Journal of Applied Physical Science International

Volume 16, Issue 1, Page 23-42, 2024; Article no.JAPSI.12136
ISSN: 2395-5260 (P), ISSN: 2395-5279 (O)

Mössbauer Spectroscopy and Scanning Electron Microscopy Studies of Road Dust Sediments in Urban Environment of Sofia – The Bulgaria's Capital City

Boyan Bonchev [a*], Nikolay Velinov [b] and Ventzislav Rusanov [a]

[a] Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72 Tsarigradsko Shose Blvd., 1784 Sofia, Bulgaria.
[b] Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: https://doi.org/10.56557/japsi/2024/v16i18720

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://prh.ikprress.org/review-history/12136

Original Research Article

Received: 27/03/2024
Accepted: 01/06/2024
Published: 05/06/2024

ABSTRACT

The annual and daily maximum permissible values applicable to the concentrations of fine particles with diameter up to ten micrometers (Particles Micrometers 10, PM10) in the city of Sofia as well as in several other Bulgarian cities and regions have been found to exceed the limit values more than

**Corresponding author: E-mail: boyan.bonchev@gmail.com;*

Cite as: *Bonchev, Boyan, Nikolay Velinov, and Ventzislav Rusanov. 2024. "Mössbauer Spectroscopy and Scanning Electron Microscopy Studies of Road Dust Sediments in Urban Environment of Sofia – The Bulgaria's Capital City". Journal of Applied Physical Science International 16 (1):23-42. https://doi.org/10.56557/japsi/2024/v16i18720.*

2.5 times for 90 days per year. Air quality is one of the main factors determining the quality of life. According to the European Commission, air pollution is still the most serious environmental and health problem in the EU, with annual deaths estimated at around 400 000 people. Two methods have been chosen for the study of road dust deposits containing fine iron-containing particles in the city of Sofia: Mössbauer spectroscopy and scanning electron microscopy with the possibility of X-ray fluorescence analysis and determination of the chemical elemental composition of the objects, as well as their size and shape. The Mössbauer spectroscopy studies at liquid nitrogen temperature allow making at least semi-quantitative estimates of the content of ultrafine iron-containing particles with superparamagnetic properties. Iron is included mostly in the form of oxides and hydroxides. The presence of a large amount of fine dust particles of metallic iron, α-Fe, is clear evidence of a significant technogenic contribution to the pollution of Sofia's air. The finest dust component with concentrations between 10 and 20% is in a superparamagnetic state and is observed as fine incrustations on the surface of silicates. In places with intense traffic and large-scale construction activities, an increased concentration of man-made dust sediments is noticed.

Keywords: Urban dust sediments; iron-containing particles; mössbauer spectroscopy; scanning electron microscopy; X-ray fluorescence analysis; superparamagnetic ultrafine particles.

1. INTRODUCTION

Air quality is one of the main factors determining the quality of life. According to the European Commission, air pollution is still the most serious environmental and health problem in the EU, with annual deaths estimated at around 400 000 people. This problem also affects Bulgaria, as for years the capital Sofia and other large metropolises in the country have had a problem with air pollution with fine dust particles [1-4].

By definition, PM10 is particulate matter with a diameter of 10 micrometers or less. PM2.5 is particulate matter 2.5 micrometers or less in diameter. PM2.5 is generally described as fine particles. The Municipality of Sofia took some actions to improve the quality of atmospheric air in Sofia - for example, partial changes from fossil fuels petrol and diesel to gas and electricity for public transport. A limited number of solid fuel heaters were replaced with more modern ones and chimney filters for fine dust particles were installed. Information boards were placed at key locations to provide information not only on the concentration of PM10, but also on the concentration of some gas components (NO_2, SO_2, O_3, etc.) in the polluted air of Sofia. Unfortunately, very soon after their installation, the information boards were damaged, stolen, simply did not work or displayed incorrect data. The press and mass media constantly point out that the main source of air pollution is the burning of solid fuels for heating. In our view, there are other sources of pollution, such as heavy urban traffic. The annual and daily maximum permissible values applicable to the concentrations of fine particles with diameter up to ten micrometers (Particles Micrometers 10, PM10) in the city of Sofia as well as in several other Bulgarian cities and regions have been found to exceed the limit values more than 2.5 times for 90 days per year. Unfortunately, the measures that are taken to improve the quality of the environment and especially of the air in Sofia and other large cities in Bulgaria are often spontaneous and have a partial political character. For this reason, there is a citizens' initiative for personal networked measurement devices, which appear to be the only source of reliable quantitative PM10 concentration data [5]. The problem of air pollution, road depositions and dust sediments is a global environmental problem, widely discussed in the scientific literature, for example in [6,7] and the literature cited therein.

The main goal of the present study is to investigate the road dust sediments containing fine iron-bearing dust particles in the city of Sofia, as an indirect indicative method for air quality assessment. The study is not the first of its kind, and the most informative method for conducting it is Mössbauer spectroscopy [8]. Applying Mössbauer spectroscopy, Rusanov and co-authors have proven contamination of the air of Sofia with fine iron-containing dust particles PM10, deposited after the Chernobyl nuclear power plant accident [9]**.** Other authors [10] also used Mössbauer spectrometric measurements and detected iron-containing atmospheric aerosols collected during the Chernobyl accident, and not only then, in various polish settlements. The quantitative or semi-quantitative speciation of iron-containing terrestrial or anthropogenic

dust and the source of its origin remains a challenge and is the second goal of this work.

2. MATERIALS AND METHODS

2.1. Dust Sediments Samples Collection

To obtain a representative sample from each sampling location, dust sediments samples were collected from three separate points approximately 1 m away from one another on the street lane along the curb. All sampling was conducted with non-magnetic paddles and brushes to avoid magnetic separation of the deposited components. The material from the individual sites was mixed into one sample with a total mass of about 10 g, representative of the respective locality. In the laboratory the powder material was sieved with a 1 mm mesh to separate the coarse particles. To obtain a finely dispersed fraction from the samples for the Mössbauer spectroscopy measurements, the material was sieved once more through a 63 μm sieve. Preparation of only the finest dust component for the measurement with Mössbauer spectroscopy is necessary because of the very low energy, 14.4 keV, of the gamma-quanta from the Mössbauer transition. The location and numbering of the samples is summarized in Table 1. Material was collected from two of the sampling sites during the winter and summer periods of 2017. The locations selected for sampling were not chosen randomly. It is generally accepted that our selected places are among the most polluted in Sofia. The construction activities related to James Bourchier metro station and the neighboring European Union and Vitosha stations are sources of heavy man-made pollution. The area of Eagle Bridge is one of the most polluted places due to the heavy traffic. Conversely, Lyulin metro station and the surrounding area is an area with a low degree of man-made pollution.

2.2 Scanning Electron Microscope and X-Ray Fluorescence Analysis

The iron concentration, size determination of the iron-containing components, and the elemental composition for all samples were precisely investigated by means of an X-ray fluorescence analysis (Energy Dispersive X-Ray Fluorescence, EDXRF analysis), using a LYRA I XMU scanning electron microscope with a detector Quantity 455, X-Flash 5010300 of BRUKER. The energy resolution of the micro analyzer at standard line Mn, K_α was 127 eV. In these studies, both objects with sub-micron dimensions and surfaces with an area of up to a quarter of a square millimeter were analyzed. Many images were acquired at different magnifications in backscattered (BSE) and secondary electron (SE) modes. Observations and measurements were conducted in the SEM laboratory at the Faculty of Physics of University of Sofia.

2.3 Mössbauer Spectroscopy Investigations

Mössbauer spectroscopy measurements of dust sediments samples were performed in transmission geometry at room and liquid nitrogen temperatures with a standard spectrometer working in constant acceleration mode. Mössbauer sources ^{57}Co in Rh matrix and activity of about 25 mCi were used. A proportional counter filled with krypton was used to detect the Mössbauer γ-quanta (14.4 keV). For velocity calibration a 25 μm α-Fe foil was used. All isomer shifts are referred to this standard at room temperature. The spectra were approximated with the software packets CONFIT 2000 [11]. Road dust sediments samples were placed into Teflon cuvettes with thin bottoms (0.5 mm), each with an area of 1.3 cm2 and surface density of 150 mg/cm2. All Mössbauer

Table 1. Localization and numbering of the samples. In the winter and summer periods of 2017 material was collected from two of the sampling sites. The sampling was chosen in the middle of the winter and summer season in order to determine the influence of meteorological conditions on sediment type

	Sample	Localization in capital city Sofia	Collection date
1	1149-17Mv	Metro station James Bourchier Blvd.	June 2017
2	1145-17Mv	Metro station James Bourchier Blvd.	January 2017
3	1143-17Mv	Eagle Bridge	June 2017
4	1144-17Mv	Eagle Bridge	January 2017
5	1148-17Mv	Metro station Lyulin	January 2017

measurements of the samples were performed in the Institute of Catalysis at the Bulgarian Academy of Sciences.

3. RESULTS AND DISCUSSIONS

3.1 Results from Scanning Electron Microscopy

The discussion of the original results focuses first on the scanning electron microscope studies of the microparticles. Microparticles are fine dust particles from atmospheric pollution with a particle size in the range of 0.1 ÷ 100 μm. By reducing the size of the objects in the deposits, the so-called ultrafine dust particles can be defined - with sizes smaller than 0.1 μm. Particles with a size below 100 nm will be called ultrafine nanoscale objects. The dust samples are from the winter and summer seasons. As a rule, winter dust sediments are coarser-grained with a maximum object size of about 50-60 μm.

