolved [6–7]. Here, we report a case study of investigation of the nature of particulate matter collected in Sofia.

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EXPERIMENTAL

Materials

Studied powder materials were collected in one of the most polluted areas in Sofia – “Orlov most” square, according to the results obtained by Lidar detector.

Lidar mapping experiments were performed by equipment operating in the EARLINET Sofia Lidar Station in IE-BAS Laser Radars Laboratory. The scanning lidar is based on Cu vapour laser emits simultaneously 2 waves (510.6 nm and 578.2 nm) with a frequency 5–8 kHz. Lidar monitoring system was used for remote scanning from a single position (Lidar Station) over the whole Sofia area, covering the entire urban area and the surroundings. Lidar maps of good quality were obtained for radial operational distances above 25 km from the Lidar Station [8].

Characterization Methods

Elemental analysis was done using Inductively coupled plasma – Atomic emission spectroscopy (ICP-AES), Perkin Elmer 5000 spectrophotometer. The chemical composition of sample was determined by means of classical silicate analysis (in mass%).

Powder X-ray diffraction patterns were registered using TUR M62 diffractometer with $\text{CoK}\alpha$ radiation within the range of 5 to $80^\circ 2\theta$ with a constant step $0.02^\circ 2\theta$. Phase identification was performed with the X'Pert program using ICDD-PDF2 Database [9].

Mössbauer spectra were recorded by Wissenschaftliche Elektronik GmbH electromechanical apparatus (Germany), operating at a constant acceleration mode. A $^{57}\text{Co}/\text{Rh}$ source and an $\alpha\text{-Fe}$ standard were used. The Mössbauer spectra were collected at room temperature. The parameters of hyperfine interactions of the obtained spectral components were calculated by CONFIT program: isomer shift (IS), quadrupole splitting (QS), hyperfine effective field (H_{eff}) as well as line width (FW) and component relative weight (G). Computer fitting was based on the least squares method.

The morphology of materials was studied using a JEOL SEM T-200 scanning electron microscope. Before SEM observations, the samples were covered with vacuum-deposited carbon and gold films in order to amplify picture contrast.

Infrared (IR) spectra of the samples were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) by material dilution in KBr pellets (0.5% of studied substance). The spectra were collected in the far and in the middle infra-

red regions using 100 scans at a resolution of 4 (data spacing 1.928 cm^{-1}).

X-ray photoelectron measurements have been carried out on the ESCALAB MkII (VG Scientific, now Thermo Fisher Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10^{-10} mbar using twin anode $\text{MgK}\alpha/\text{AlK}\alpha$ X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra are recorded at the total instrumental resolution (as it was measured with the FWHM of $\text{Ag}3d_{5/2}$ photoelectron line) of 1.06 and 1.18 eV for $\text{MgK}\alpha$ and $\text{AlK}\alpha$ excitation sources, respectively. The energy scale has been calibrated by normalizing the C1s line to 285.0 eV. The processing of the measured spectra includes a subtraction of X-ray satellites and Shirley-type background [10]. The relative concentrations of the different chemical species are determined based on normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [11].

RESULTS AND DISCUSSION

Analysis of major elements presented in studied PM is key point for better interpretation of all other analyses. However a specific and challenging problem of dust analysis is the small available mass for analysis, its apriori unknown elemental composition and its chemical complexity with elements varying from main component level to trace elements. Alumino-silicate compounds were found to be a substantial part of the PM content being SiO_2 (46.53%) and Al_2O_3 (20.12%), respectively. CaO (3.79%), K_2O (1.99%), MgO (1.22%), Na_2O (0.26%), SO_3 (0.25%), TiO_2 (0.93%), P_2O_5 (0.33%) are also presented. The metals with major concentrations in PM were Fe_2O_3 (16%), CuO (12%) and MgO (20%), respectively. Small quantities of Ni, Cr, Pb and Zn oxides less than 1% were also registered.

