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ELEMENTAL COMPOSITION OF AIR PARTICULATE (PM10) IN SOFIA BY EDXRF TECHNIQUES

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ABSTRACT

Particulate matter (PM) and its fraction PM10, belong to the major air pollutants in urban environment, because of their effects on air quality and human health. It is important to study in greater details the impact of different PM10 sources on the mass concentration when exceeding the air quality limit and its target values, observed in Sofia. In order to investigate the PM10 variations in connection with the elemental composition and the influence of the meteorological conditions, winter and summer campaigns with standardized low-volume PM10 sampler were organized at National Institute of Meteorology and Hydrology (NIMH) Sofia, in 2012. In the present paper the results for PM10 mass concentration and its elemental composition are compared and discussed. In general PM10 concentrations are higher in February (17.7-160.1 $\mu g.m^{-3}$) than those measured in July (15.5-42.7$\mu g.m^{-3}$), because of the different meteorological conditions. The ED-XRF technique is applied to determine more than 20 elements (P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, I, Ba, Pb) in the filter samples. The concentrations of some of the elements are under the detection limits of EDXDR, in particular for the PM10 summer filter samples. The elemental concentrations are lower in July than in February with an exception for the crustal elements Ca and Fe.

Keywords: urban air pollution, PM10, elemental composition, EDXRF analyses.

INTRODUCTION

The suspended particulate matter (SPM) in air is generally a complex, multi-phase system of all airborne solid and low vapor pressure liquid particles, with aerodynamic particle sizes from 0.01 to more than 100 µm. Studies on the health effects of SPM in ambient air have been focused increasingly on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10 µm. SPM can be presented as total suspended particulate (TSP), PM10, PM2.5 and PM1. PM10 is particulate matter with an aerodynamic diameter of 10 µm or less, PM2.5 (fine PM) is with an aerodynamic diameter of 2.5 µm or less. Aerosol is considered as primary or secondary depending of its formation [1]. 21 % of the urban population in Europe is exposed to PM10 concentrations above the EU reference value of 50 µg m^{-3} (a 24-hours mean concentration) [2]. Sofia has the highest health risk of air pollution in comparison with other Bulgarian cities, because of the topography of the closed Sofia valley surrounded by mountains, and the presence of different industrial, traffic and domestic pollutant sources which could affect the most populated area in the country. The harmful impact of PM depends not only on the size but to a significant extent on the chemical composition of the aerosol particles. Therefore, it is an important task to characterize the chemical composition of particulate matter as a whole and of PM10 in particular. The European Union has established ambient air quality standards for certain toxic elements, such as lead, cadmium, arsenic, nickel, mercury and the carcinogenic benzo[a]pyrene [3]. Air quality guidelines are recommended by the World Health Organization for other elements [4].

In general, the origin of the trace elements in air particulate can be from: Soil dust - most of the crustal elements with high concentrations of Si, Al, Fe, Ca and partialy of K, with an important contribution to the coarse aerosol [5]; Vehicles emitted elements as Cu, Zn, V, Sb, Pb and Ni have been widely used as representative markers for vehicle sources [5]; For Biomass burning – the representatives are mainly K, Ca, Mn and Sr, especially during the periods when the wild fires occurs [6]; Industrial sources - many elements such as Ti, V, Cr, Cu, Zn, Sb, Fe, Ni and As may be associated with metallurgical and chemical industries. Source of Ti, Cr, Fe, Ni, As, Rb, Sn and Ba could be fly-ash particles resulting from high-temperature processes, such as coal burning [7]; Sea salt aerosol is the main source of Na, Cl and K [1, 8].

The methods applied to determine multielemental trace concentrations in airborne particulate matter, mostly require sample digestion, often followed by extraction and further analyses by Atomic Absorption Analyses (AAS); inductively coupled plasma atomic emission and mass spectrometry (ICP-AES/ MS) ([8, 9]. On the other hand, the ion beam analysis techniques, such as the Rutherford backscattering spectroscopy (RBS) and the particle-induced X-ray emission (PIXE) [10] and X-ray fluorescence spectrometry (ED-XRF) [6, 9, 11] are fast and do not require sample pretreatment. Between them XRF has the advantage to be a non-destructive method.