Fig. 1 presents the results of an X-ray fluorescence analysis of a sample from James Bourchier metro station, June 2017. The spectrum was obtained when scanning a selected surface with an area of approximately a quarter of a square millimeter. The figure also shows a scanning electron microscopic image of the sample obtained in backscattered electron (BSE) mode. The result of the analysis shows that the dominant chemical element is silicon, probably in the form of silicon dioxide, containing large amounts of the elements Na, Al, K and Ca. Iron is also detected as a micro impurity in the spectrum. Man-made particles with a specific shape and chemical composition are rarely observed - for example, the thin rod-like object in the middle of the photograph. Some particles have a pronounced single crystal habit.

The images in Fig. 2 were obtained at two different magnifications in secondary electrons (SE) mode. The right-hand part represents fragmented silicate particles at a higher magnification which often show smooth surfaces. The surfaces of silicate particles are encrusted with submicron particles showing a high iron content. To serve as an example, several of them are marked with red circles in the right-hand part of Fig. 2.

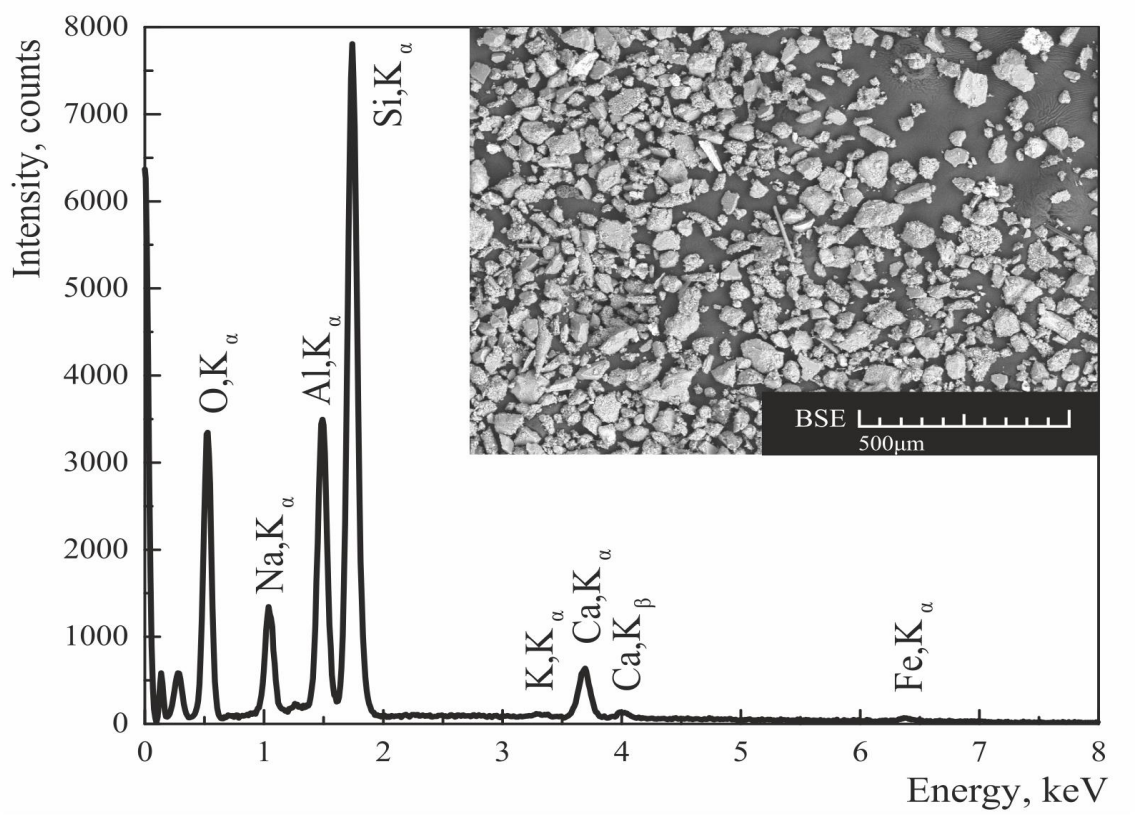

Fig. 1. Results of an X-ray fluorescence analysis and a scanning electron microscopic image of the sample obtained in backscattered electron (BSE) mode

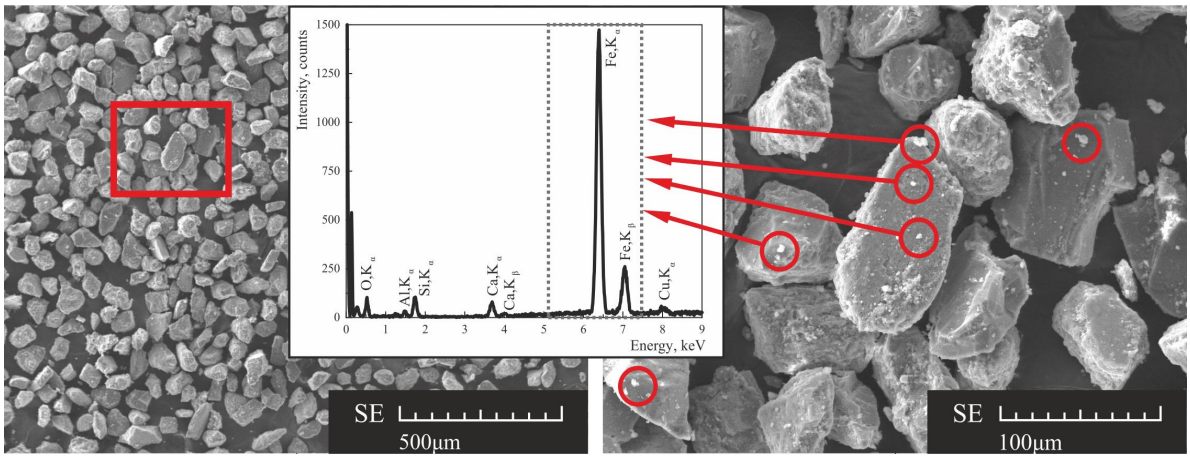

Fig. 2. Scanning electron microscopy images from fine dust particles obtained at two different magnifications in secondary electrons (SE) mode. The right-hand part represents silicate particles fragmented at a higher magnification, from the area marked with a rectangle in the left-hand part of the photography. The results of an X-ray fluorescence analysis, obtained from a single several-micron particle, marked in the right-hand part with red circles, are presented in the center of the figure

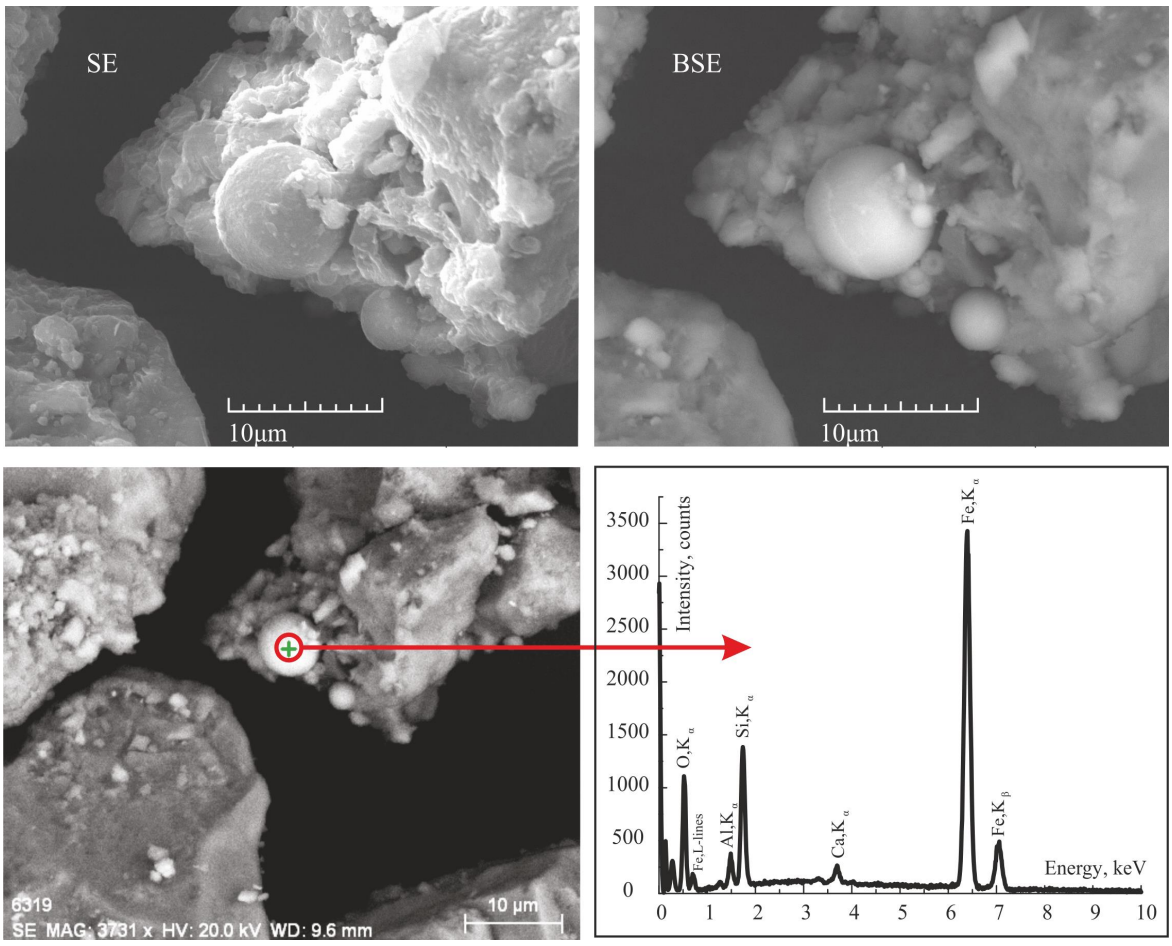

Fig. 3. Electron microscopic images obtained in different modes show a spherical object embedded in a silicate matrix. The elemental composition is dominated by iron. A typical technological man-made object – a drop of α-Fe.

