

Characterization of Chosen Products of Combustion Processes

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Abstract

The basic form of pollution is characterized by a microscopic size and solid state and it is called particulates or particulate matter. Unfortunately, these forms undergo a variety of transformations, which consequently can sometimes be easily modified and even cause an increase in their toxicity. This work was devoted to join the composition of various materials being residues after different combustion processes with the distribution of elements and molecules within studied surfaces. The content of chosen elements was determined using ICP-MS and ICP-OES methods. Elemental and/or molecular distribution was studied using surface sensitive techniques, SEM-EDS and ToF-SIMS. The obtained results revealed that the composition and morphology of particles are strongly influenced by the type of material and combustion conditions.

Keywords: airborne particles, surface studies, ToF-SIMS, SEM-EDS, ICP

Introduction

In recent years a lot of studies have been devoted to obtaining detailed information on both the surface and internal composition of different airborne particles. Generally, the size of particles emitted from different emission sources ranges from tens of μm to tens of nm. Particulate air pollution is a serious problem because of high toxicity of emitted elements and compounds concerning potentially serious environmental impact. Although considerable reductions in toxic metals emissions have been introduced, a high amount of undesirable substances is incorporated into the atmosphere. During combustion variable amounts of elements are emitted as gaseous and solid-phase pollutants and partially captured by fly ash. We should take into consideration the fact that the properties of material formed during combustion are unpredictable.

For that reason the characterization of various types of residual substances after combustion is necessary [1-5].

Great attention has been paid to assess the anthropogenic emissions and their changes in time. Many papers mostly deal with reporting chemical bulk data without focusing on the analysis of individual particles. The determination of toxic element content is also a key parameter in assessing their influence on the environment and human health [6]. For instance, diesel exhaust particles can be adsorbed on the surface of particulate matter with 2.5 μm of diameter and form the so-called complex particles (they contain carrier particle and adsorbed particle) [7]. These particulates are usually emitted from engines (diesel and gasoline), in car emissions or are produced during the process of fuel combustion [5].

The toxicity of particles formed in combustion processes depends on their chemical composition, size and morphology. Information about the elemental quantitative composition of different particles can be obtained by a variety of analytical techniques such as inductively coupled

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plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectroscopy (AAS), or neutron activation analysis (NAA). However, these methods allow analyzing a volume of the sample and do not provide information concerning molecular composition, morphology and elemental and/or molecular distribution. Recently the most commonly applied techniques appropriate for surface studies are scanning electron microscopy SEM equipped with energy dispersive spectrometer EDS and time-of-flight secondary ion mass spectrometer ToF-SIMS. Hence, it is possible to relate the surface morphology and distribution of chosen elements and/or molecules to their chemical composition [6, 8].

The Łódź region is an area situated almost in the centre of Poland with one of the worst air pollution in the country. It covers approximately 400 km² with a dense population of about 1 mln. There are many factories and power plants with insufficient ash removal systems. Additionally, almost 40% of households are still dependent upon their own heating systems not equipped with any ash removal devices. Moreover, the contribution of traffic component to total air particulate matter is also important [9]. Elements typically associated with emissions from different sources play a crucial role in atmospheric circulation at a regional level within the investigated area. For that reason it seems to be advisable to monitor and control the levels of elements incorporated into the air and environment.

This study is dedicated to a better understanding of the influence of local emissions on the chemical composition of products of different types of combustion processes. In the present work the concentration of elements in bottom ash, fly ash, ash, soot and slag was determined by the use of ICP-OES and ICP-MS techniques. Surface content of elements and compounds and their surface distribution were investigated with the use of ToF-SIMS and SEM-EDS. The aims of this work was to determine the composition of different particles and to distinguish different types of particles connected with various pollution sources.

