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SURFACE PROPERTIES OF PARTICLES EMITTED  
FROM SELECTED COAL-FIRED HEATING PLANTS  
AND ELECTRIC POWER STATIONS IN POLAND:  
PRELIMINARY RESULTS

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**Keywords:** Particulates emission, coal-fired power and heating stations, surface chemical composition, X-ray photoelectron spectroscopy (XPS), specific absorption.

**Abstract:** The surface properties of particles emitted from six selected coal-fired power and heating plants in Poland have been studied in this work for the first time. Samples were collected beyond the control systems. Surface composition of the size-distributed particles was obtained by photoelectron spectroscopy (XPS).

The reflection of the smallest, submicron particles was also measured to calculate their specific/mass absorption. The surface layer of the emitted particles was clearly dominated by oxygen, followed by silicon and carbon. The sum of the relative concentration of these elements was between 85.1% and 91.1% for coarse particles and 71.8–93.4% for fine/submicron particles. Aluminum was typically the fourth or fifth, or at least the sixth most common element. The mass absorption of the submicron particles emitted from the studied plants ranged from 0.02 m<sup>2</sup>g<sup>-1</sup> to 0.03 m<sup>2</sup>g<sup>-1</sup>. Only specific absorption obtained for the “Nowy Wirek” heating plant was significantly higher than in other studied plants probably because the obsolete fire grate is used in this heating plant.

The obtained results suggest that the power/heating-plant-emitted fine particles contain less carbonaceous material/elemental carbon on their surfaces than those that are typical in urban air.

## INTRODUCTION

Numerous epidemiological studies demonstrate positive association between ambient concentrations of airborne particulate matter and increased adverse respiratory and cardiovascular events [1–4], including morbidity and mortality [5, 6]. The presence of particles suspended in the air (atmospheric aerosol) is caused by the emission of solid particles (or their gaseous precursors) from various natural and anthropogenic sources.

Therefore, in order to reduce adverse health effects related with the inhalation of airborne particles, the reduction of the emission level is needed.

However, not only total mass of emitted particles is important but also their structure and chemical composition. Significant political and economic transformations in Poland during the last thirty years changed sources of the anthropogenic pollution but the share of hard coal and lignite in the fuel balance in Poland still exceeds 62% [7]. On the other hand, it should be mentioned that due to the applications of advanced technology in Poland, the emission of dust from power plants fired with hard or brown coal has decreased in the last twenty to thirty years. At present, slag and fly ash are captured in boilers and the dust remaining in the used equipment is utilized or stored on waste dumps, hence only from 0.2 to 0.5% of fly ash is released into the atmosphere. Although a number of industrial sources have been removed or significantly modernized, the “industrial” emission of airborne particles, especially from the coal-fired power and heating plants, is considered to contribute still more than 65% of emission of PM<sub>10</sub> (airborne particles having aerodynamic diameter up to 10 μm). In some cities, however, this contribution is much smaller, especially during smog episodes. It is related with the high municipal emission of air pollutants in Poland and growing significance of the vehicular emission of particulate matter [8–10].

Experience with coal combustions, based mainly on the results obtained in the USA, the UK and Scandinavia, has shown that the ash particle size distribution is typically bimodal with a majority of ash in the coarse mode. A fraction of ash forming constituents is vaporized during the combustion process forming fine submicron ash particles by nucleation of refractory oxides followed by growth due to coagulation and condensation of vapors [11, 12]. Also the morphology of the fly ash is very interesting, especially when considering ash deposit formation. The deposition mechanisms and thus the deposition rates are different for vapors, submicron ash and super-micron ash [13–15]. Vapors are deposited on the heat exchanger surfaces by condensation or chemical reaction. The major deposition mechanisms for submicron particles are thermophoresis and Brownian diffusion for the finest particles. Coarse ash particles impact on the heat exchanger surfaces with a high probability, but often they do not adhere to the surface [12]. Their retention on the deposit is facilitated if the deposit surface or the surface of the impacting particle is formed of sticky material [12]. Recently, some studies on the emission of air pollutants from selected coal-fired power plants in Poland, including airborne particles, polycyclic aromatic hydrocarbons (PAHs), as well as polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (dl-PCBs), and hexachlorobenzene (HCB), have been carried out [16–19]. Such studies, describing new aspects of chemical and physical properties of fly ashes are still very interesting (see for example [20]).