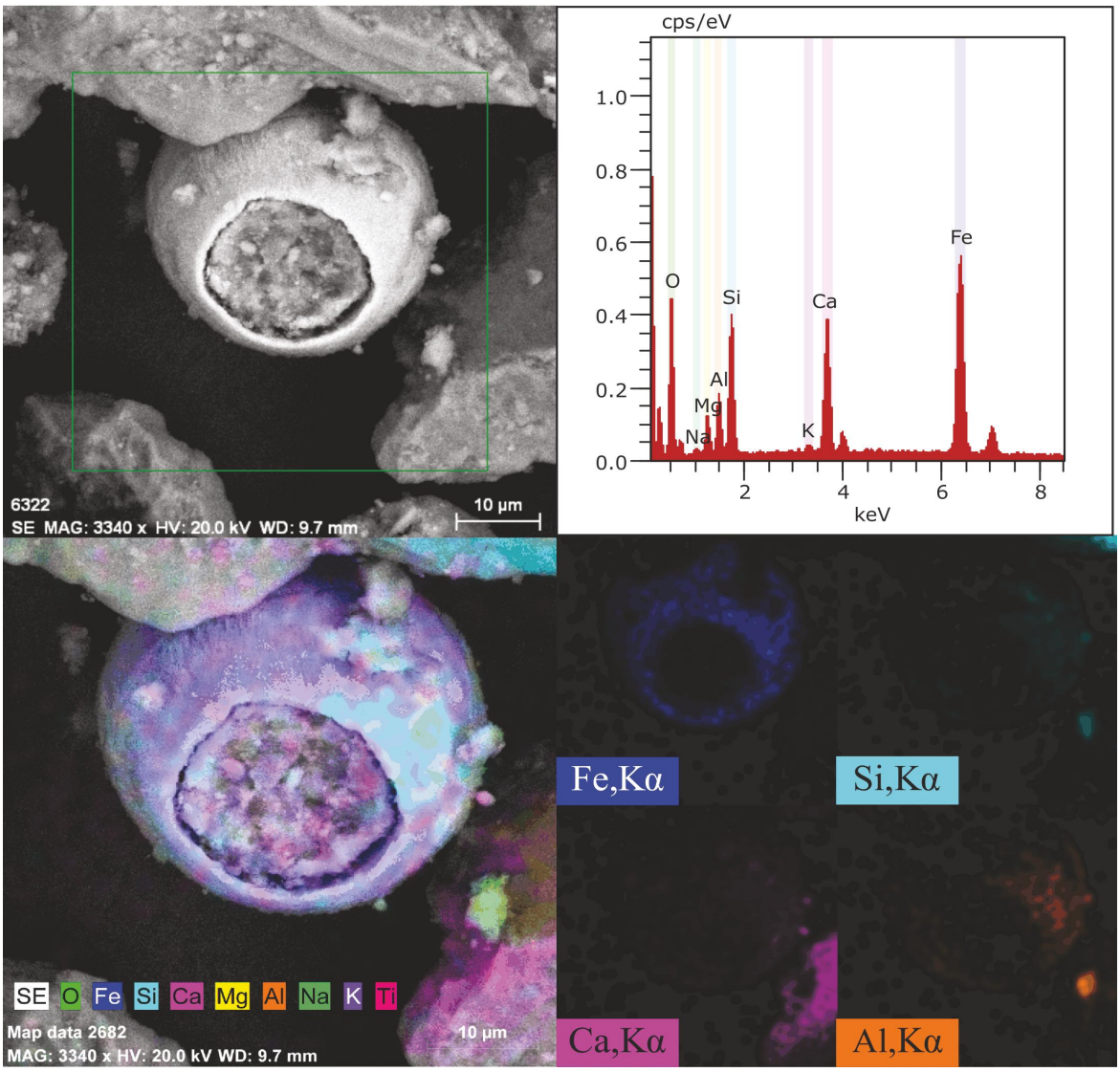

Fig. 4. Complex results of the study of a hollow iron microsphere filled with silicate material, additionally containing the elements Ca, Al and Mg in the form of their oxides or carbonates. (left-hand part) Scanning electron microscopy images and map data for the selected elements. (right-hand part) X-ray fluorescence spectrum obtained from the hollow iron microsphere and images obtained by detection of selected chemical element X-ray emission. For example, the detection of characteristic Fe, K_α line confirms that the spherical shell contained mainly iron

The central part of Fig. 2 presents the results of an X-ray fluorescence analysis obtained from a single particle. In the spectrum of these microparticles, the dominant chemical element is iron. The weak lines of Al, Si and Ca are connected to the silicate pad. By passing through the microparticles, the electron beam of the scanning electron microscope with energy of 20 keV and a diameter of about 0.5 µm also excites the characteristic X-ray emission of the elements that build the silicate basis. It can be concluded that the designated particles are monoelement iron particles with a micro impurity of copper. The origin of these microparticles is certainly technogenic since monoelement iron particles of natural origin are very rare in nature. These are the objects that will be characterized by Mössbauer spectroscopy in the next part.

Fig. 3 presents the results of the complex study of an exotic object that will turn out to be a drop of α-Fe. Electron microscopic photographs in different modes show a spherical object embedded in a silicate matrix. The elemental composition is dominated by iron. Additionally, signals from the elements Si, Al and Ca are

observed in the X-ray fluorescence spectrum from the silicate matrix. An α-Fe subspectrum is often unambiguously identified in Mössbauer spectra, which is further evidence of the presence of technogenic α-Fe particles. Similar spherical micro-objects of α-Fe have been frequently discussed and reported in mass media and popular science studies of the ruins of the World Trade Center after the attacks on September 11, 2001. Their occurrence is explained by melting and partial evaporation of the huge metal structure of the buildings.

Fig. 4 presents the complex results of the study of another exotic object, a hollow iron microsphere filled with silicate material, additionally containing the elements Ca, Al and Mg in the form of their oxides or carbonates. The object is assumed to be of man-made origin and arose, like the object in Fig. 3, during welding work carried out during the construction of the James Bouchier subway station.

Various other strange objects were observed such as ceramic fibers, possibly from the air filters of construction machinery, shavings of galvanized or tinned sheet metal and others. As a final example, Fig. 5 presents the results of the study of an exotic object, a microcrystal with a monocrystalline habit. The elemental composition corresponds to mineral zirconate $ZrSiO_4$, also known as a cheap imitation of diamonds in the jewelry industry.

3.2 Results of Mössbauer Spectroscopic Studies

First, it was shown by the Kopcewicz family that Mössbauer spectroscopy can be successfully used to study iron-containing aerosols and their properties as well as to determine their concentration in atmospheric air [12-14]. The monograph [15] includes and discusses these studies among many others as examples of exotic applications of Mössbauer spectroscopy. During the weathering processes, a large amount of iron oxides, hydroxides and iron-containing clay, and silicate materials in the form of ultradisperse particles is lifted from the earth's surface and transported into the troposphere. These components can be blown by winds over large areas and distances. The specifics of these processes and the possible investigation with Mössbauer spectroscopy are summarized in the monograph again by the Kopcewicz family [16]. Many other physicochemical analytical methods could certainly be successfully used as well. We will mention just one example from the work of Elzinga et al. [17] and the literature cited there for XANES studies in combination with other methods for quantifying speciation of Fe-bearing minerals in anthropogenic urban dust.

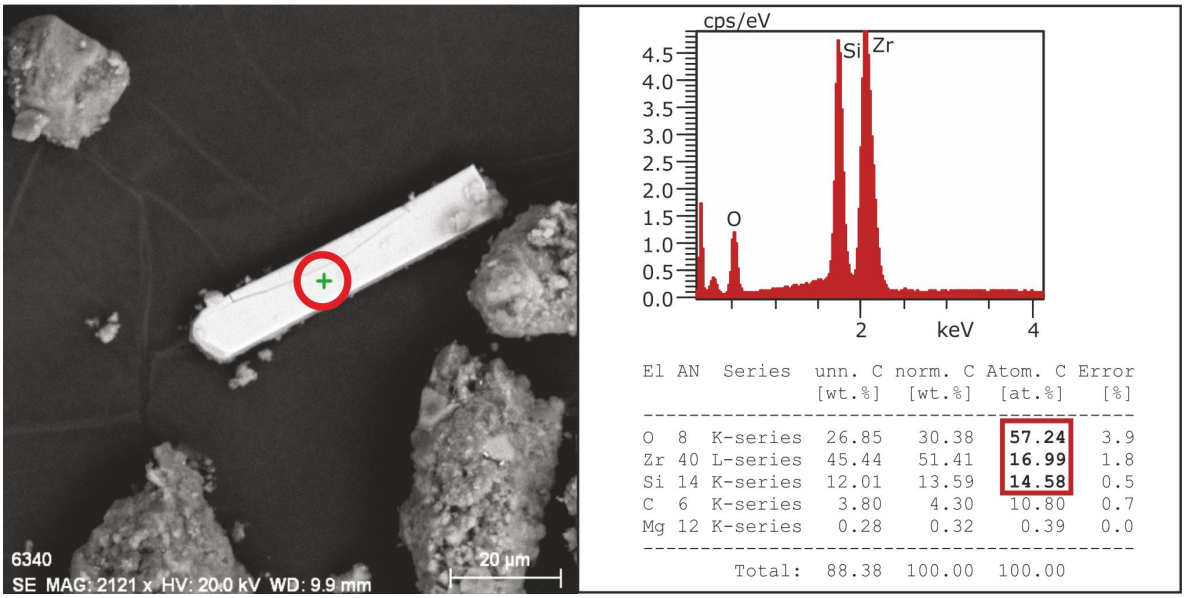

Fig. 5. Scanning electron microscopy image (left-hand part) and (right-hand part). The result of the X-ray fluorescence examination confirms Zr, Si and O as the main chemical elements in the composition. The elemental composition corresponds to the mineral $ZrSiO_4$, a zirconate also known as a cheap imitation of diamonds in the jewelry industry