Experimental Procedures

Materials

Investigated samples were collected from four different sources: small- and large-scale power plants localized in Łódź and the region, a hospital incinerating room and fireplaces in private houses. In the ICP-AES and ICP-MS studies, elemental composition of 36 samples consisting of bottom ash and two fractions of fly ash from power plants, slag and soot from domestic furnaces, and slag and ash from a hospital incinerating room were measured. SEM-EDS and ToF-SIMS analysis was performed for chosen samples of bottom ash and fly ash (power plants), soot (domestic fireplaces) and ash (hospital incinerating room). Generally, manual sampling was carried out

in each case, except samples of fly ash coming from power plants, which were collected using electro-filters. Fractions over and below 10 µm were obtained using a cascade impactor. Sample collection was conducted during two months. Samples were dried for 24 h at 100°C, ground in a ball mill, sieved through a 0.5-mm screen and stored in polystyrene containers.

Methods

Before analysis the material was mineralized in teflon vessels with a mixture of 3 ml of spectrally pure nitric acid and 1 ml of hydrochloric acid, and placed in a microwave system, Milestone MLS-1200 MEGA. The content of elements was determined by inductively coupled plasma mass spectrometer OptiMass 8000, GBC (Cd, Cr, Cu, Pb and Sr) and inductively coupled plasma atomic emission spectrometry IRIS-AP, Thermo Jarrell Ash (Al, Ba, Fe, Mn). Standardization was made using a multi-element standard solution Merck VI. Each sample was determined three times and the RSD in most cases was below 5%. Elemental composition of the samples was characterized by scanning electron microscopy using a Hitachi S-4700 equipped with energy dispersive spectrometer, ThermoNoran. Before microscope measurements the samples were placed on the carbon plasters and coated with Pd/Pt (SEM) or carbon target (EDS) by Cressington 208 HR system. The accelerating voltage was 25kV. EDS maps were collected from micro areas corresponding to SEM pictures at various magnifications (x1,000, x3,500). Additionally, the secondary ion mass images were recorded with a ToF-SIMS IV (ION-TOF GmbH, Muenster, Germany) in order to obtain information concerning differences in their surface composition and chemistry. Contrary to EDS analysis, which provide information concerning elemental composition of the surface, secondary ion mass spectrometry additionally allowed us to obtain information at the molecular level. ToF-SIMS measurements (positive and negative ion spectra and images) were carried out using ⁶⁹Ga⁺ primary ion gun and high mass resolution time of flight mass analyzer. Secondary ion images were recorded from an approximately 500 µm × 500 µm² area of the sample surface. During measurement the analyzed area was irradiated with the pulses of 25 keV Ga⁺ ions at 10 kHz repetition rate and an average ion current of 1 pA. Secondary ions emitted from the bombarded surface were mass separated and counted in time-of-flight (ToF) analyzer. In the case of SEM-EDS maps and ToF-SIMS images the brightness of a particular area in the image increases with the increase of surface concentration of selected elements or compound in this area.

Results

The analytical quality of the obtained results and reliability of the methods (ICP-AES, ICP-MS) were checked by the determination of elements in the Certificate Mate-

rial of Soil NCS ZC 73001. The agreement between the analytical values for the certificate material and measured results was satisfactory. The obtained results are presented in Table 1.

Table 2 presents the range (min. and max. values) and average concentration of investigated metals in 36 sam-

ples of studied materials after various combustion processes determined with the use of ICP-MS and ICP-AES methods (depending on the expected content of elements the choice of methods used was done – low concentration for ICP-MS, high concentration for ICP-AES). On the basis of the obtained quantitative results we can state that

Table 1. Results of the measurement of the Certificate Reference Material of Soil NCS ZC 73001 [mg/kg], (U uncertainty).