The main aim of the present work is to investigate the advantages and limits of the EDXRF technique to characterize the variations of the elemental composition of PM10 in the urban air.

EXPERIMENTAL

PM10 sampling was carried out at the site of NIMH Central Meteorological Station (CMS) during winter (February 2012) and summer (July 2012). Twenty-four hour samples were collected according to EN-12341 on 47 mm quartz fiber filters (Whatman 1851-047-QMA), using certified low volume air sampler Tecora Echo PM (flow rate of ~38 l/min). Filters were weighed before and after sampling with an analytical balance (Mettler Toledo, AG135). The conditioning of the filters was for 48 - 96 hours in a temperature and humidity controlled room ($T = 20\pm2^{o}C$, $RH = 50\pm5$ %). Temperature differences between pre-sampling and post-sampling weighing were usually within 1°C and relative humidity - within 10 %. The average mass at least 3 repetitive weightings (blank /loaded) is for the results used further.

The sampling procedure and the used equipment is of the same type as applied in the Executive Environmental Agency (ExEA) of Ministry of Environment and Waters (MoEW) network for air pollution monitoring, thus permitting comparative assessment with ExEA data set [12].

The exposed quartz fiber filters were analyzed by EDXRF in Institute of Nuclear Research and Nuclear Engineering-Bulgarian Academy of Sciences (INRNE-BAS). Three spectrometric systems have been applied:

- The first one is equipped with a Si (Li) detector with 25 μ Be window and 170 eV energy resolution at 5,9 keV Mn-Ka line (PGT). This system is combined with an exciting head, based on an annular source Am-241 and three secondary targets (Mo, Dy, Sn).
- The second system is equipped with a Si pin diode detector, Peltier cooling, with 7 μBe window at 140 eV (KETEK). One exciting head, especially designed for low Z elements determination, is supplied with three radionuclide sources Fe-55.
- The third system is equipped with a Si pin diode detector, Peltier cooling, with 7μ Be window at 140 eV (KETEK). One exciting head with source of Pu-238, is especifially designed for analyzing elements with Z between 17 and 35.

The XRF spectra were analyzed with the specialized software X-Ray-Fit1 [13]. By these three spectrometric systems it was possible to determine more than 20 elements: P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, I, Ba, Pb. The low concentrations in the filter samples require long measurement time – 10000 s.

An available suitable standard for XRF analysis of aerosol filters in the INRNE Lab is the Community

Bureau of Reference BCR, Reference material 128, "Fly ash on filter". In this reference material only a few elements are presented. Therefore, 5 filters from the experimental campaign in February 2012 with different mass loadings were chosen, corresponding to different atmospheric conditions and used as "internal standards". These 5 filters were analyzed in the AGH University, the Krakow laboratory, and after that - on the spectrometric systems in INRNE-BAS. In addition, the same 5 filters were measured in the laboratory in IMI, Zagreb, and in the Albanian Centre of Applied Nuclear Physics. This intercomparison exercise has helped to evaluate the elemental concentrations in the PM10 samples collected in 2012.

RESULTS AND DISCUSSION

Systematic monitoring of the air particulate fraction PM10 in the urban atmosphere of Sofia is performed since about 2005 by the monitoring stations of the Ministry of Environment and Waters (MoEW) and the Ministry of Health (MH). Analysis of the annual variation of PM10 and a relation to NIMH TSP data in Sofia during the period 2005-2011, can be found in [14].

PM10 data from the urban monitoring stations of the Executive Environmental Agency (ExEA) of MoEW are presented in Fig.1. Well distinguished seasonal patterns are observed with maximums in the cold period of the year (first and fourth quarter) for all urban stations. Minimums are observed in the summer months, when the mixing conditions in the atmosphere are better due to more intensive turbulent diffusion that results in lower measured concentrations. The PM10 concentrations in Fig. 1 show similar seasonal variations because of the key impact of the meteorological conditions influencing the mixing in the urban atmosphere over the territory of Sofia.

The high correlation between mean monthly PM10 concentrations ($R^2 = 0.86; 0.96$) show that the processes forming the PM10 concentration fields at Drujba, Pavlovo, Orlov most and Nadejda are the same, in spite of their locations in different directions from the city center of Sofia (at 5 - 8 km distance).

PM10 seasonal patterns (like those observed in Sofia, Fig. 1) are observed in other European regions with a prevailing continental climate [15].