As an example of a research, not only with Mössbauer spectroscopy, but also with the application of the neutron activation analysis method [18,19] can be cited. Iron of extraterrestrial origin can also be detected in small concentrations during special sampling. When meteors enter the atmosphere, vaporized meteoric material condenses, oxidizes and forms ultradispersed particles. It is believed that as a result of the nuclear reaction $^{56}Fe(n,\gamma)^{57}Fe$ during nuclear tests in the atmosphere the concentration of ^{57}Fe in the natural isotopic mixture was increased. An attempt to prove these processes was made in the series of works of the Kopcewicz family [12-14]. Kopcewicz drew attention to the fact that the filters taken during the deposition of Chernobyl pollution contained higher concentrations of iron oxides and hydroxides as well as a specific chemical composition (more magnetite Fe_3O_4), compared to filters taken before the accident. The authors claim that they also registered an increase in the isotopic concentration of ^{57}Fe in the natural isotopic mixture [12]. The last two main conclusions were verified by new measurements carried out with filters taken in Sofia by Rusanov and co-authors in the publication [9] cited previously. A substantial increase in the concentration of magnetite particles was demonstrated, but the second conclusion was not confirmed. Several control measurements were also carried out on filters taken years after the accident on days characterized by a highly dusty atmosphere (windy summer days) and on days with a clean atmosphere (winter days after a heavy snowfall), showing very strong changes in the concentration of iron under different shapes in the air of Sofia [9]. At this point, mention should be made of the work of Devell and co-authors [20] which is perhaps the first study of micrometric radioactive, "hot" particles from the Chernobyl fallout, conducted with scanning electron microscopy, autoradiography, beta- and gamma-spectroscopy. Very close to our current work is the recently published [21], which applies the same analytical methods - Mössbauer spectroscopy, scanning electron microscopy and additionally magnetometric measurements and X-ray diffraction studies of airborne magnetic technogenic particles in soils as a record of anthropocene pollutions.

The discussion of the experimental spectra starts with the most complex one since it contains all the subspectra that are also observed in the spectra of the other samples. For each of the five samples, RT indexing was used for measurements at room temperature and LT for measurements at liquid nitrogen temperature.

The RT-1 and LT-1 spectra represent the Mössbauer results obtained from the study of a dust sediment sample collected during the summer season of 2017 around the James Bourchier subway station. The measurements were carried out at room temperature and liquid nitrogen temperature, respectively. RT-1 is approximated by five Zeeman sextets and six quadrupole doublets, and LT-1 is approximated by four Zeeman sextets and four quadrupole doublets. The Mössbauer parameters of the two spectra are summarized in Table 2. Due to the similar compositions and close Mössbauer parameter values of the different samples, tabulated data is presented only for these two spectra.

In both spectra, RT-1 and LT-1, the S1 subspectrum with the largest Zeeman splitting corresponds to the mineral hematite, α-Fe_2O_3 [22]. The experimental line widths are normal, which is an indication of the presence of high particles crystallinity. The origin of hematite in the sample may be natural due to the widespread occurrence of the mineral. A technogenic origin of the hematite cannot be excluded because it is the ultimate stoichiometric member and a very stable product in various oxidation processes.

The RT-1 spectrum was taken above the Morin temperature ($T_M = 260\,\mathrm{K}$), and the LT-1 spectrum - below it. The IS isomer shift as well as the hyperfine magnetic field in LT-1 are larger than in RT-1. The change in the quadrupole splitting QS value at LT-1 is noticeable, which is due to the Morin phase transition. The measured value of the quadrupole splitting differs strongly from the known table values [23], which is probably due to a large amount of impurity atoms. Other authors, by temperature-dependent Mössbauer spectroscopy, also observed a decrease in the Morin transition temperature and other properties of hematite in the presence of impurity atoms [24].

The ratio of the partial areas of the two subspectra is two in favor of LT-1. This difference is largely due to the fact that hematite particles below 8 nm in size exhibit superparamagnetic behavior at room temperature. Since LT-1 was measured below the blocking temperature T_B, the fine dust particles exhibit antiferromagnetic properties and a significant part of the area of the

superparamagnetic component (D2 doublet) is transferred to the S1 sextet area. This may be the second reason for the difference between the measured and the reference values of the quadrupole splitting of the hematite particles from the LT-1 spectrum (Table 2).

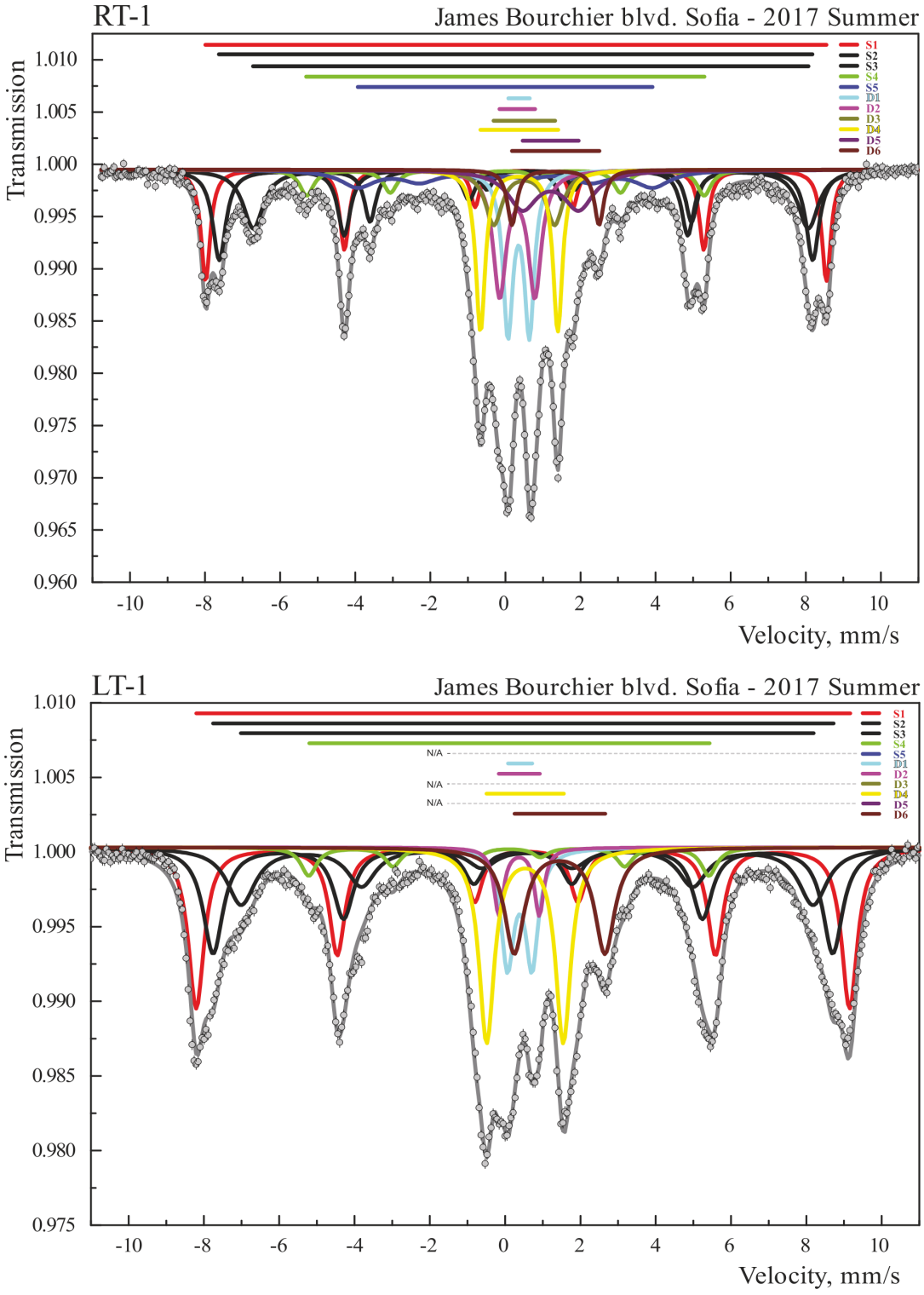

Fig. 6. Mössbauer spectra RT-1 and LT-1 obtained from the road dust sediments sample collected during the summer season of 2017 around the James Bourchier metro station

Table 2. Summarized Mössbauer parameters of spectra RT-1 and LT-1. In brackets the uncertainly of the last digital is given. Overall, the Mössbauer spectroscopic analysis provides valuable information about the composition, origin, and magnetic properties of dust sediment samples, shedding light on both natural processes and anthropogenic influences in the study area.