Unfortunately, the surface properties of the emitted particles are still unknown although new species produced from chemical reactions in the atmosphere occur on the particle surface. Besides, the chemical composition of the surface of particles also plays an important role in determining health effects, because the surface is directly accessible to biological fluids after inhalation. The X-ray photoelectron spectroscopy (XPS) is a surface analysis technique and in recent years, a number of researchers have used XPS to analyze particulate matter collected onto filters [21–27]. However, the surface composition of airborne particles emitted from the power plants probably has not been investigated yet.

The environmentally-oriented studies of emitted particles should also include optical analysis in addition to chemical/structural analysis. In particular, particle sizes in

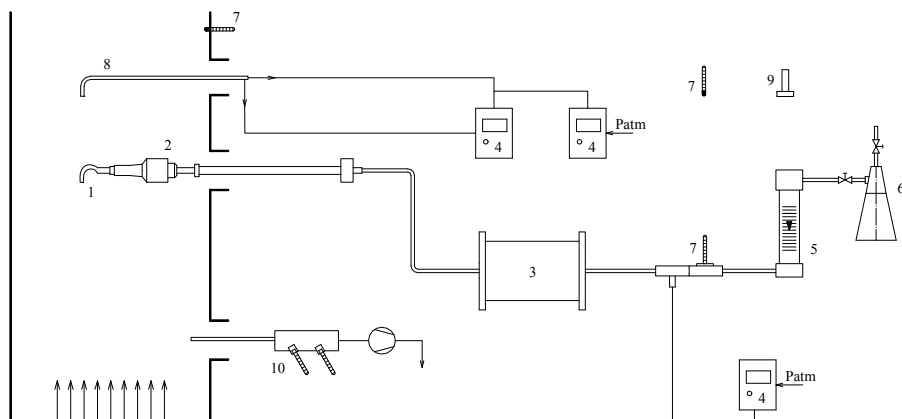
the range 0.1–2.5  $\mu\text{m}$  are most effective in light scattering and thus have a major effect on visibility. On the other hand, the optical properties of particles are closely related with the structure of their surface.

The aim of this research was to determine the surface properties of particles emitted from selected coal-fired power and heating plants in Poland, being the greatest in Europe. Particles emitted from these sources are present in atmospheric air in a number of European countries, mainly in Scandinavia.

## METHODS

Table 1 shows the technological parameters of the examined plants and the combusted fuel.

The fly ash was sampled from the flow of exhaust gases with a six-stage cascade impactor (Andersen Mark III), configured similarly to the particles sampler used to measure the dust emission (Fig. 1).



FLUE GASES

Fig. 1. Schematic presentation of the particles sampling system

- 1 – Sampling Tube, 2 – Cascade Impactor, 3 – Dehumidifier, 4 – Differential Pressure Sensor, 5 – Flow Meter, 6 – Pumping Device, 7 – Thermometer, 8 – Prandtl Tube, 9 – Barometer, 10 – Humidity Sensor

Samples were collected beyond the used control system. This device, like other conventional in-stack cascade impactors uses the inertial force to remove particles from the inhaled air. The sized particle collections are made on the substrate located under the air jets accelerated from stage to stage. The sampling process was performed according to the sampler operating manual, keeping isokinetic condition between the main and aspirated flow of exhaust gases. The mass of collected particles on each impactor stage was determined by weighing. Next, the cut-size aerodynamic diameter ( $d_{50}$ ) of each stage was determined. The backup filter provides one more sized cut. Computations were based on the measurement of volume and temperature of the up-taken gas and aerodynamic characteristics of the impactor (diagrams of cut points versus flow rate at stack conditions). Table 2 shows the ranges of these calculated cut-size diameters.

Table 1. Characteristics of studied coal-fired electric power stations and heating plants

Item	Facility	Type of boiler	Type of furnace	Power	Fuel	Flue gas de-dusting system	$\eta$ (%)	Flue gas desulfurization system	$\eta$ (%)
1	Nowy Wirek Heating Plant	WLM 5	Mechanical stocker	5.8 MW	Hard coal	Cyclone (SP)	89.0	None	
2	Gliwice Heating Plant	WP 70	Pulverized-fuel fired furnace, tangential furnace	81 MW	Hard coal	Electro-filter (SP)	99.0	None	
3	Opole Power Station	BP1150	Pulverized-fuel fired furnace, tangential furnace	360 MW	Hard coal	Electro-filter	99.6	Wet lime (SP)	95.0
4	Belchatów Power Station	BB1150	Pulverized-fuel fired furnace, tangential furnace	360 MW	Brown coal	Electro-filter	99.6	Wet lime (SP)	95.0
5	Siersza Power Station	OP380	Pulverized-fuel fired furnace, tangential furnace	120 MW	Hard coal	Electro-filter	99.6	Dry-scrubbing, Fabric filter (SP)	87.0 >99.6
6	Nowa Heating and Power Plant	OPG 230	Pulverized-fuel fired furnace, tangential furnace	Steam: 230 t/h	Hard coal, Waste gases	Electro-filter (SP)	99.0	None	