ELEMENT/METHOD (Emission line [nm] /isotope)	CERTIFICATE ± U [mg/kg]	EXPERIMENTAL ± RSD [mg/kg]	RECOVERY [%]
Al*/ICP-OES 396.152{66}	7.31 ± 0.11	7.01 ± 0.01	95.90
Ba/ICP-OES 233.527{111}	613 ± 12	610 ± 10	99.51
¹¹¹ Cd/ICP-MS	0.105 ± 0.013	0.093 ± 0.005	88.57
⁵³ Cr/ICP-MS	58 ± 2	60 ± 0.9	103.4
⁶⁵ Cu/ICP-MS	19 ± 1	18 ± 0.3	94.74
Fe*/ICP-OES 259.940{100}	2.92 ± 0.03	2.90 ± 0.06	99.31
Mn/ICP-OES 260.569{99}	681 ± 13	690 ± 16	101.3
²⁰⁸ Pb/ICP-MS	22 ± 2	21 ± 0.5	95.45
⁸⁸ Sr/ICP-MS	226 ± 5	221 ± 4	97.79

* values in [%]

Table 2. The min. and max. (range), and average concentration of chosen elements in 36 studied products (bottom ash, fly ash, ash, soot, slag) emitted by different pollution sources during combustion process determined by ICP-AES and ICP-MS methods [mg/kg].

Average (min.-max.) [mg/kg]								
Al	Ba	Cd	Cr	Cu	Fe	Mn	Pb	Sr
130 (19.5-345)	3.97 (1.22-19.1)	0.06 (0.03-0.71)	0.96 (0.15-28.1)	3.19 (1.62-18.4)	59.5 (36-350)	39.7 (10.2-350)	1.50 (0.23-20.1)	5.12 (1.09-14.1)

Table 3. Concentration of chosen elements in selected studied samples formed during different combustion processes determined by ICP-AES and ICP-MS methods [mg/kg].

Sample	Concentration of elements in products of combustion process ± RSD [mg/kg]								
	Al	Ba	Cd	Cr	Cu	Fe	Mn	Pb	Sr
Bottom ash (small-scale power plant)	34.4 ± 0.21	16.1 ± 0.11	0.52 ± 0.01	5.12 ± 0.08	12.4 ± 0.09	350 ± 11.5	155 ± 2.23	14.1 ± 1.01	4.21 ± 0.09
Bottom ash (big-scale power plant)	25.4 ± 0.19	10.2 ± 0.13	0.31 ± 0.02	6.53 ± 0.06	10.9 ± 0.05	330 ± 10.2	120 ± 1.32	10.5 ± 0.06	3.74 ± 0.06
Fly ash < 10 µm (big-scale power plant)	19.5 ± 0.21	6.94 ± 0.15	0.09 ± 0.01	10.5 ± 0.09	5.13 ± 0.05	100 ± 1.65	26 ± 0.12	6.92 ± 0.13	1.82 ± 0.03
Soot from domestic fireplaces	46.2 ± 1.15	18.2 ± 0.05	0.68 ± 0.04	4.92 ± 0.11	12.3 ± 0.03	150 ± 2.76	80 ± 0.85	20.1 ± 0.15	12.5 ± 0.59
Slag from domestic fireplaces	130 ± 5.43	16.2 ± 0.29	0.51 ± 0.02	20.5 ± 0.34	14.8 ± 0.43	250 ± 7.91	130 ± 1.76	16.7 ± 0.13	10.3 ± 0.38
Ash from incinerating room in hospital	345 ± 8.53	19.1 ± 0.38	0.71 ± 0.03	28.1 ± 0.69	18.4 ± 0.72	320 ± 10.3	345 ± 12.6	15.9 ± 0.11	8.31 ± 0.04