Sub-spectrum		IS [mm/s]	QS [mm/s]	B_{hf} [T]	Partial Area [%]	Γ_{exp} [mm/s]	Substance
S1	RT-1	0.39(1)	-0.22(1)	51.4(1)	13.4(8)	0.30(1)	α-Fe_2O_3, hematite
	LT-1	0.52(1)	0.09(1)	53.9(1)	25(1)	0.51(2)	
S2	RT-1	0.28(1)	0.00(1)	49.1(1)	15.3(9)	0.42(3)	Fe_3O_4, magnetite A-site
	LT-1	0.47(1)	0.00(1)	51.1(1)	21(1)	0.64(6)	
S3	RT-1	0.68(1)	0.01(1)	45.9(1)	12.8(8)	0.66(4)	Fe_3O_4, magnetite B-site
	LT-1	0.58(2)	0.01(1)	47.2(2)	16(1)	0.91(7)	
S4	RT-1	0.01(1)	0.01(1)	32.9(1)	5.0(7)	0.45(5)	α-Fe
	LT-1	0.10(1)	0.01(1)	33.0(1)	4.3(4)	0.50(1)	
S5	RT-1	-0.01(5)	0.01(1)	24.4(4)	7(1)	1.1(2)	Ferro-superparamagnetic component
	LT-1	–	–	–	–	–	
D1	RT-1	0.35(1)	0.57(1)	–	10(1)	0.32(2)	γ-FeOOH, lepidocrocite
	LT-1	0.39(1)	0.65(6)	–	7(1)	0.42(5)	
D2	RT-1	0.32(1)	0.94(4)	–	10(2)	0.42(5)	Superparamagnetic component
	LT-1	0.37(1)	1.07(6)	–	3(1)	0.31(8)	
D3	RT-1	0.50(3)	1.62(5)	–	6(2)	0.5(1)	Iron in silicates and glasses
	LT-1	–	–	–	–	–	
D4	RT-1	0.37(1)	2.06(1)	–	9.7(7)	0.30(1)	Iron in clay minerals
	LT-1	0.53(1)	2.03(1)	–	14.3(8)	0.49(2)	
D5	RT-1	1.20(4)	1.50(7)	–	7.1(9)	0.96(7)	Carbonates, siderite
	LT-1	–	–	–	–	–	
D6	RT-1	1.34(1)	2.32(2)	–	3.3(5)	0.30(4)	Olivine, Pyroxene
	LT-1	1.45(1)	2.41(2)	–	10.1(8)	0.64(4)	

At room temperature magnetite Fe_3O_4 is represented by two sextets corresponding to the A (S2) and B (S3) positions of the iron atoms in the spinel crystal structure. At the temperature of liquid nitrogen, the Mössbauer spectrum is significantly complicated due to suppression of electron delocalization from the donor–acceptor bond between Fe^{2+} and Fe^{3+} in the B-positions below the Verwey temperature ($T_V = 118\,\mathrm{K}$). The theoretical ratio of intensities A:B = 1:2 is very rarely fulfilled as it is in this case, indicating that magnetite is non-stoichiometric. The latter is also a strong indication of its man-made origin as an initial product of oxidation processes. It was found in large quantities around industrial areas, highways with intense traffic, even in Chernobyl radioactive deposits [9,10,13,14,18,19].

The partial areas of the two sextets for the A and B positions show an increase in the LT-1 spectrum relative to RT-1. It should be mentioned that magnetite particles with a size below 8 nm exhibit superparamagnetic properties at room temperature, too. The increase of S2 and S3 in the LT-1 spectrum at low temperatures is associated with a decrease in the relative area of the doublet component D2. The latter is also associated with magnetite particles exhibiting superparamagnetic properties. Again, this leads to a transfer of a part of the area of the superparamagnetic component (doublet D2) to the area of sextets S2 and S3 because the low temperature measurement was performed below the blocking temperature T_B.

The presence of sextet S4, which has the parameters of α-Fe, is clear evidence of an anthropogenic origin of much of the contamination. Fine dust particles with the structure of α-Fe and terrigenous origin are practically not found in nature. Due to the high degree of symmetry in the body-centered cubic crystal lattice of α-Fe, a practically zero value of the quadrupole splitting, and a very weak temperature dependence of the hyperfine magnetic field are expected. In the case of low-temperature measurements a temperature isomer shift occurs [12] as a result of the second-order Doppler effect. This results in the appearance of a noticeable additional shift in all subspectra. For the temperature difference between room temperature and the liquid nitrogen temperature, it is less than one natural line width, 0.097 mm/s, which often is not discussed by some authors. There is no significant difference in the partial areas of the S4 subspectrum measured at both temperatures.

In the RT-1 spectrum, the S5 subspectrum has a small magnetic Zeeman splitting and very large experimental line widths. The latter is proof of the presence of fine dust particles with sizes in the range of 2.5 ÷ 10 μm. As the particle size decreases for ultrafine dust particles, the sizes become smaller than 0.1 μm. These sizes are smaller than the size of the magnetic domains typical of magnetically ordered materials. The violation and weakening of the magnetic interaction at room temperature leads to a decrease in the intracrystalline magnetic field and a very strong broadening of the lines. The wide particle size distribution is also important. The spectrum remains a magnetic Zeeman sextet, but the parameters are unusual for iron oxides. A transition from ferro-, antiferro-, ferrimagnetic properties of magnetic particles to superparamagnetic properties at room temperature is observed. In the low-temperature measurement we find the complete absence of the S5 subspectrum (Fig. 6, Table 2). The reason for this is the complete transition of the ferro-superparamagnetic component, often called the "transition component", into a ferromagnetic one at liquid nitrogen temperature. A detailed study of such transients related to magnetic particle size and temperature influence in the case of cobalt ferrite is demonstrated in the publication [25].

Of the quadrupole doublet subspectra the D1 doublet is of significant intensity in both the RT-1 and LT-1 spectra. This is associated with γ-FeOOH, the mineral lepidocrocite - one of the most abundant iron hydroxides in nature. Its origin is probably natural although it is also a product of corrosion processes. There were no phase transitions in the temperature range in which the measurements were carried out. As expected, a Mössbauer parameters isomer shift, quadrupole splitting and line widths at low temperatures in LT-1 are of increased values. The relative area of D1 remains the same in both spectra RT-1 and LT-1. The Néel temperature for lepidocrocite is T_N = 77 K, but no sextet is observed in LT-1, which is probably due to low crystallinity and substitutions of Fe atoms with Al. Additionally, the measurement was carried out at a temperature about one degree higher. A transition to a magnetically ordered state would be observed at lower temperatures, depending on the number of defects and the amount of substituting Al atoms [23].

The doublet with larger quadrupole splitting D2, which is always associated with iron oxides that have gone into the superparamagnetic state, is essential to our considerations. This fraction should refer to the particles of the smallest sizes. In many cases it is a matter of nanometric sizes or tens of nanometers, and systems of such particles are defined as ultradisperse. The ultrafine superparamagnetic fraction transitions into a ferro-, ferri-, or antiferromagnetic state in measurements performed at liquid nitrogen temperature. The phase transition occurs at the blocking temperature T_B, which is different for different components, depending on the particle size and composition, but is usually higher than 77 K.

The iron in various silicates and glasses is of natural origin. At room temperature, the relative area is low, approximately 6%. The doublet shows wide lines. In LT-1 this subspectrum is not observed as a separate component. The most likely reason for this is its overlap with the doublet due to iron-bearing clay minerals, D4. In most cases the Mössbauer parameters increase with the temperature decrease, which results in an overlap of the lines.

Iron-bearing clay minerals are also of natural origin. On decreasing the temperature to nitrogen, the D4 doublet increases its area significantly. This is largely due to its overlap with D3. As for the other components, the increase in the probability of recoilless absorption *f* at low temperature leads to an increase in the areas of the subspectra.

Iron in carbonate minerals, of which the best known is the mineral siderite $FeCO_3$, which is also of natural origin, has a small contribution to the total area of the RT-1 spectrum and is not observed in LT-1. The reason for this is again the overlap of this subspectrum with lines of other components.

The group of olivines and pyroxenes is characterized by a relatively high iron content in the minerals. Here again, like D4, the doublet greatly increases its area at LT-1, due in part to its overlap with D5, and in part to the increased probability of recoilless absorption at the liquid nitrogen temperature.

Regarding the relative contribution of the magnetic and non-magnetic components in the spectra with rough uncertainty values we can summarize as follows: for RT-1, the total part of the magnetic components in the spectrum is 54(1)%, and the total part of the non-magnetic component is 46(1)%; for LT-1 the common parts of the components are 65(1)% and 35(1)% , respectively.

The RT-2 and LT-2 spectra represent the Mössbauer results obtained from the measurement of a dust sediments sample collected during the winter season of 2017 around the James Bourchier subway station and measured at room temperature and liquid nitrogen temperature, respectively. RT-2 is approximated by four Zeeman sextets and five quadrupole doublets and LT-2 is approximated by four Zeeman sextets and four quadrupole doublets (Fig.7).

Due to a similar composition and close Mössbauer parameter values of the samples, only the observed differences in the spectra will be discussed. The first significant difference is the absence of sextet S5 in both the RT-2 and LT-2 spectra. SEM studies show that the particles in the samples taken during the winter periods are larger, which suggests a decrease in the absolute amount of fine dust particles. The second significant difference is associated with doublet D2. At liquid nitrogen temperature measurement, the entire superparamagnetic component D2 transforms to the magnetic subspectra of LT-2.

The relative contribution of the magnetic and non-magnetic components in the spectra with rough uncertainty values can be summarized as follows: for RT-2 the total part of the magnetic components in the spectrum is 34(1)%, and the total part of the non-magnetic component is 66(1)%; for LT-2 the common parts of the components are in the spectrum LT-1 are 49(1)% and 51(1)%, respectively.