(SP) – Sample-taking point, located after the flue gas cleaning system (de-dusting/or desulfurization devices),

 $\eta$  – Cleaning efficiency

Table 2. Ranges of the cut-size diameters of the used cascade impactor (Andersen Mark III) during the sampling processes

Impactor stage	Cut-size diameter $d_{50}$ [ $\mu\text{m}$ ]		
I	12.8	(Siersza Power Station) – 15.0	(Nowy Wirek Heating Plant)
II	7.4	(Siersza Power Station) – 9.8	(Nowy Wirek Heating Plant)
III	5.25	(Siersza Power Station) – 6.6	(Nowy Wirek Heating Plant)
IV	3.3	(Siersza Power Station) – 4.5	(Nowy Wirek Heating Plant)
V	2.3	(Siersza Power Station) – 2.8	(Nowy Wirek Heating Plant)
VI	1.1	(Siersza Power Station) – 1.4	(Nowy Wirek Heating Plant)
Backup filter	less than (1.0–1.4)		

To better characterize the collected particles the micrographs of some samples from all the studied plants were made by scanning electron microscopy combined with a LINK 860 energy dispersive spectrometer (Si-Li detector, beryllium window, analytical range from Na to U). During SEM observation and X-ray microanalysis an accelerating voltage of 25 kV and a beam current of  $2 \times 10^{-6}$  A were applied. These experimental conditions have been selected to obtain high X-ray count rates and good quality of SEM micrographs. During the study campaign typically 3–5 sets of samples were collected from each plant using the described above six-stage Andersen cascade impactor. One set of samples was used for the electron microscopy study while the second was used for the XPS analysis and third for the optical measurement. The XPS spectra of aerosol samples were obtained with monochromatized Al  $K\alpha$  radiation using a PHI 5700/660 Photoelectron Spectrometer (Physical Electronics, USA).

Surface analysis by XPS is accomplished by irradiating a sample with monoenergetic soft X rays and analyzing the energy of the detected electrons. The photons have limited penetrating power in a solid on the order of 0.01 micrometer. They interact with atoms in the surface region, causing electrons to be emitted by the photoelectric effect [28]. The emitted electrons have kinetic energies ( $KE$ ) given by:

$$KE = hv - BE - fs \quad (1)$$

where:  $hv$  – is the energy of the photon,

$BE$  – is the binding energy of the atomic orbit from which the electron originates,

$fs$  – is the spectrometer work function.

Each peak of the recorded spectrum is characteristic for a certain electron energy level of a certain element. The electron binding energies are characteristic for each element. However, in compounds, the binding energies are not absolutely constant but depend on the chemical environments due to modification of the valence electrons distribution. These differences in relation to pure elements in the electron binding energies are called chemical shifts [28]. Using the catalog of the chemical shifts, the compounds were identified.

A hemispherical mirror analyzer determined the energy of the electrons with a resolution of approximately 0.3 eV. During the X-ray analysis a voltage of 15 kV was applied. X-ray

emissions from a surface area of  $800 \times 2000 \mu\text{m}$  were measured with a  $45^\circ$  angle between the X-ray beam and the sample surface. Each analysis session took approximately 5 hours. All measurements were performed under UHV (ultra high vacuum) conditions, 10-10 Torr.

Calibration for the spectra was made using the carbon C1s peak (285.0 eV). The Multipak Physical Electronics program has been used for the analysis of the obtained data. This program enables quantification of the XPS spectra utilizing the peak area and the peak height sensitivity factors. The standard atomic concentration calculation provides a ratio of each component to the sum of all detected elements. Only those elements for which the specific line is clearly visible in the spectrum were considered.