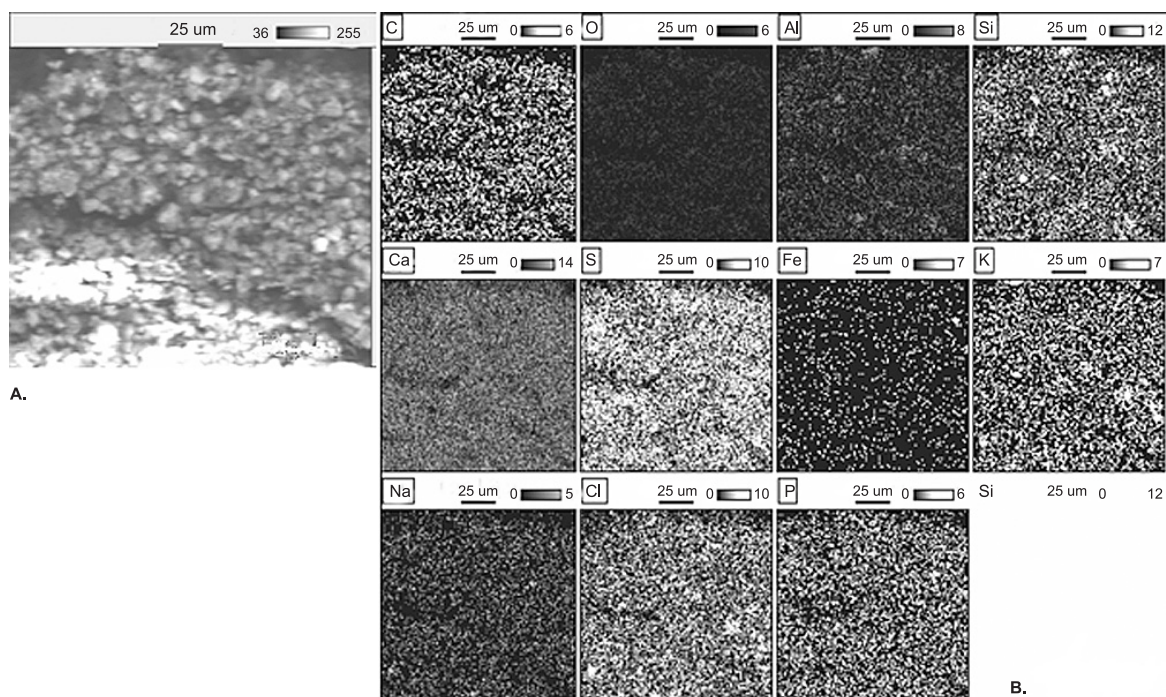


Fig. 1. SEM micrograph (A) and EDS corresponding map of distribution of chosen elements (B) showing the composition of bottom ash from a small-scale power plant in the Łódź region; x1.000.