The RT-3 and LT-3 spectra represent the Mössbauer results obtained from a dust sediment sample collected during the summer season of 2017 around the Eagle Bridge and measured at room temperature and liquid nitrogen temperature, respectively (Fig. 8).

This location in the central part of the capital city is known for high air pollution mainly due to heavy traffic. RT-3 is approximated by four Zeeman sextets and five quadrupole doublets, and LT-3 is approximated by four Zeeman sextets and three quadrupole doublets (Fig. 8).

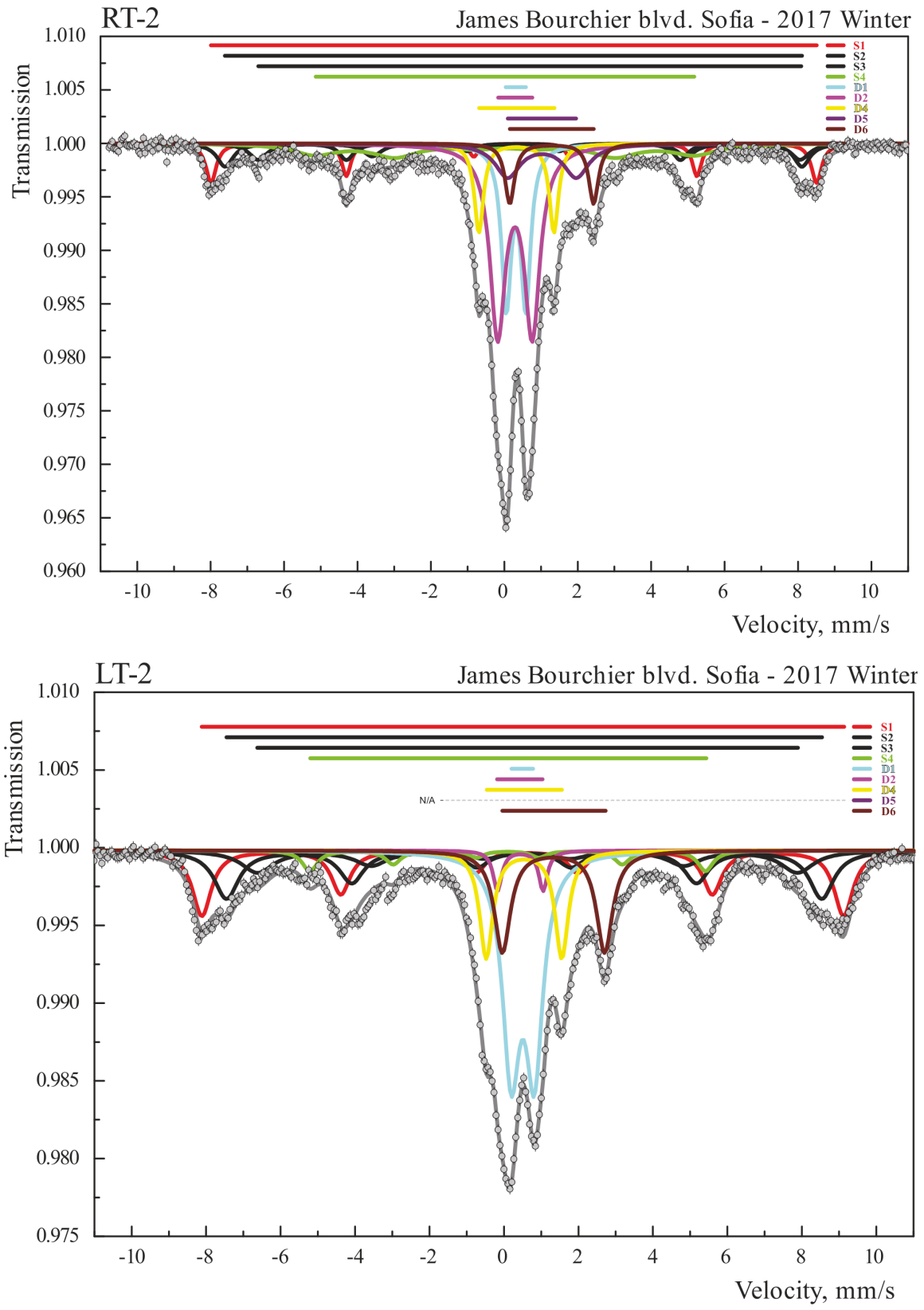

Fig. 7. Mössbauer spectra RT-2 and LT-2 obtained from the dust sediment sample, collected during the winter season of 2017 around the James Boucher metro station

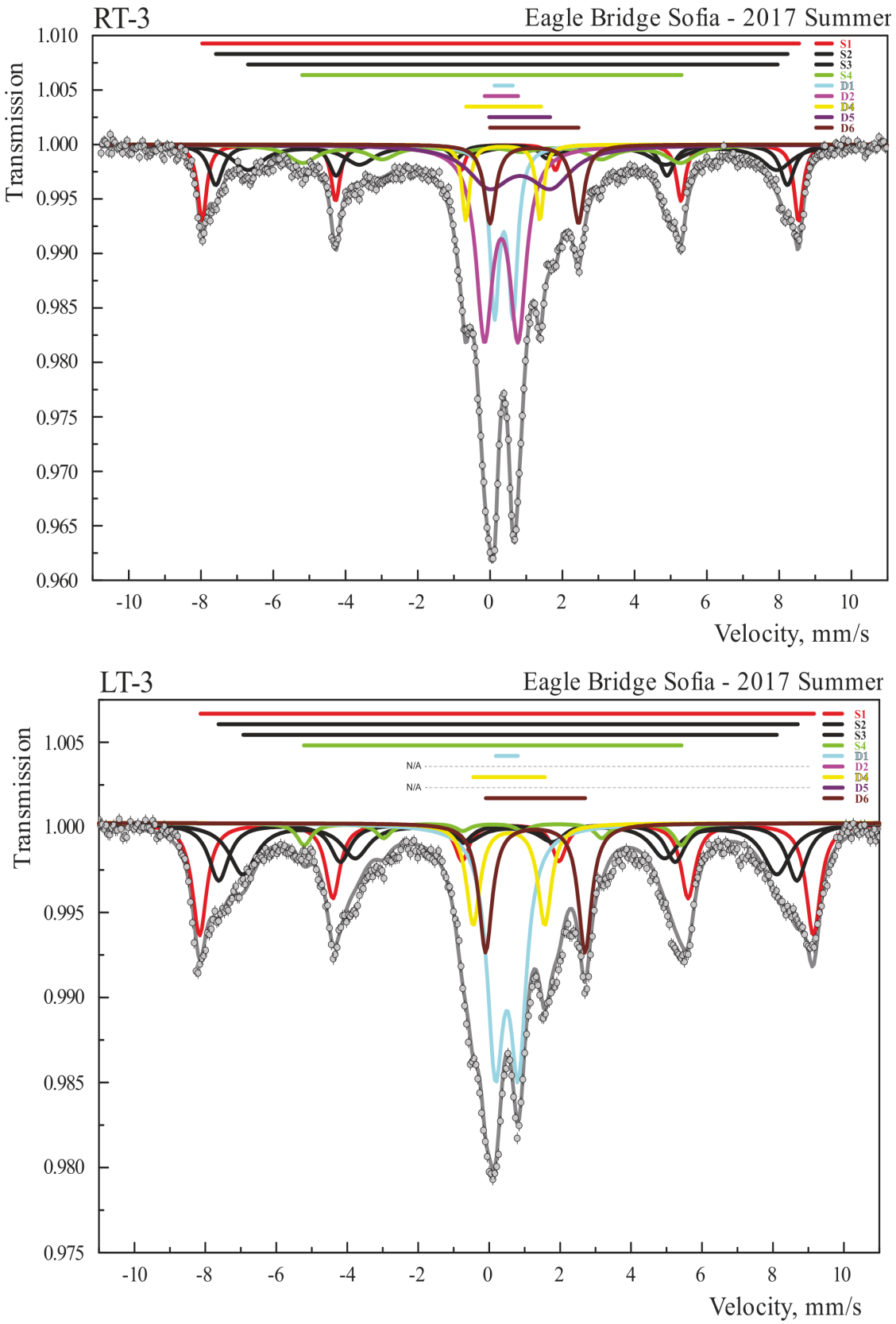

Fig. 8. Mössbauer spectra RT-3 and LT-3 obtained from the road dust sediment sample, collected during the summer season of 2017 around the Eagle Bridge