The reflectance of the particulate filter deposit was determined using a digital smoke stain reflectometer (Model 43D, Diffusion Systems Ltd., London, UK), which measures the reflection of the white light incidence in percent. One blank (per ten exposed) filter was used to standardize the reflectance of the reflectometer to 100. Next, the blank filter was replaced by an exposed filter and the reflectance was read. Each filter was measured five times in different places of the filter to document the homogeneity of the filter. The reflectance (average of the five readings) was transformed into an "absorption coefficient" (ISO 9835,1993), according to the equation [29]:

$$a_p = \frac{A}{2V} \ln \frac{R_0}{R} \quad (2)$$

where:  $a_p$  [ $\text{m}^{-1}$ ] – absorption coefficient (obtained for PM2.5 or for PM10),  
 $A$  [ $\text{m}^2$ ] – loaded filter area,  
 $V$  [ $\text{m}^3$ ] – samples volume,  
 $R_0$  [%] – reflectance of the blank filter,  
 $R$  [%] – reflectance of the filter with collected particles.

Dividing the absorption coefficient  $a_p$  [ $\text{m}^{-1}$ ] by the concentration of particles the mass (specific) absorption was

$$\sigma_p = \frac{a_p}{C} \quad (3)$$

where:  $\sigma_p$  [ $\text{m}^2/\text{g}$ ] – mass absorption coefficient (specific absorption).

Because concentration is defined as  $C = m/V$ , where  $m$  is the mass deposited on the filter surface, it can be finally written:

$$\sigma_p = \frac{A}{2m} \ln \frac{R_0}{R} \quad (4)$$

where:  $\sigma_p$  [ $\text{m}^2/\text{g}$ ] – mass absorption coefficient (specific absorption).

To measure the reflection coefficient the sampled particles must be homogeneously distributed on large enough surfaces. Therefore, reflection measurements could be carried

out only for the smallest particles, collected on the final (backup) filter. The reason is that the in-stack cascade impactor, used in our studies for source emission particle size distribution measurements, collects the sized particles in small piles on a substrate. This type of collection is due to the impact design, where like in most other in-stack impactors, stages have a number of rectangular slits (or small holes) to accelerate the particles [30].

## RESULTS AND DISCUSSION

### *General characteristics of emitted particles*

The examples of the micrographs of collected particles and the results of the X-ray analysis of the chosen particles (marked with a cross) are presented in Figs 2 and 3.

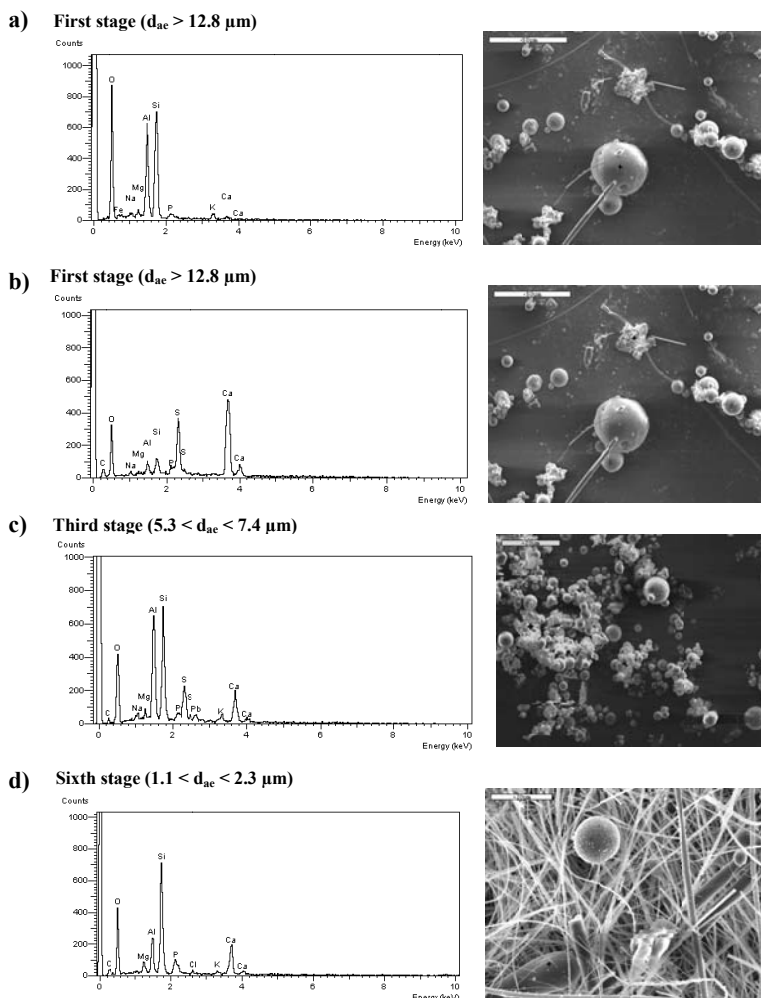
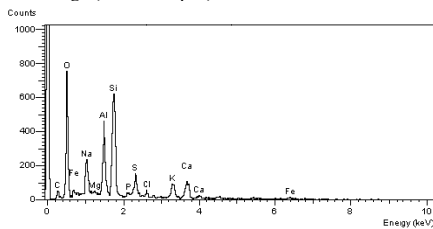