SEM images are shown on Fig. 1. It can be very well seen that PM greatly vary in size from nanometers to several tenths of micrometers. The most of particles are observed to be an aggregates of small particles. The size distribution and differences in the material morphology are registered at higher magnification (Fig. 1a, 1b and 1c).

Powder XRD (Fig. 2) show the presence of low intensity and broad X-ray diffraction peaks laid on non-selective background in pattern of studied sample. The main crystallite phases registered in X-ray diffractogram are silicate, aluminosilicate, carbonate, silicate hydroxide and sulfate phases. The characteristic patterns of quartz SiO_2 (78-1252), anorthite (73-0264), Mn silicate (12-0215), calcite CaCO_3 (03-0596) and K-Mg silicate hydroxide (26-

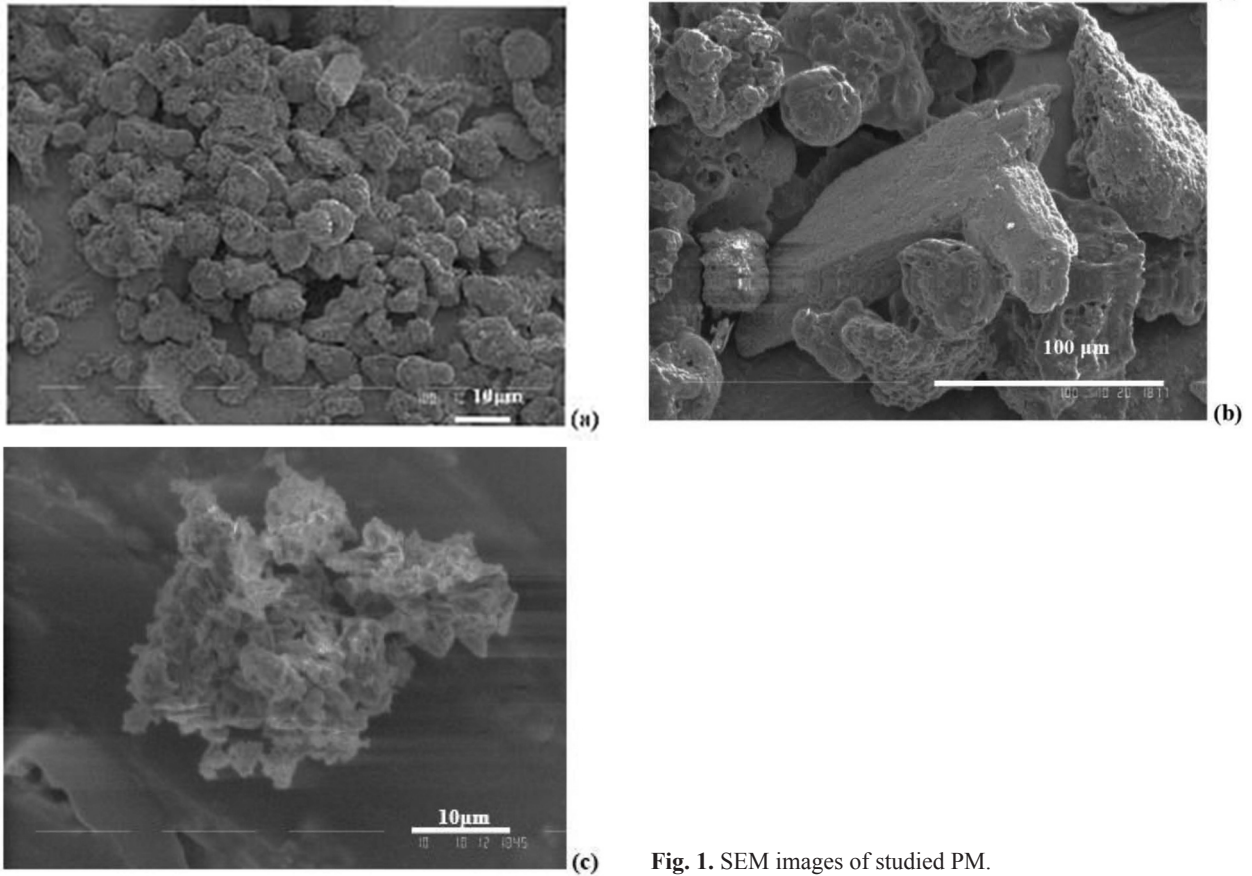


Fig. 1. SEM images of studied PM.