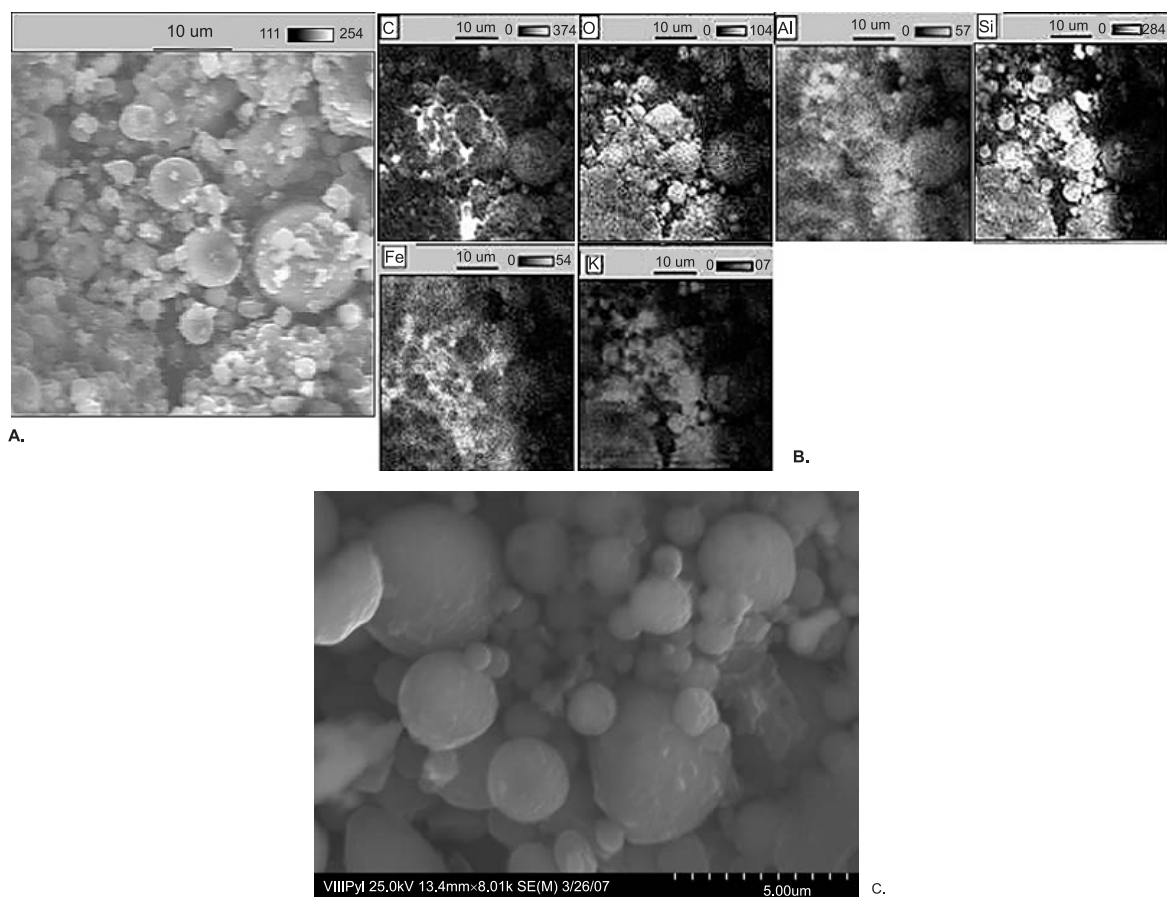


Fig. 2. SEM micrograph (A) and EDS corresponding map of distribution of chosen elements (B) showing the composition of fly ash from a large-scale power plant in Łódź; x3.500 and SEM picture of fly ash, x8.000 (C)