Fig. 2. Micrographs of particles emitted from the Siersza Power Station and elemental spectra of selected particles (marked with the cross)

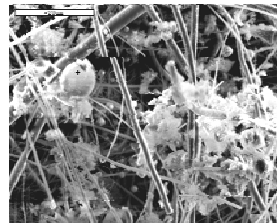
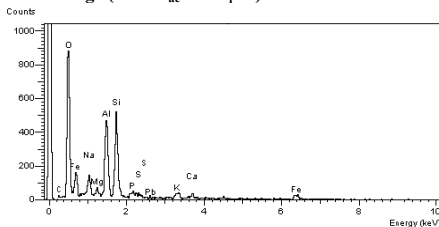
Figure 2 shows the particles emitted from the “Siersza” power station. This picture, as well as the elemental spectra of selected particles, are representative for most of the obtained micrographs collected from almost all plants, except the “Nowy Wirek” heating plant. From the analysis of these and other micrographs the general impression is that the spherical particles were definitely dominant. On the contrary, Figure 3a demonstrates the coarse particle collected behind dust controlling installation of the “Nowy Wirek” heating plant where the mechanical fire grate is used. This device is probably the reason of the emission of such large particles.

The X-ray analysis shows that in a whole mass of collected particles silicon, aluminum and oxygen are dominant in elements' rating. The content of other elements varies, probably according to coal chemistry or combustion technology. In fact, such results could be expected because the previous works (e.g. [31]) demonstrated that the relatively high contents of Al, Si, Fe, S, Ca, Na, and K of the coal mineral matter and the high temperature reached during coal combustion in conventional power stations account for the characteristic composition and mineralogy of fly ash: aluminosilicate glass (amorphous component) and high temperature crystalline phases such as mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), quartz ( $\text{SiO}_2$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ). Therefore, particles emitted from the

**a) First stage ( $d_{ac} > 15.0 \mu\text{m}$ )**



**b) Fourth stage ( $4.5 < d_{ac} < 6.6 \mu\text{m}$ )**



**c) Sixth stage ( $1.4 < d_{ac} < 2.8 \mu\text{m}$ )**

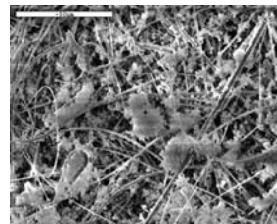
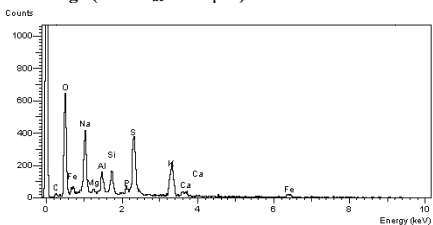


Fig. 3. Micrographs and elemental spectra of selected particles (marked with the cross) emitted from the Nowy Wirek Heating Plant



studied heating and power plants in Poland seem to be similar to fly ash studied in other countries.

### Surface properties

An example of XPS spectrum for the collected particles is shown in Fig. 4. Before the detail analysis it should be mentioned that an important limitation of this technique is the loss of volatile species under UHV conditions, particularly organic species from soot [21].

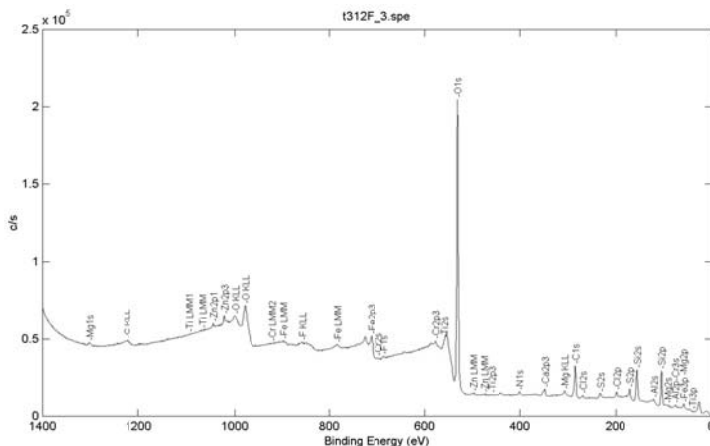


Fig. 4. Example of the XPS spectrum in the energy range 0–1400 eV for the particles collected from flue gases