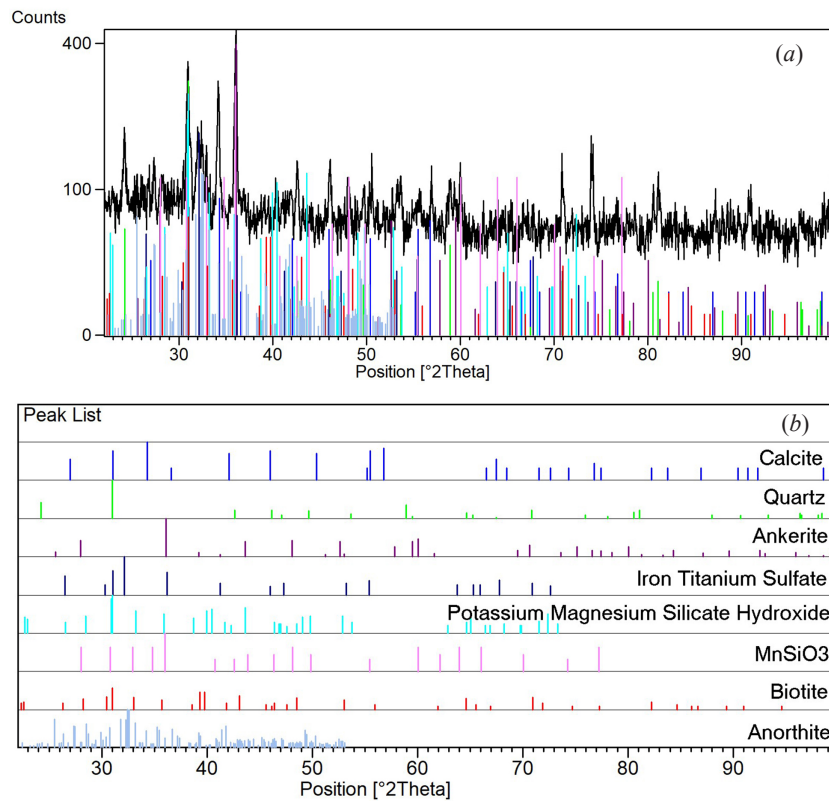


Fig. 2. X-ray diffraction pattern of PM material (a) and analysis (b) showing peaks derived from the pattern compared to the JCPDS standard pattern numbers.

1322) were resolved in the registered diffractogram. Lesser amounts of ankerite (79-1348), Fe-Ti sulfate (28-0500) and biotite (42-1414) were found also. Registered X-ray amorphous halo peaks and non-selective background were the reason not to present quantity results about the estimation of listed phases. Small intensity and high width of diffraction peaks of all registered crystallite phases indicates their small particle size and low crystallinity degree. These observations are in good consideration with previous studies of air pollutants [2, 4–5].

Additional information about chemical composition, chemical bonds and surface functional groups of the studied PM material was obtained by IR study in far and middle infrared regions. Spectra are shown on Figure 3. Possibilities of this method are limited during multicomponent systems investigation and are reduced to determination of present functional groups in the studied sample. Conclusion concerning presence of definite chemical compound cannot be done because of partial and/or total characteristic bands overlapping. Spectra analysis showed presence of inorganic carbonate(s) (714, 876, 1425 cm^{-1}) and surface carbonate groups (714, 876, 1038, 1441, 1545, 1640, 1660, 1719 cm^{-1}). About inorganic phosphate/ phosphate rests availability can be judged from bands positioned at 529, 914, 1038, 1080 cm^{-1} since the range around 1000 cm^{-1} is characterized by increased absorption and it is typical of PO_4 group vibrations. Sulfur containing components of the studied sample were also registered by characteristic bands of sulfates (621, 1080 cm^{-1}) and organic compounds containing thiol group S-H (664, 697, 1267, 2521 cm^{-1}). Despite low