Winter and summer experimental campaigns were organized in chosen representative winter and summer months for measuring of PM10 in Sofia at NIMH-CMS (central meteorological station) in February (from 6 to 25) and in June (from 2 to 26) 2012. The averaged meteorological data are based on synoptic data from the NIMH-CMS Sofia and analyses. February 2012 was colder than the normal (with -3.4°C mean monthly value) and July was warmer (25°C) than normal [16].

The winter experiment performed in February 2012 was characterized with cold and cloudy weather with low wind velocity and stable snow cover during the sampling period. The daily mean relative humidity was in the range of 63 – 90 %, and calm weather prevailed, especially for the period from 19 to 23 February.

The PM10 concentrations in February (Fig. 2a) are significantly higher than in July (Fig. 2b), regardless

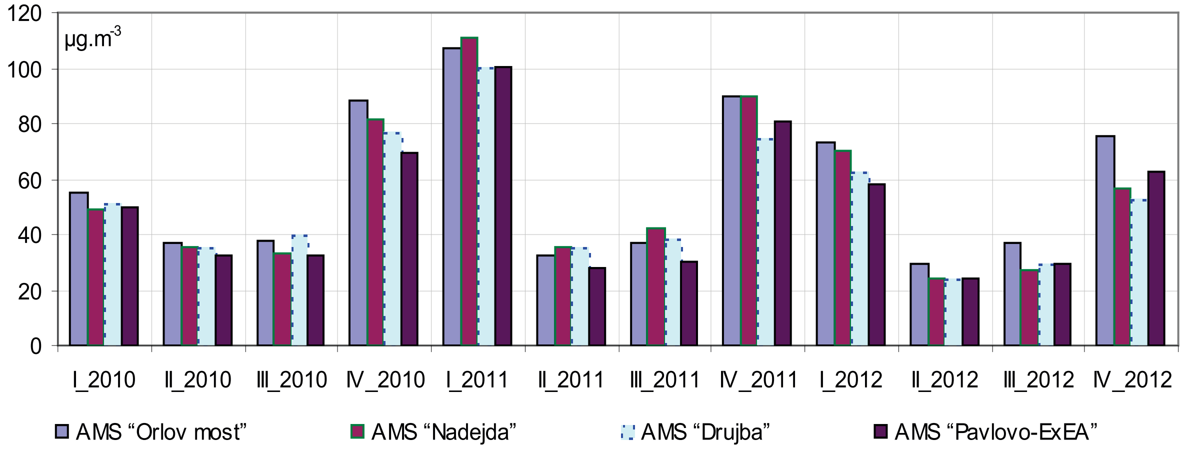

Fig. 1. Mean PM10 quarterly concentration in air quality monitoring stations (AMS) in Sofia, 2010-2012. (ExEA data, http://riosv.riew-sofia.org/)

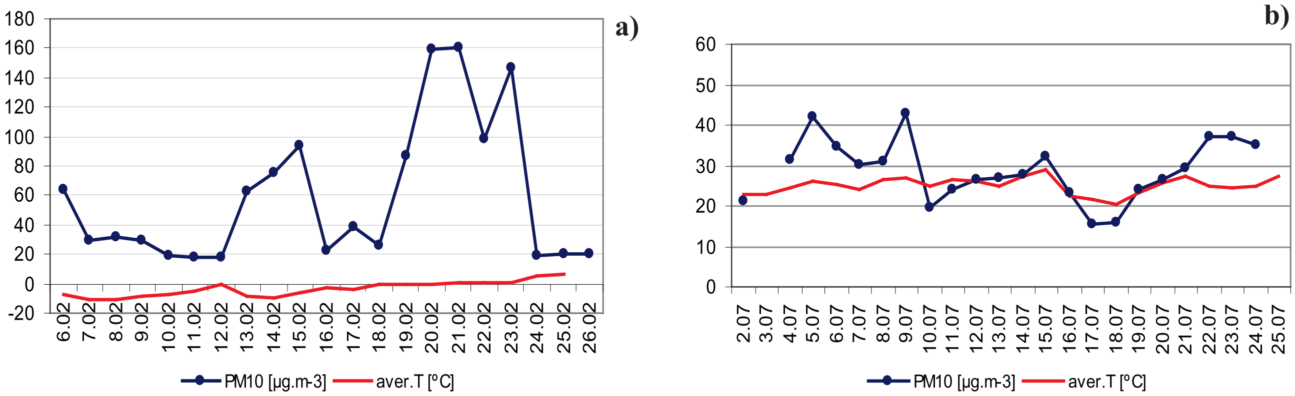

Fig. 2. Mean 24-hours PM10 concentration at NIMH Sofia station in a) February and b) July 2012 and mean daily temperature [°C].

