1. Introduction

Airborne particulate matter (PM) is composed of inert carbonaceous cores with multiple layers of various adsorbed molecules including metals, organic pollutants, acid salts and biological elements such as endotoxins, allergens, and pollen fragments [1]. This term refers to solid and liquid particles (dust-size pollutants) that are dispersed into ambient air [2]. Particulate matter contains organic compounds (soot, polycyclic aromatic hydrocarbon [PAH]) or inorganic compounds (metals, sulfates, nitrates, and other inorganic species), or combinations of both organic and inorganic constituents [3]. It can be classified into primary and secondary particles based on the mechanism of their formation. PM may be emitted directly (primary PM) or be formed in the atmosphere (secondary PM). Both types of particles are subjected to growth and transformation, since there can be formation of secondary material on the surface of existing particles.

Electron microscopy has proved to be an ideal tool for characterization of individual particles. TEM and SEM coupled with energy dispersive X-ray spectrometers (EDX or EDS) characterization is well suited to provide information on individual particles; for example: morphology, elemental composition, mixing state, crystal structure, particle number, metals identification, crustal elements [4,5]. Using automation procedures, large numbers of individual particles in the size range from 100 nm up to 1 mm in diameter can be studied, providing high statistical significance. Electron microscopy can provide valuable information on the composition, sources, and atmospheric transformations as well as the number and volume-size distribution of atmospheric aerosols.

Abstract: In years 2006-2010 particulate matter analysis was undertaken for dust samples collected from Gdansk and London area in order to compare their morphology and composition. Part of those studies was devoted to analysis of particulate matter (PM) bearing metals. Characterization of the morphology and size of the particles collected onto the filters was performed using a scanning electron microscope (SEM) and transmission electron microscope (TEM). Both electron microscopes were equipped with energy dispersive X-ray spectrometers to identify the elemental composition of the particles. On analysis of the X-ray spectra acquired by both TEM and SEM, the particles were divided into 10 groups as follows: Al-rich, Ba-rich, Ca-rich, Cl-rich, Fe-rich, Mg-rich, Na-rich, S-rich, Si-rich. Speciation of the particles based on the major element and accompanying minor elements yielded 34 particle types. However, some pairs of elements repeat, for instance: Na-Cl and Cl-Na, Al-S and S-Al, Si-Al and Al-Si, Si-Ca and Ca-S. These are undoubtedly the same types of particles; variation in peak heights of the major and minor elements is normal in a mixed particle population.

Keywords: Energy dispersive X-ray spectrometry • EDX • EDS • Electron microscopy • Particulate matter

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These data are essential for the assessment of health effects of airborne particles, but cannot be obtained by mass measurement alone [6]. Energy-dispersive X-ray spectrometry is a microanalysis technique acquired from small regions of the specimen illuminated with a focused electron beam [7]. The elemental composition of a phase is determined using the characteristic X-ray spectrum of the examined specimen. It is a non-destructive analytical method for elemental analysis, with a potential detection limit of 0.1–0.5 wt% for most elements [8]. The EDS solid state detector is capable of identifying elements with atomic numbers equal to or greater than five (boron). EDS can provide rapid qualitative analysis with adequate standards. Quantitative analysis of elemental composition with a sampling depth of a few microns depends on the average density of the particle. Quantification is difficult for elements with atomic number below six (carbon) [9].

The aim of the project was to determine types of particles bearing metals in two different urban agglomerations with the use of electron microscopes equipped with elemental composition detectors.

2. Experimental Procedure

In years 2006-2010 particulate matter analysis was undertaken for dust samples collected from Gdansk and London area in order to compare their morphology and composition. Part of those studies was devoted to analysis of PM bearing metals. In Gdansk, samples were collected in the one atmosphere monitoring station. The station was placed near busy crossroad in the city center. In Hillingdon district, samples were collected in two stations. Both stations were placed close to A4 highway, one of the busiest roads in Europe.

Characterization of the morphology and size of the particles collected onto the filters was performed using JEOL JXA840A scanning electron microscope (SEM) and JEOL 2000FX transmission electron microscope (TEM). Both electron microscopes were equipped with energy dispersive X-ray spectrometers to identify the elemental composition of the particles.

The filters were cut in half. The one half was prepared for TEM analysis. It was immersed in distilled water and ultrasonically agitated for 5 minutes. The resultant suspension of particles was filtered through a 0.8 μm pore size polycarbonate membrane filter. The filters were coated with a layer of evaporated carbon and 3 mm squares cut from the active filter surface and placed onto 3 mm copper 200 mesh TEM grids. The filter material was dissolved to leave a carbon film with the particles embedded in it. Analysis of the particulate material was performed using an accelerating voltage of 100 kV at magnification between ×2,500 and ×250,000. The remaining halves of the filters were mounted onto aluminum microscope stubs and coated with a thin layer of gold, approximately 5 nm in thickness, to increase the electrical conductivity of the filter surface. The filters were examined in the SEM at an accelerating voltage of 20 kV and a working distance of 39 mm at magnifications between ×500 and ×50,000. Representative electron micrographs and X-ray spectra were acquired by both techniques.