intensity of band at 2521 cm^{-1} it is considered indicative. In this case the low intensity is not a problem because the band is positioned in infrared region, which is relatively free of interferences. Organic rests were registered by bands characteristic of CH_3 and CH_2 groups (714, 730, 1267, 1384, 1466, 2852, 2924, 2957 cm^{-1}) as it is possible to suppose that CH_2 groups are more because of the increased intensity of bands at 2852 и 2924 cm^{-1} and availability of couple of bands at 714 и 730 cm^{-1} . The investigated material surface moisture is associated with bands characteristic of presence of hydrogen bonded OH groups (3424 cm^{-1}), physically adsorbed water molecules (1631 cm^{-1}) and isolated on the surface OH groups (3740 cm^{-1}). Bands at 1038 и 3633 cm^{-1} are assigned to oxygen containing organic compound – primary alcohol. Infrared bands at 362, 412/420, 470, 529 cm^{-1} can be assigned to Fe-O vibration. Presence of nitrate (876, 1384 cm^{-1}), silicate (517/520, 529, 1038, 1080 cm^{-1}) and carbonyl (1719 cm^{-1}) groups, and CC multiple bond (2170 cm^{-1}) could not be excluded baring in mind elemental analysis, XRD and MS data.

X-ray photoelectron spectroscopy has been applied in order to monitor the surface element and their concentrations and ratios. Fig. 4 shows a survey spectrum of investigated sample. The elements as Al, Si, C, O, N, Na and Cu have been detected on the surface and their calculated concentrations are summarized in Table 1. The determined binding energies of C1s (285.0 eV), Al2p (74.8 eV), Si2p (102.8 eV), O1s (532.2 eV), Ca2p (347.7 eV), N1s (400.0 eV), Na1s (1072.3 eV), Cl2p (199.2 eV), and Cu2p (933.3 eV) are typical for Si-O, Al-Si-O, Ca-