As shown in Fig. 4, the spectrum indicates a strong, dominating peak of oxygen. This result can be partially explained by the fact that fossil fuel combustion particulate products are principally inorganic substances, and they are usually identified as oxides [32]. The silicon and carbon peaks, although much lower in comparison with oxygen, indicate significant contribution of both these elements in the surface layer of the studied particles. The calculated contributions of all detected elements contained in the submicron particles (i.e. collected on the filters) as well as contained in all the other sampled particles (i.e. averaged levels for stages I–VI) are presented in Table 3. As it can be seen, the surface layer of the particles sampled on the impactor stages I–VI was clearly dominated by oxygen followed by silicon and carbon.

The sum of relative concentrations of these elements in the coarse particles is between 85.1% (for the “Opole” electric power station) and 91.1% (for the “Nowa” heating and power plant). Aluminum is typically the fourth or fifth, or at least the sixth most common element constituting 2.14–4.87% of all the elements found in the surface layer of particles larger than one micrometer in aerodynamic diameter. Generally, similar contributions of the detected elements were found in the surface layer of submicron particles. It is interesting to note that the surface ratio of S to Al on the coarse particles for four plants (No.: 2, 1, 6, 3) ranges from 0.18 (“Opole”) to 0.88 (“Bełchatów”) but for two plants (No.4 and No. 5) it exceeds 1.0 (“Siersza” – 1.0 and “Nowy Wirek” – 1.1) suggesting that

Table 3. Surface composition of particles emitted from the studied plants

Element	Relative concentration of element [%] in the surface layer of particles											
	1. Gliwice Heating Plant		2. Opole Electric Power Station		3. Belchatów Electric Power Station		4. Siersza Electric Power Station		5. Nowy Wirek Heating Plant		6. Nowa Heating and Power Plant	
	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
O	60.58 (1.08)	54.13	56.14 (1.21)	51.93	58.18 (2.56)	58.40	54.13 (2.29)	54.94	53.78 (2.63)	47.84	44.13 (5.73)	43.22
Si	16.69 (0.47)	13.70	18.49 (1.05)	15.43	17.38 (1.28)	16.95	11.33 (4.16)	18.80	15.42 (3.07)	0.64	11.44 (3.74)	12.76
C	9.38 (0.80)	14.59	10.44 (3.16)	10.90	12.56 (4.07)	15.19	22.00 (2.82)	19.70	20.20 (4.26)	23.31	35.55 (8.70)	36.50
Al	4.87 (0.54)	6.98	3.81 (0.54)	3.93	2.51 (0.24)	1.43	2.54 (0.49)	2.84	2.14 (0.30)	0.00	3.07 (0.52)	3.10
F	1.97 (0.51)	2.78	5.10 (1.34)	9.62	1.97 (0.85)	0.31	0.35 (0.13)	0.00	0.25 (0.12)	0.00	0.41 (0.23)	0.55
Na	1.23 (0.16)	1.60	0.84 (0.30)	0.52	0.66 (0.17)	0.00	0.54 (0.37)	0.29	2.26 (0.76)	8.17	0.87 (0.36)	0.26
S	1.44 (0.30)	1.60	0.68 (0.44)	1.15	2.20 (0.36)	1.79	2.62 (1.14)	0.70	2.27 (0.99)	9.94	1.17 (0.61)	0.98
Ca	0.99 (0.17)	0.41	2.20 (0.32)	3.53	2.18 (0.56)	0.84	4.21 (1.80)	2.06	1.48 (0.31)	0.00	1.44 (0.25)	1.64
N	1.16 (0.15)	1.03	0.72 (0.21)	1.15	0.80 (0.52)	0.93	0.13 (0.08)	0.06	0.52 (0.11)	2.81	0.39 (0.20)	0.36
K	0.60 (0.13)	0.94	0.35 (0.10)	0.22	0.05 (0.03)	0.00	0.00 (0.00)	0.06	0.75 (0.24)	4.45	0.04 (0.04)	0.00
P	0.29 (0.09)	0.76	0.16 (0.12)	0.56	0.02 (0.02)	0.00	0.01 (0.02)	0.00	0.04 (0.04)	0.12	0.42 (0.24)	0.21
Mg	0.52 (0.12)	0.67	0.64 (0.25)	0.58	1.00 (0.34)	0.51	1.39 (0.66)	0.50	0.32 (0.12)	0.00	0.65 (0.47)	0.40
Ti	0.11 (0.04)	0.13	0.09 (0.05)	0.18	0.10 (0.06)	0.03	not found	not found	0.04 (0.05)	0.00	0.06 (0.07)	0.00
Cr	0.00 (0.00)	0.00	0.00 (0.00)	0.00	0.00 (0.00)	0.30	0.00 (0.00)	0.00	0.03 (0.05)	0.04	not found	not found
Fe	0.12 (0.03)	0.43	0.07 (0.08)	0.00	0.36 (0.25)	1.99	0.22 (0.18)	0.01	0.21 (0.13)	1.15	0.20 (0.14)	0.00
Co	0.01 (0.01)	0.09	0.04 (0.08)	0.08	0.00 (0.00)	0.00	not found	not found	not found	not found	0.12 (0.18)	0.00
Ni	0.03 (0.02)	0.09	0.03 (0.07)	0.00	0.00 (0.00)	0.00	not found	not found	not found	not found	not found	not found
Cu	0.01 (0.01)	0.02	0.00 (0.00)	0.00	0.00 (0.00)	0.00	not found	not found	0.06 (0.05)	0.10	not found	not found
Cl	0.02 (0.01)	0.05	0.12 (0.14)	0.16	0.002 (0.004)	1.02	0.51 (0.21)	0.02	0.14 (0.05)	0.61	0.03 (0.03)	0.00
Zn	0.01 (0.01)	0.02	0.02 (0.02)	0.05	0.002 (0.004)	0.32	not found	not found	0.09 (0.07)	0.83	0.02 (0.03)	0.00
As	0.01 (0.01)	0.00	0.00 (0.00)	0.00	0.00 (0.00)	0.00	not found	not found	not found	not found	not found	not found
Ba	not found	not found	not found	not found	not found	not found	0.01 (0.01)	0.00	0.01 (0.01)	0.00	not found	not found