of the high number of days with snow. In 9 of 20 days the PM10 concentration exceeded the threshold value of 50 µg m^{-3}. Periods with PM10 > 60 µg m^{-3} in several consecutive days are 13 - 15 and 19 - 23 of February. The last period (from 19 to 23 Feb.) was characterized with highest PM10 measured concentrations (around 150 µg m^{-3}) explained with the anticyclonic weather, calm conditions, temperature increase (around and above zero) - the type of atmospheric conditions favorable for high air pollution episodes.

During the summer experimental campaign in July 2012, the weather was hot with high summer temperatures, low wind (daily mean < 1.5 m s^{-1}) and mean relative humidity below 60 %, with scarce

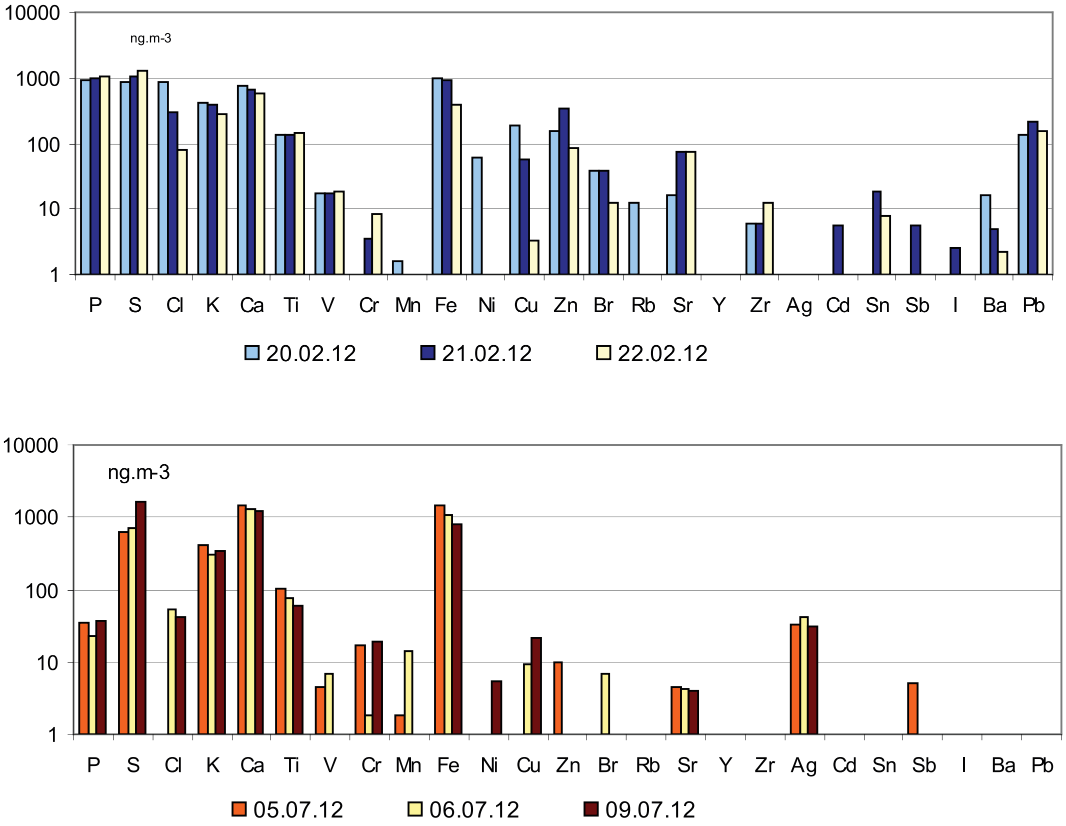

Fig. 3. Elemental composition of PM10 samples in selected days in February and July 2012.

Table 1. Mean daily concentration and range of PM10 and elements determined by EDXRF.