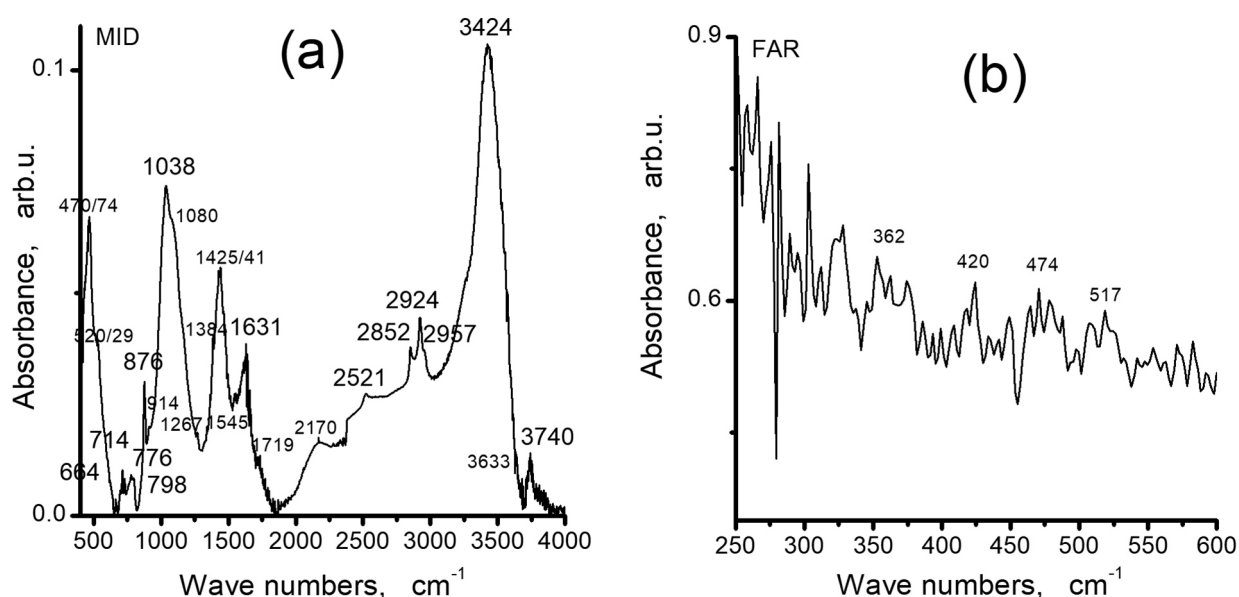


Fig. 3. Infrared spectra of powder PM in the middle (a) and in the far infrared regions (b).

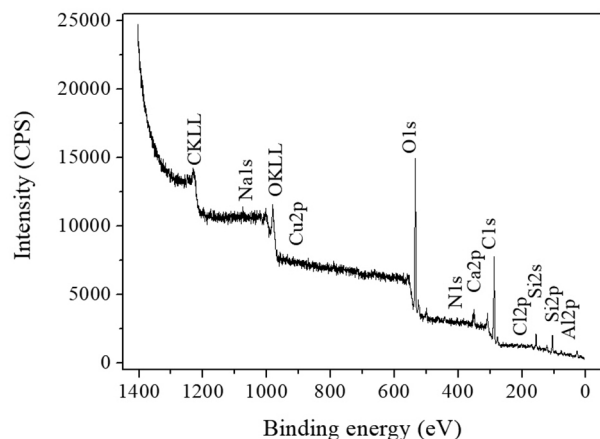


Fig. 4. Survey X-ray photoelectron spectrum of powder PM.

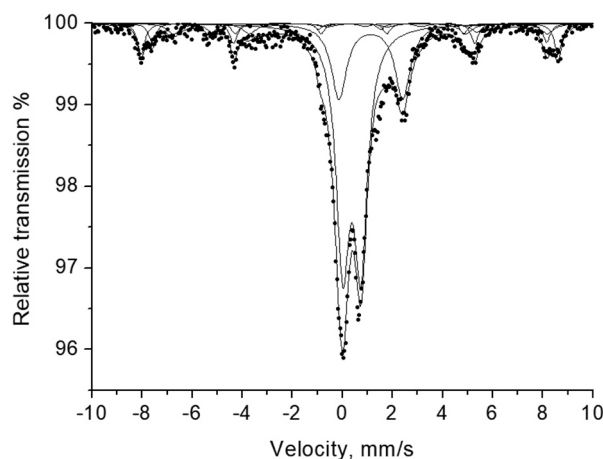


Fig. 5. Mössbauer spectrum of PM sample.

CO₃, C-H-N, C-H-NO_x, C-H-N-Cl, Na-C-H-N-Cl, Cu-Cl-C-N-H-O, Cu-O bonding, respectively [12]. So, the analysis shows that the surface of investigated PM sample consists mainly of silicate, aluminosilicate compounds and of organic and inorganic carbon phases.

So we have collected a data set of studied PM sample, however no clear conclusions about the presented chemical compounds, their quantity and dispersion were possible. On the other hand the iron is not the only transition metal found in particulate matter, but it is one of the predominant ones. Furthermore the elemental analysis of sample showed a bigger iron content in studied PM than in the usual ones. In this regard ⁵⁷Fe Mössbauer spectroscopy was applied and this allows us to become deeper into the PM characteristics.