3. Results and Discussion

3.1. Classification of the PM

Dust particles were divided based on the content of the main element. As the main one the particles with maximum signal in EDX/EDS spectrum were selected. In the case when Si was the main element, the signal source was always checked if comes from filter fiber (Fig. 1). It consists in comparison of spectrum showing the base content (filter) with spectrum taken for tested particle. If Ca peak height in the sample was from 0.18 to 0.21 of Si peak height, then as the main element the one with secondly the highest content in the particle was chosen. The value of peak height was determined basing on the analysis series of unused filter content. Elements with signal value lower than main element were also classified and treated as additional component. However, their signal value was greater than other existing elements. This procedure was utilized for fast and simple classification of particles in relation with their composition. The scheme of proceedings is given in Fig. 2.
On analysis of the X-ray spectra acquired by both TEM and SEM, the particles were divided into 10 groups as follows: Al-rich, Ba-rich, C-rich, Ca-rich, Cl-rich, Fe-rich, Mg-rich, Na-rich, S-rich, Si-rich. Speciation of the particles based on the major element and accompanying minor elements resulted in 34 particle types. However, some pairs of elements repeat, for instance: Na-Cl and Cl-Na, Al-S and S-Al, Si-Al and Al-Si, S-Ca and Ca-S. These are undoubtedly the same types of particles; variation in peak heights of the major and minor elements is normal in a mixed particle population.

3.2. Main particle types

3.2.1. Al-rich
The most often Al-rich particles were present, which contain in their composition great quantity of Si, rather than S. This type of particles usually creates huge agglomerates of very fine particles with diameter of approximately 10 nm. The second type of particles observed was chosen for particles with the size from 0.3 μm to 2 μm and irregularly shaped. Particles with S content were characterized by their roundness and size of approximately 1 μm (Fig. 3).

3.2.2. Ba-rich
Fig. 4 shows an irregularly shaped flat particle. The X-ray spectrum contains peaks for barium and sulphur. Barium sulphate is an ubiquitous material often found in airborne dusts.

3.2.3. C-rich
C-rich particles contained in their composition apart from carbon also Al, O and S. This type of particles was characterized by irregular shape and size of approximately 1 μm. Great carbon content might suggest that these particles originated from combustion process (Fig. 5).

3.2.4. Ca-rich
Figs. 6 and 7 are typical examples of calcium sulfate (gypsum). The crystalline habit of gypsum ranges from rosettes, shown in the figures to laths. X-ray analysis of the particles shows peaks for calcium and sulfur with other minor elements which originate from adjacent or adherent small particles (Fig. 6 and 7). These particles are typically from construction or refurbishment of buildings and are common in urban dusts. The large particle (ringed in Fig. 7) is an iron flake.

3.2.5. Cl-rich
Particles with great content of Cl were mainly composed of significant quantity of Na as well. Probably, these particles are aerosols of sea salt brought with the wind to the place where samples were collected. Salt particles show the typical cubic habit of regular square prisms shape in contrast to other particle types with irregular shapes (Fig. 8).
3.2.6. **Fe-rich**

This type of particles contained addition of Cl, Cu, Sn and Mn. Generally, these were big particles with the size approximately 10 µm. They had regular edges and homogenous structure (Fig. 9).

3.2.7. **Mg-rich**

Apart from Mg, particles contained also huge quantities of Cl and S. Independently of additional elements amount, this type of particles had usually the diameter of approximately 5 µm and approximate shape (Fig. 10).

3.2.8. **Na-rich**

Particles rich in Na contained also Cl and Ca. Probably, these were marine aerosols, similar to Cl-rich particles. They also had much the same composition and size. Generally, these particles formed masses with flat many-sided surface. They appeared as cubic crystals of very tiny sizes from 2 - 4 µm (see Fig. 11).

3.2.9. **S-rich**

This was very diverse dust group. Individual PM differed among each other in respect of the morphology and composition. Particles of this kind contained also in their composition Al, Ca, Cl and Si. S-rich particles may create complex structures with highly developed shapes or compose irregularly shaped particles and these of simple surface (Figs. 12 and 13).

3.2.10. **Si-rich**

This type of particles was the largest group in the respect of quantity. Apart from Si, in most cases, it contained Al and Fe. This group was probably composed of particles from natural sources (like rock weathering, transferring of very fine sand by wind) (Fig. 14).

On the filters from Gdansk, eight dust groups were categorized. These were Al, C, Ca, Cl, Mg, Na, S and Si-rich. Apart from sulfate dusts, the largest group
contained mineral particles with calcium, silicon and aluminum content. A significant number of particles with magnesium were also identified. These were not found in the samples collected in Hillingdon.

In samples collected at atmospheric monitoring stations in Hillingdon, nine particle kinds were determined. They were particles rich in Al, Ba, C, Ca, Cl, Fe, Na, S, Si. In comparison with samples from Gdansk,
we found higher number of particles with iron, carbon and rich in Ca. Ba particles were only found in samples from Hillingdon. Particles rich in Cl and Na were present in smaller number of samples from Hillingdon than those from Gdansk. This is undoubtedly because Gdansk is a coastal city and Hillingdon is inland.

According to the results obtained, mineral particles, combustion dusts and biological particulates dominated and predominantly metallic particulate matter comprises only a small percent of all dusts analyzed. Particles with metals Fe, Zn, Cu, Ti, Ba, and Mn were mostly present in Hillingdon.

4. Conclusion

The use of energy dispersive X-ray detectors combined with electron microscopy provides a unique method of rapid morphological and elemental analysis of single particles allowing the speciation of the particles and offers an insight to their origin. This information obtained can be used for many purposes from tracking of pollution sources to predictions about air quality related to health.

Dust collected in Gdansk contains mainly Al, C, Ca, Cl, Mg, Na, S and Si. However, samples taken in Hillingdon contain mainly Al, Ba, C, Ca, Cl, Fe, Na, S and Si. This indicates that the composition of dust varies in different cities. It is worth to stress that in the analyzed samples (mostly in Hillingdon) metals were often present.

In comparison with samples from Gdansk, we found higher number of particles with iron, carbon and rich in Ca. Barium particles were only found in samples from Hillingdon. Particles rich in Cl and Na were present in smaller number of samples from Hillingdon than those from Gdansk.

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