“Coarse” – particles collected in all the stages of the cascade impactor (the presented relative concentration is the mean calculated for these particles, collected in stages from 1 to 6). In brackets are standard deviations.

“Fine” – particles collected on the backup filter (practically these particles can be treated as the submicron particles).

sulfur substantially enriched the surface composition of these particles. Although it is difficult to explain these differences precisely, this result may be important because it is speculated that surface S plays a role in reducing surface Fe(III) to Fe(II) [27]. In fact, the large surface of fly ash causes the enrichment of these particles in various elements which condense during cooling of combustion gases [33, 34].

The distribution of carbon in the surface layer of the submicron particles emitted from these plants can be grouped as follows: the highest value obtained for the “Nowa” plant – 36.50%, next for “Nowy Wirek” – 23.31%, “Siersza” – 19.70%, and “Gliwice” – 14.59%, and finally, the lowest value obtained for “Opole” – 10.90%.

The analysis of the results obtained in this work so far indicates that although the relative contents of carbon in the surface layer of the examined dust is significant, the detected level does not exceed 36.5% (for particles emitted from the “Nowa” heating and power plant) being mainly below 20%. It needs to be emphasized that carbon is always the dominant surface element in atmospheric aerosol particles in urbanized areas and constitutes over a half of all the identified elements [21, 23, 25, 35]. Also the data recently obtained in Zabrze, Poland show that the relative surface concentration of elemental carbon in airborne PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> ranges from about 78% to 81%, depending on the fraction and season [36]. It is important to note that the analyzed carbon is really present on the surface of the studied particles, especially – fine particles. In fact, another interpretation of the obtained results for coarse particles could be possible assuming that silicate and oxide fly-ash big particles are mixed on the same sample with fine carbonaceous (mainly soot) particles. In this case the upper 50-nm layer of such a bulk aerosol would produce the same spectrum as is presented in Fig. 4, since both fly-ash and soot particles would contribute to it. Although the analyzed particles were sampled by the cascade impactor, hence the size ranges of collected particles were relatively narrow, this hypothesis cannot be totally excluded for coarse particles. Anyway, the difference in the surface concentration of elemental carbon between fine particles emitted and suspended in the air indicates that the power/heating-plant-emitted particles contain less carbon on their surface than those that are typical in urban air. Besides, the presented results seem to support the opinion about the decreasing role of heating and power plants as sources of emission of airborne particles in Poland during the last two decades. Although additional studies on this subject are needed, recently Juninen et al. [37] have obtained the source contribution estimates for PM<sub>10</sub> and associated toxic air pollutants in Krakow, Poland, during the pollution episodes, confirming this hypothesis. According to their report the major cause for the extreme pollution levels was demonstrated to be residential heating by coal combustion in small stoves and boilers (>50% for PM<sub>10</sub>), whereas road transport (<10%), and industry (4–15%) played a lesser role. On the other hand, it is also possible that some particles emitted from these industrial sources are intensively enriched with carbon during translocation from the emitted trail of pollution to the ground layer of air in urban areas. The submicron particles, mainly sulfate, associated with microstructures of soot had been observed previously in polluted urban environments [38].