Mössbauer spectra of sample (Fig. 5) reveal a phase composition and dispersity of presented iron-containing phases. Four sextet and two doublet components were obtained after spectrum evaluation. They have the characteristic parameters of phases presented in Table 2. The first sextet component has hyperfine parameters characteristic of hematite phase – α -Fe₂O₃. The calculated value of H_{eff} is lower than the typical one of bulk hematite (52 T) which shows that particle size is about 20 nm [13–14]. Sextets 2 and 3 are characteristic for Fe₃O₄ which corresponds to iron in a tetrahedral (sublattice A) and octahedral (sublattice B) oxygen configuration in spinel Fe³⁺[Fe²⁺Fe³⁺]O₄. Mössbauer spectrum of stoichiometric magnetite consists of two sextet components resultant from presence of Fe³⁺ in tetrahedral position (Sxt2) and only one sextet (Sxt3) due

Table 1. Surface atomic concentration of powder PM

Elements	Cl1s	O1s	Al2p	Si2p	Na1s	Cl2p	Ca2p	Cu2p	N1s
Concentration, at. %	48	31	3	12	0.42	1	3	0.22	1

Table 2. Mössbauer parameters obtained after PM spectrum evaluation

	IS, mm/s	QS, mm/s	Heff, T	FWHM, mm/s	G, %
Sx1	0.37	-0.09	51.7	0.25	8
Sx2	0.28	0.00	49.0	0.25	5
Sx3	0.66	0.00	46.4	0.56	6
Sx4	0.06	0.00	10.6	0.46	3
Db	0.37	0.72	–	0.53	56
Db	1.13	2.54	–	0.63	21

to electron dislocation between octahedrally coordinated ions Fe^{2+} and Fe^{3+} , so-called mixed valency state $\text{Fe}^{“2.5+”}$ [13–14]. Partial oxidation of magnetite and/or the presence of maghemite phase – $\gamma\text{-Fe}_2\text{O}_3$ leads to a reduction of the “2.5+” component intensity paralleled by an increase of the relative intensity of a sextet attributed to tetrahedrally-coordinated Fe^{3+} . According to previous investigations the hyperfine parameters of the fourth sextet should be regarded to Fe^0 in metal phase. IS not equal to 0mm/s, i.e. this is the intermetallic phase, which includes not only iron, but also other elements [13]. The first of doublet components (Dbl1), which is the main Fe-bearing phase presented in the spectrum of the sample, show that Fe is in paramagnetic (glass phases, sulfates, etc.) or superparamagnetic (SPM) phases with nanometric size (oxides or hydroxides) [15–16]. The second paramagnetic component (Dbl 2) is indicative for the presence of Fe^{2+} in aluminosilicate glass, ankerite, iron-containing carbonates, biotite or other phase [15–17].

The obtained results using Mössbauer analysis were successfully combined with the observations of the other characterization methods in this study. This allows us to make conclusions about chemical composition of studied PM sample, both crystal and amorphous phases, as well as about the quantity and dispersion of compounds. The main phases registered in the sample are silicate, aluminosilicate and sulfate compounds, as well as an organic and inorganic (carbonate and coal) carbon phases. The obtained bigger than usual content of iron in PM could be regarded to the airborne particles produced by transport and mainly by car engine performance [13]. The main source of silicate and aluminosilicate compounds was recognised to be born by natural and anthropogenic sources and the last ones are connected by street and house reparation activities [4–5]. Combustion products and residuals from the exhaust gases originating from power plants, small houses and different engines [1–5, 13, 15–16] could be also regarded to their sources after preparation of characterization procedure for atmospheric particulate matter monitoring.

CONCLUSIONS

This paper is an investigation on the nature of particulate matter collected in the area of Orlov most square, in Sofia. The physicochemical characteristics of the studied PM sample revealed its high heterogeneity and complexity. It was shown that detailed information about iron-bearing compounds could be obtained using Mössbauer spectroscopy, which allows us to get information about the phase composition and the size of the particles

because the hyperfine parameters are affected by the difference in the microscopic environments of the iron ions. Drawing conclusions from the experiments discussed in this study is not an easy task. It demonstrates that, in spite of advancements, a lot of efforts should be put in regard to suggest the common characterization procedure to distinguish PM emissions from different sources or individual PM components. However we are motivated to continue to further progress. Preparation of a methodology will be used for quantifying and characterizing the PM and also will enable further activities in order to reduce the atmospheric PM pollution.

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