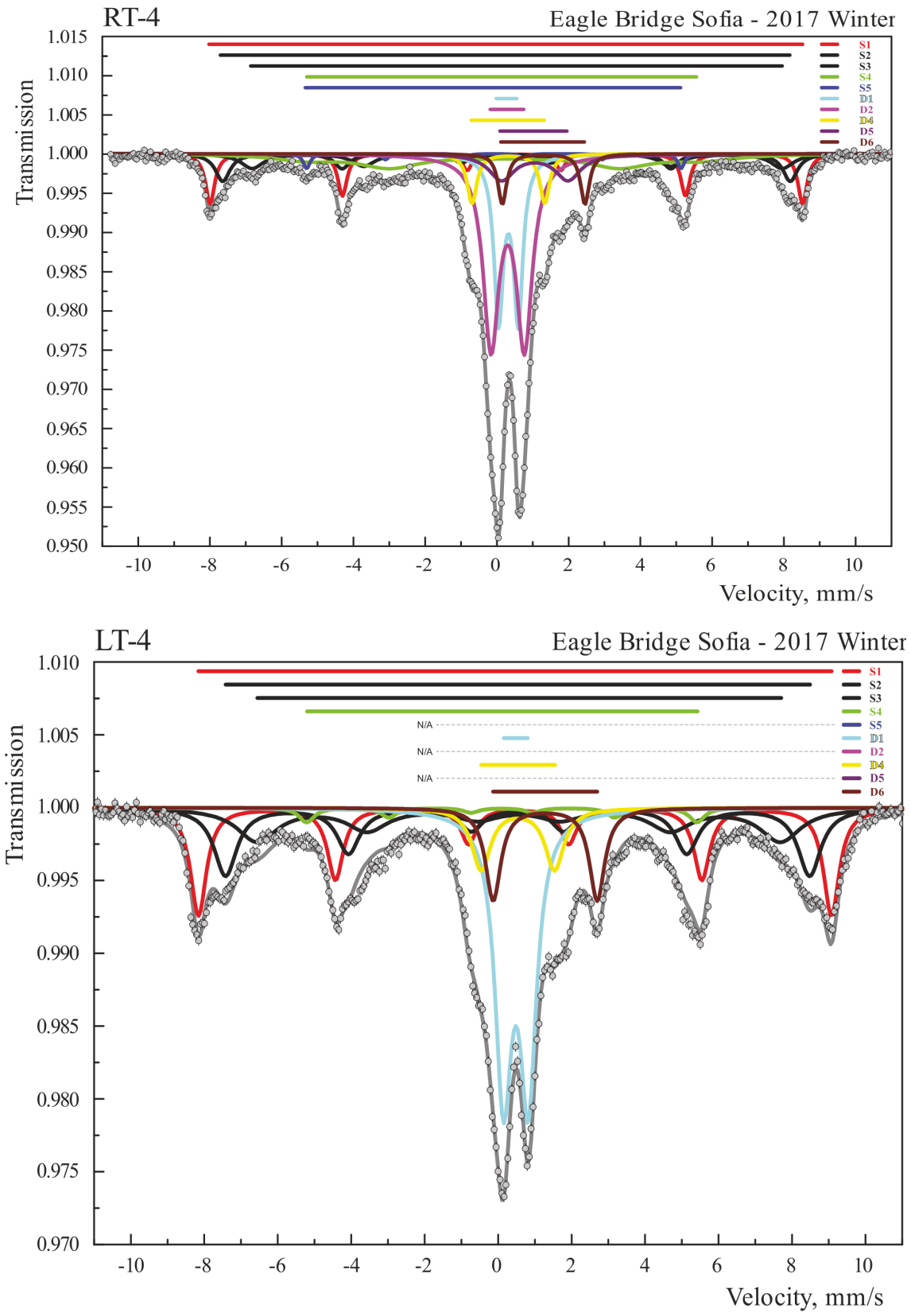

Fig. 9. Mössbauer spectra RT-4 and LT-4 obtained from the road dust sediment sample, collected during the winter season of 2017 around the Eagle Bridge

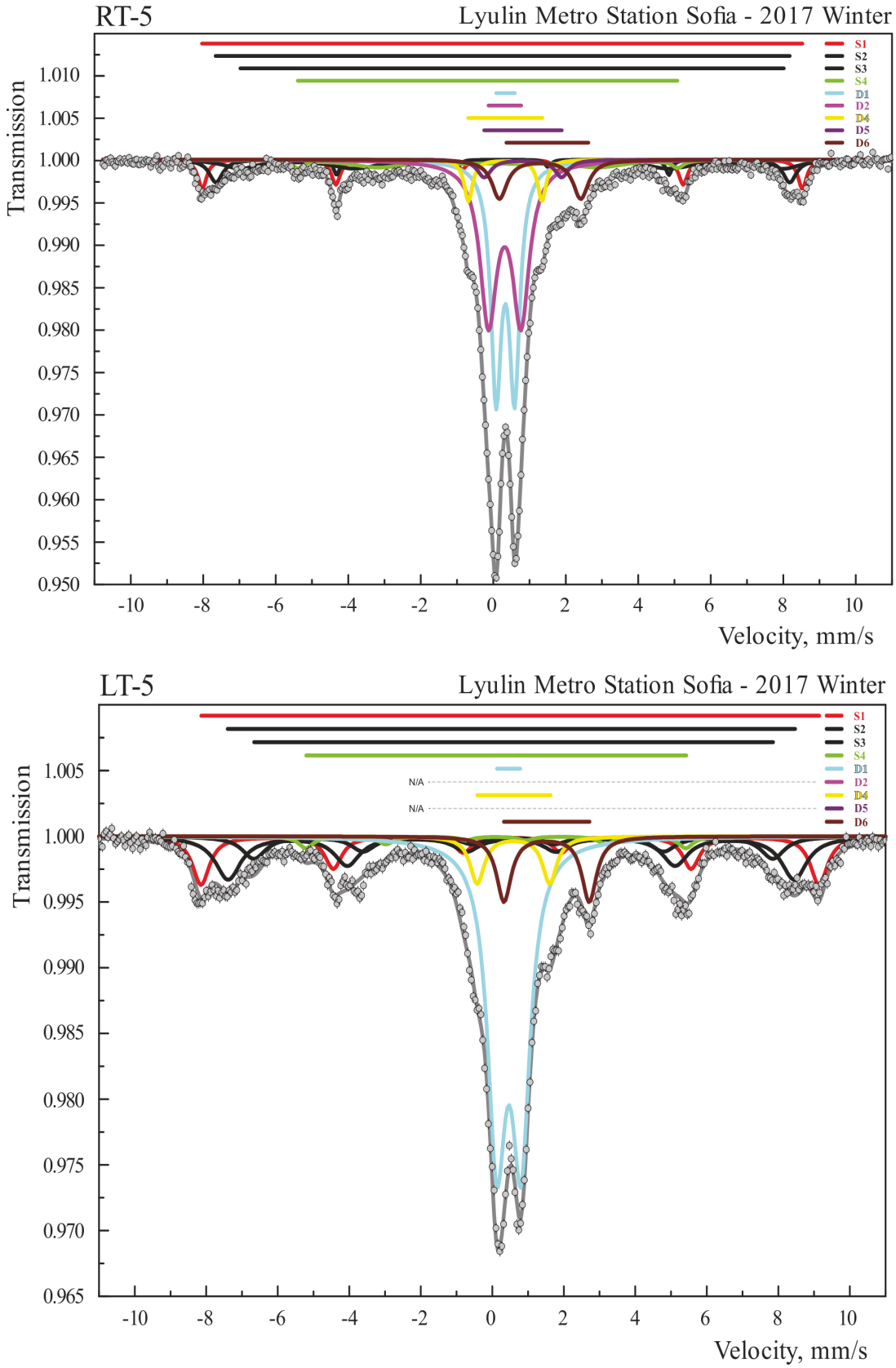

Fig. 10. Mössbauer spectra RT-5 and LT-5 obtained from the road dust sediment sample, collected during the winter season of 2017 around Lyulin metro station

From the sextet subspectra at RT-3, S5 is absent, associated with the transition component from ferro-, antiferro-, ferrimagnetic properties of magnetic particles to superparamagnetic properties. This is the main difference observed when compared to the other James Bourchier metro station summer sample measured at room temperature, RT-1. It can be concluded that the particles are of a smaller size and have already passed into the superparamagnetic state. This is confirmed by the large partial area of the D2 doublet at RT-3, corresponding to the superparamagnetic component of the sample. It is noteworthy that the spectrum measured at liquid nitrogen temperature, LT-3, is with a completely missing D2 doublet. The measurement at liquid nitrogen temperature was carried out below the blocking temperature T_B, and under these conditions, the entire fraction of fine and ultrafine dust particles transitioned into the magnetically ordered phase.

Regarding the relative contribution of the magnetic and non-magnetic components in the spectra with rough uncertainty values, we can summarize as follows: for RT-3 the total part of the magnetic components in the spectrum is 41(1)%, and the total part of the non-magnetic components is 59(1)%; for LT-3 the common parts of the components are 57(1)% and 43(1)%, respectively.

The RT-4 and LT-4 spectra represent the Mössbauer results obtained from the dust sediment sample, collected during the winter season of 2017 around the Eagle Bridge, and measured at room temperature and liquid nitrogen temperature, respectively. The RT-4 is approximated with five Zeeman sextets and five quadrupole doubles, and the LT-4 is approximated with four Zeeman sextets and three quadrupole doublets (Fig. 9).

These spectra and their corresponding parameters are very close to those obtained from measuring the sample taken during the summer period from the Eagle Bridge location. During the winter period, in RT-4, the S5 subspectrum is observed. It is associated with the component that undergoes a smooth transition from ferro-, antiferro-, ferrimagnetic properties of magnetic particles to superparamagnetic ones. This is consistent with SEM results, where winter fractions were shown to be coarser-grained than summer ones.

Regarding the relative contribution of the magnetic and non-magnetic components in the spectra with rough uncertainty values we can summarize as follows: for RT-4, the total part of the magnetic components in the spectrum is 40(1)%, and the total part of the non-magnetic component is 60(1)%; for LT-4 the common parts of the components are 57(1)% and 43(1)%, respectively.

The RT-5 and LT-5 spectra represent the Mössbauer results obtained from a dust sediment sample collected during the winter season of 2017 around Lyulin metro station and measured at room temperature and liquid nitrogen temperature, respectively. RT-5 is approximated by four Zeeman sextets and five quadrupole doublets, and LT-5 is approximated by four Zeeman sextets and three quadrupole doublets (Fig. 10).