Element	February, 2012			July, 2012		
	Average ng m^{-3}	Range ng m^{-3}	N*	Average ng m^{-3}	Range Ng m^{-3}	N
PM10	63300	17700÷160100	19	28900	15500÷42700	22
P	534.1	18÷1052	16	30.6	5÷97	9
S	975.6	288÷2740	19	742.3	274÷1620	18
Cl	117.3	8÷868	19	31.1	7÷55	15
K	259.9	55÷495	19	235.8	114÷417	18
Ca	338.2	7÷751	19	854.0	514÷1435	18
Ti	69.2	2÷149	19	37.9	9÷104	18
V	9.1	1÷19	17	3.8	1÷8	16
Cr	8.3	2÷23	12	7.4	1÷20	17
Mn	60.2	2÷174	3	8.1	1÷18	17
Fe	356.9	53÷993	19	714.0	290÷1537	23
Ni	37.6	21÷62	3	5		1
Cu	43.2	2÷183	16	16.5	5÷30	6
Zn	102.1	1÷440	16	14.4	2÷32	7
As				65.1	21÷152	3
Br	24.2	8÷51	14	4.7	3÷7	2
Rb	6.7	3÷13	9	5		1
Sr	22.5	1÷75	15	5.2	1÷12	17
Zr	7.4	3÷12	7			
Ag				34.09	16÷50	23
Cd	5.8	2÷14	8			
Sn	8.8	3÷19	7			
Sb	6.1	3÷11	9	6.6	2÷16	16
I	3.4	1÷8	10			
Ba	9.5	1-26÷	15			
Pb	75.5	5÷209	13	44		1

(N* is the number of samples in which the given element is measured).

precipitations. These meteorological conditions are favourable for air pollutants dispersion and lead to low measured PM10 concentrations (< 50 μg m^{-3}). Relatively high concentrations were measured on 5th, 6th and 9th of July, when low Eastern winds were prevailing. Lower concentrations were measured on 16th and 17th of July with a Western wind of 2-3 m s^{-1} (Fig. 2b).

The elemental composition of PM10 in days with high mass concentration in February and July is presented in Fig. 3. It is well seen that more elements with concentration above the detection limit are measured in winter than in the summer. The concentrations of most of the analyzed elements are lower in summer, excluding calcium and iron. The average concentrations of Ca and Fe in summer are about 2 times higher in respect to the winter (Table 1). This can be explained with the relatively higher impact of soil dust in the summer, in comparison to the specific conditions with permanent snow cover in February 2012. The Pb concentration was measured in one sample in July in opposite to more regular Pb presence in the February samples.

It is important to note that the concentrations plotted in Fig. 3 are shown on a logarithmic scale. While the macro elements can be analyzed in all of the PM10 samples in February, some of the microelements like Sn and Sb are below the limits of detection approximately in half of the winter samples. Other microelements, like Ni are measured in a few samples in February and in one in July. The concentrations of macro elements K, Ca, Fe are in the range from less than 50 to 1000 ng m^{-3} in winter and from 100 to 1600 ng m^{-3} in summer. The phosphorous concentration is in the same range only in