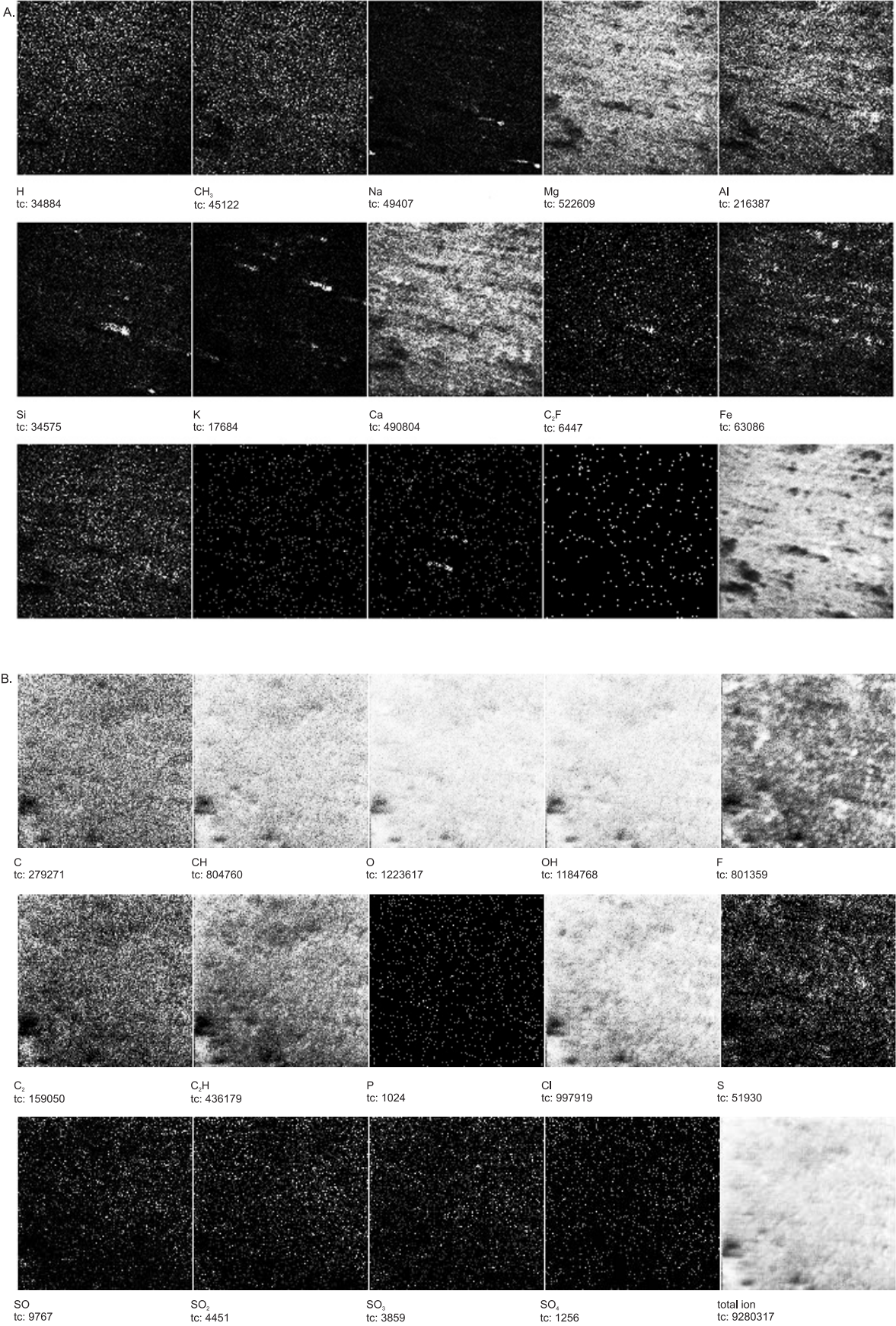


Fig. 3. ToF-SIMS positive (A) and negative (B) ion images of fly ash from a large-scale power plant in Łódź, collected from a microarea of 500x500µm²

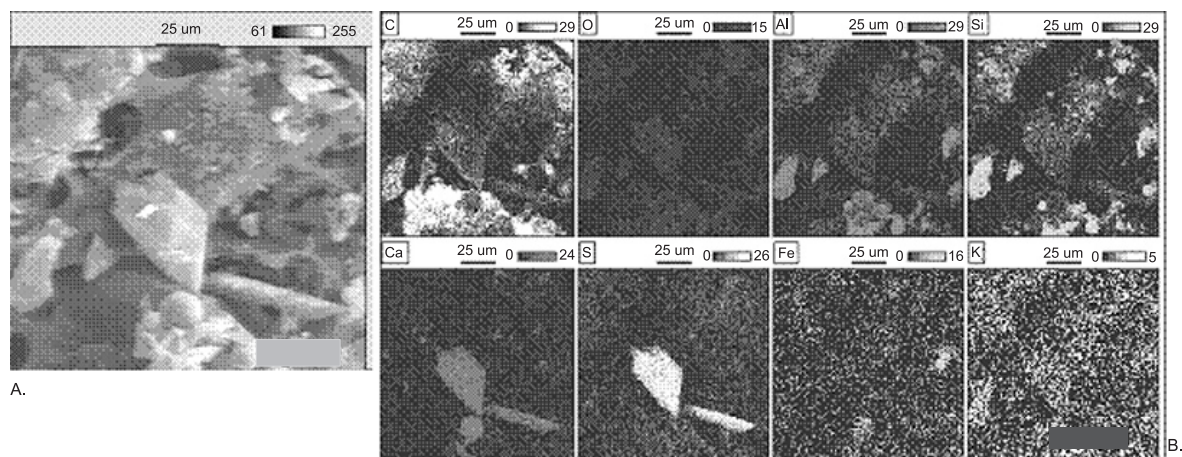


Fig. 4. SEM micrograph (A) and corresponding EDS map of distribution of chosen elements (B) showing the composition of soot from domestic fireplaces collected from the chimney-stalk; x1.000.