The spectrum measured at liquid nitrogen temperature, LT-5, completely lacks the D2 doublet. This temperature is below the blocking T_B for the fraction of fine and ultrafine dust particles in the sample, and the corresponding fraction has transferred to the magnetically ordered state. It is noteworthy that the low concentration of magnetic components in the spectra. The relative contribution of the magnetic and non-magnetic components in the spectra with rough uncertainty values can be summarized as follows: for RT-5 the total part of the magnetic components in the spectrum is 28(1)%, and the total part of the non-magnetic component is 72(1)%; for LT-5 the common parts of the components are in the spectrum LT-1 are 43(1)% and 57(1)%, respectively. The partial areas of the quadrupole doublets, which are always associated with natural minerals of terrigenous origin, are very high, which is explained by the fact that Lyulin Residential Area is the westernmost part of Sofia, the capital city. It can be concluded that of all controlled locations, this is the place with the lowest atmospheric air pollution. It is known that the westerly transfer is dominant for the air masses above Sofia, which excludes the transfer of man-made pollution. For the most fine particles weathered and transported into the troposphere may be of natural, terrigenous origin.

4. CONCLUSIONS

The main results are related to a qualitative and semi-quantitative study of iron-containing particles in the road dust sediments in urban environment of Sofia. It should be specified that

the focus is on fine dust particles whose sizes vary from 2.5 ÷ 10 μm, the so-called PM10. Additional research provides information on the presence of ultrafine dust particles, the sizes of which are submicron and even nanometric. The two research methods chosen are Mössbauer spectroscopy and scanning electron microscopy with the possibility of X-ray fluorescence analysis and determination of the chemical elemental composition of the objects as well as their size and shape. The Mössbauer spectroscopy studies at liquid nitrogen temperature allow making, if not quantitative, at least semi-quantitative estimates of the content of ultrafine iron-containing particles with superparamagnetic properties. The main results of the study can be summarized as follows:

1. In places with intense traffic and large-scale construction activities, an increased concentration of man-made dust deposits is noticed, which is an expected result. Additionally, weathering and transportation increase air pollution with dust particles.
2. Iron-containing chemical compounds, minerals and alloys are diverse. Iron is included in the form of oxides and hydroxides. Most of these components may have a terrigenous origin, but a technogenic one cannot be excluded.
3. The presence of a large amount of fine dust particles of metallic iron, α-Fe, is surprising. Small amounts of cementite, Fe_3C, are probably also present in the spectra. The presence of these components in the spectrum is clear evidence of a significant technogenic contribution of the dust deposits and contributes to the pollution of Sofia's air with fine dust particles. Their origin must be connected to the wear and tear of internal combustion engines and the intense road traffic in the capital. The statement that fossil fuels are the main pollutant of fine particulate matter may be incomplete. Technogenic pollution is also a major contributor. The vehicle fleet in Sofia is very old and vehicle inspections are carried out formally. This needs to be corrected to reduce the technogenic component of pollution.
4. The main amount of contamination is related to various silicate, clay and carbonate mineral components whose terrigenous origin is unquestionable. Particles with sizes of tens of microns are entirely associated with the terrigenous silicate component. The technogenic component is relatively smaller in size, which is in the submicron and even nanometer range. As shown by Mössbauer spectroscopic studies at liquid nitrogen temperature, the finest dust component with concentrations between 10 and 20% is in a superparamagnetic state. Man-made iron-containing particles are observed as fine incrustations on the surface of silicates. Several exotic fine dust objects of diverse shapes and chemical compositions were observed.

ACKNOWLEDGMENTS

This research was funded by the National Roadmap for Research Infrastructure 2020-2027 for the National Cyclotron Centre funded by the Bulgarian Ministry of Education and Science**.**

The authors are obliged to Prof. D. Jordanova for making samples available. We thank very much Prof. S. Russev for his assistance in the scanning electron microscope studies. Thanks are due to Mrs. M. Nikolova for the critical reading of the manuscript. We are very grateful to Prof. D. Tonev for his interest in this work and helpful discussions and for the opportunity to work at INRNE. Prof. V. Rusanov gratefully acknowledges the continuous support of the Alexander von Humboldt Foundation.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. European Commission. (n.d.). Marked improvement in Europe’s air quality. Accessed On:November 24, 2022. Available:https://ec.europa.eu/commission/presscorner/detail/en/ip_20_2168
2. EUR-Lex - 32008L0050 - EN - EUR-Lex. (n.d.). Accessed On: March 20, 2023. Available:https://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX%3A32008L0050

3. EUR-Lex. (n.d.). EUR-Lex - 62015CJ0488 - EN - EUR-Lex.
Accessed On: November 24, 2022.
Available:https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A62015CJ0488
4. European Commission. (n.d.). Air quality: Commission decides to refer BULGARIA. Accessed On: November 24, 2022,
Available:https://ec.europa.eu/commission/presscorner/detail/en/ip_20_2150
5. AirBG.info- Sofia. (n.d.).
Accessed On: https://airsofia.info/
6. Casotti Rienda L, Alves CA, Nunes T, Soares M, Amato F, Sánchez de la Campa A, Kováts N, Hubai K, Teke G. PM10 Resuspension of Road Dust in Different Types of Parking Lots: Emissions, Chemical Characterisation and Ecotoxicity. Atmosphere. 2023;14(2):305.
Available:https://doi.org/10.3390/atmos14020305
7. Amato F, Pandolfi M, Viana M, Querol X, Alastuey A, Moreno T, Spatial and chemical patterns of PM10 in road dust deposited in urban environment. Atmospheric Environment. 2009;43(9):1650–1659.
Availablehttps://doi.org/10.1016/J.ATMOSENV.2008.12.009
8. Gütlich Ph, Bill E, Trautwein AX. Mössbauer spectroscopy and transition metal chemistry: Fundamentals and Applications. Springer-Verlag; 2011.
9. Rusanov V, Gushterov V, Winkler H, Trautwein AX. Iron-containing atmospheric aerosols in the Chernobyl fallout. Hyperfine Interactions. 2005;166(1–4):625–630.
Available:http://dx.doi.org/10.1007/s10751-006-9331-4
10. Kopcewicz B, Kopcewicz M. Mössbauer study of iron-containing atmospheric aerosol collected during the chernobyl accident. Industrial Applications of the Mössbauer Effect. 2002;657–665.
Available:https://doi.org/10.1007/978-94-010-0299-8_72
11. Žák T, Jirásková Y. CONFIT: Mössbauer spectra fitting program. Surf. Interface Anal. 2006; 38:710-714.
Available:https://doi.org/10.1002/sia.2285
12. Kopcewicz B, Kopcewicz M. Mössbauer study of iron-containing atmospheric aerosol collected during the Chernobyl accident. Hyperfine Interact. 2002;139/140(1–4):657.
Availablehttps://doi.org/10.1023/a:1021243400103
13. Dzienis B, Kopcewicz M. Tellus. 1973;XXV:213.
14. Kopcewicz B, Kopcewicz M. Tellus. Tellus. 1978;30:562.
15. Gonser U. (Ed.). Mössbauer Spectroscopy II:The Exotic Side of the Method. Springer Berlin Heidelberg. 1981;25
Available:https://doi.org/10.1007/978-3-662-08867-8
16. Kopcewicz B, Kopcewicz M. Mössbauer. In K. R. Spurny (Ed.), Analytical Chemistry of Aerosols. Lewis Publishers. 1999;185.
17. Elzinga EJ, Gao Y, Fitts JP, Tappero R, Iron speciation in urban dust. Atmospheric Environment. 2011;45(26):4528–4532.
Available:https://doi.org/10.1016/j.atmosenv.2011.05.042
18. Wiesinger G, Ismail SS. Characterization of Fe bearing compounds in environmental samples. Hyperfine Interactions. 1990; 57(1–4):2319–2325.
Available:https://link.springer.com/article/10.1007/BF02405806
19. Wiesinger G, Ismail SS. Nuclear methods in environmental research. Hyperfine Interactions. 1991;66(1–4):203–220.
Available:https://link.springer.com/article/10.1007/BF02395868
20. Devell L, Tovedal H, Bergström U, Appelgren A, Chyssler J, Andersson L. Initial observations of fallout from the reactor accident at chernobyl. Nature. 1986;321(6067):192–193.
Available:https://doi.org/10.1038/321192a0
21. Wilczyńska-Michalik W, Michalik JM, Kapusta C, Michalik M. Airborne magnetic technoparticles in soils as a Record of Anthropocene. Atmosphere 2020;11(1):44.
Available:https://doi.org/10.3390/ATMOS11010044
22. McCammon C. Mineral Physics and Crystallography, A handbook of

physical constants, AGU reference shelf 2, mössbauer spectroscopy of minerals. American Geophysical Union; 1995.

23. Cornell RM, Schwertmann U. The iron oxides: structure, properties, reactions, occurrences and uses. Wiley Verlag; 2003.
24. Popov N, Ristić M, Kuncser V, Zadro K, Velinov N, Badica P, Alexandru-Dinu A, Iacob N, Kratofil Krehula L, Musić S, Krehula S. Influence of erbium doping on the structural, magnetic and optical properties of hematite (α-Fe2O3) nanorods. Journal of Physics and Chemistry of Solids. 2022;169:110857. Available:https://doi.org/10.1016/J.JPCS.2022.110857
25. Grigorova M, Blythe HJ, Blaskov V, Rusanov V, Petkov V, Masheva V, Nihtianova D, Martinez LM, Muñoz JS, Mikhov M. Magnetic Properties and Mössbauer Spectra of Nanosized CoFe2O4 Powders. Journal of Magnetism and Magnetic Materials. 1998;183:163–172. Available:https://www.sciencedirect.com/science/article/pii/S0304885397010317

Peer-review history:
The peer review history for this paper can be accessed here:
https://prh.ikprress.org/review-history/12136