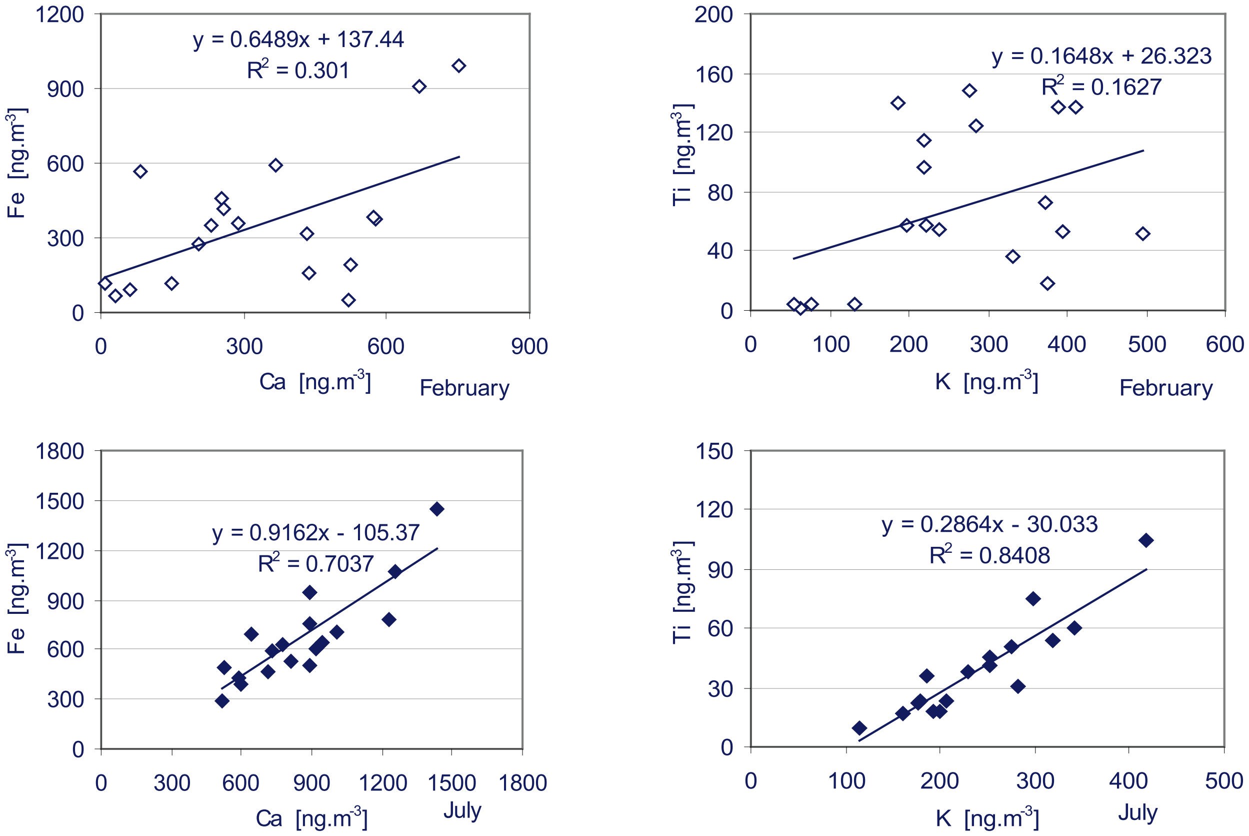

Fig. 4. Scatter plot of Fe and Ca concentrations (left panel) and K/Ti (right panel) during winter and summer experiments in Sofia 2012.

February with average of 534.1 ng m^{-3}, while in July it is much lower - average 30.6 ng m^{-3}. In February the concentrations of Cu are above 100 ng m^{-3} for certain days. In July, daily Cu concentrations are several times lower than in February. This is valid also for Ti, Zn, Mn. The results for the Pb concentration are controversial. Ag was measured in all PM10 summer samples, but in February it was not detected. The source of Ag is not identified and these results need further clarification. The most probable source could be from industrial activity in this region of Sofia.

The results presented in Table 1 show that the concentrations of crustal elements such as Fe, K, and Ti are comparable with the corresponding values for other cities, as summarized in our previous work [12].

The statistical relations between the different elements were evaluated by correlation and regression analyses. Some of these results as X-Y scatter plots are compared for the winter and the summer in Fig. 4. High R^2 value for Ca-Fe and K-Ti pairs are observed in the summer, while R^2 values for the same elements are low in winter. These results show that during summer the origin of these elements is similar and is dominated by the resuspension of soil and road dust with high Fe and Ca mean daily concentrations. In winter there is no strong correlation because of the impact of other sources, like domestic heating for K. In February high correlation is observed between Ca and P concentrations (r = 0.912); V and Ti (r = 0.896), and less, but significant in case of K and S (r = 0.695).

CONCLUSIONS

In the present study EDXRF techniques were used to characterize the PM10 elemental composition and results from winter and summer sampling campaigns of NIMH in Sofia are discussed. The results show that the EDXRF technique has been successfully applied to determine the variations in the elemental composition of PM10 for some of the analyzed elements. The reported results do not present a significant level of attention from a toxicological point of view. The concentrations of most of the analyzed elements are lower in the summer in correspondence to the lower PM10 mass concentration, excluding those of calcium and iron. In order to perform source apportionment more experimental data are needed and future experiments are planned.

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