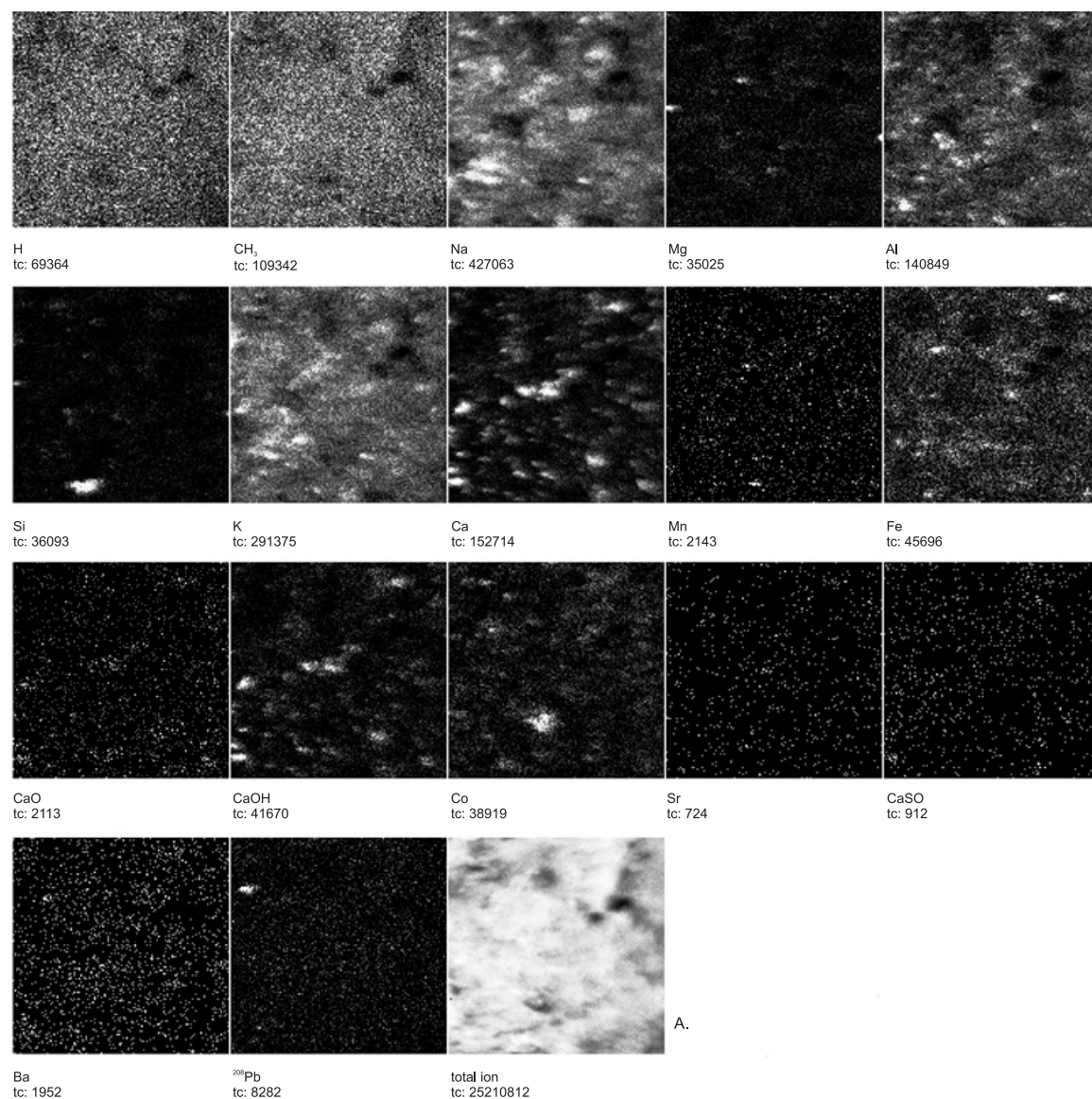


Fig. 5. Part A. ToF-SIMS positive (A) and negative (B) ion images of ash particles originating from domestic fireplaces, collected from a microarea of 500x500 μm².