Table 4 shows the values of specific (mass) absorption factor ( $\sigma$ ) for submicron particles obtained for two heating plants (“Gliwice” and “Nowy Wirek”), as well as for two electric power stations (“Opole” and “Siersza”). As it can be seen the mass absorption of the submicron particles emitted from three of the studied plants is very similar, ranging from 0.02 m<sup>2</sup>g<sup>-1</sup> to 0.03 m<sup>2</sup>g<sup>-1</sup>. Only specific absorption obtained for the “Nowy Wirek”

heating plant ( $0.36 \text{ m}^2\text{g}^{-1}$ ) is significantly (ten times) higher than in the other studied plants probably because of the use of the obsolete fire grate in this heating plant.

Table 4. Specific absorption coefficient of submicron particles emitted from selected power and heating plants

Stationary source emission	Size of studied particles [ $\mu\text{m}$ ]	Specific absorption coefficient [ $\text{m}^2\text{g}^{-1}$ ]
Gliwice Heating Plant	< 1.3	0.026
Nowy Wirek Heating Plant (mechanical fire-grate)	< 1.4	0.364
Opole Electric Power Station	<1.2	0.016
Siersza Electric Power Station	< 1.1	0.030

Although a direct comparison of mass absorption of examined dust and atmospheric aerosol particles is difficult, it can be noted that the coefficient  $\sigma$  of submicron particles from studied plants (except the “Nowy Wirek” heating plant) is from 3.3 to about 19 times smaller than the average annual level of  $\sigma$  ( $0.6\text{--}0.10 \text{ m}^2\text{g}^{-1}$ ) obtained for aerosol particles PM<sub>2.5</sub> in four cities in southern Poland [25]. Only submicron particles emitted from “Nowy Wirek” plant have the specific absorption comparable with the fine aerosol particles in Polish and European cities. For example, the following results were obtained: in Vienna  $\sigma=0.6 \text{ m}^2\text{g}^{-1}$  and in Almeria, Spain  $\sigma=0.1\text{--}0.3 \text{ m}^2\text{g}^{-1}$  [39].

It should be noted that in contrast to highly linear correlation between the absorption coefficient and the ambient elemental carbon concentration the literature data illustrate the diversity in the specific absorption  $\sigma$  along elemental carbon levels [40]. This variability is usually attributed to size distribution and the mixing state of the elemental carbon in the atmospheric particles, although this argument is still subject to debate [40]. On the other hand, for real aerosol, originated and evaluated under given atmospheric conditions, a highly correlated relationship was found between the factor  $\sigma$  and the concentration of elemental carbon, or at least the concentration of “black smoke” [41].

Although the mentioned above relationship between the specific absorption and elemental carbon content is only a simplistic view, the absorption data suggest that the concentration of absorbing carbonaceous particles is smaller in the power plant emissions than in the cities.

## CONCLUSIONS

Bulk particles emitted from the studied coal-fired heating and power plants in Poland seem to be similar to fly ash studied in other countries. Silicon, aluminum, and oxygen are the major elements of these particles.

The surface layer of the emitted particles was clearly dominated by oxygen followed by silicon and carbon. The sum of the relative concentration of these elements was between 85.1% and 91.1% for coarse particles and 71.8–93.4% for fine/submicron

particles. Aluminum was typically the fourth or fifth, or at least the sixth most common element.

The obtained data indicate that the power/heating-plant-emitted fine particles contain less carbonaceous (elemental carbon) material on their surfaces than those that are typical in urban air.

The mass absorption of the submicron particles emitted from three of the studied plants ranged from  $0.02 \text{ m}^2\text{g}^{-1}$  to  $0.03 \text{ m}^2\text{g}^{-1}$ . Only specific absorption obtained for the heating plant "Nowy Wirek" is significantly higher than in the other studied plants probably because of the use of the obsolete fire grate in this heating plant.

The absorption data suggest that the content of fine absorbing carbonaceous particles is smaller in the power/heating plant emissions than in the urban aerosol.

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