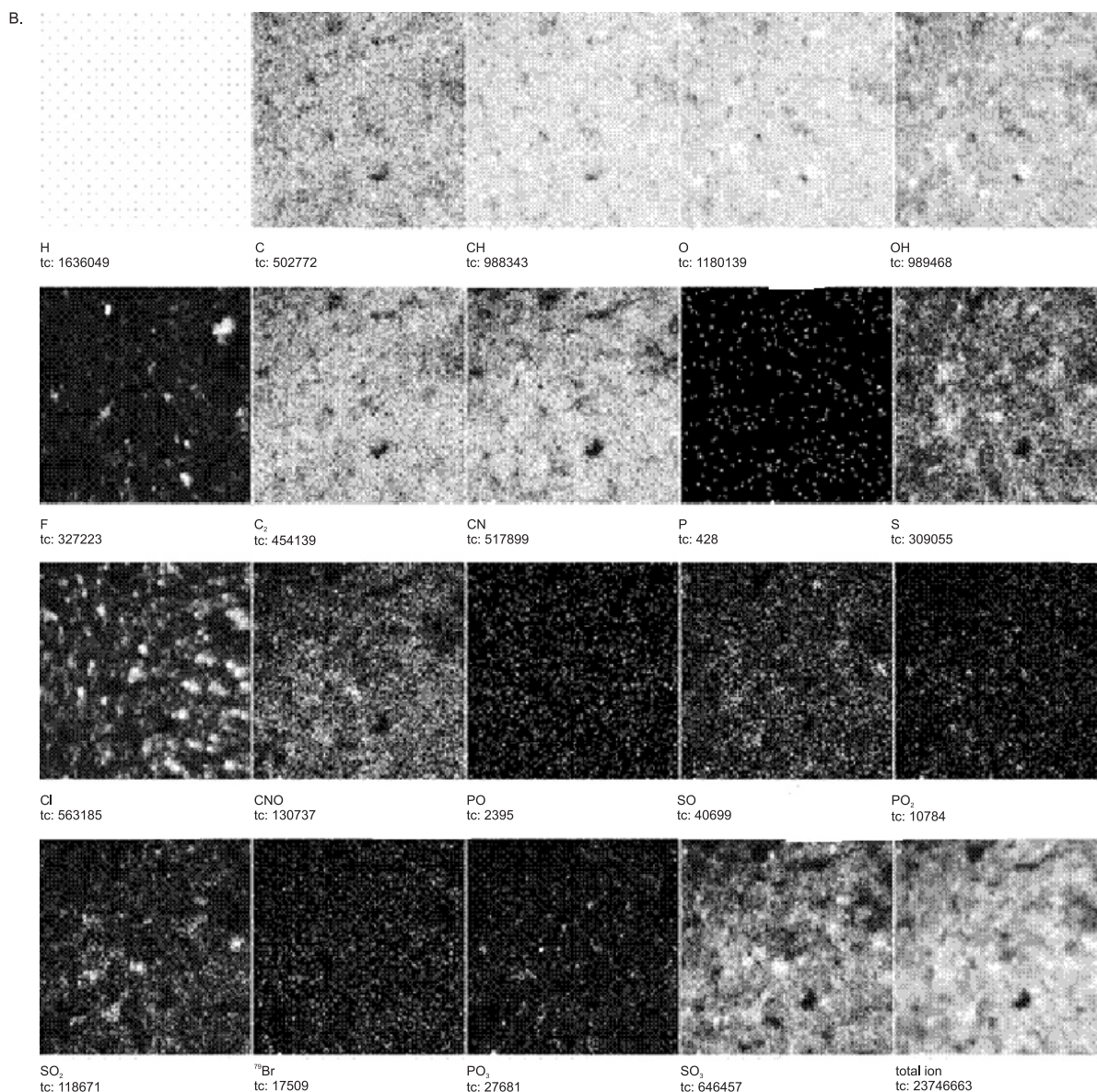


Fig. 5. continued. Part B

the concentration of elements varies greatly, especially in the case of such elements as Al, Fe and Mn, for which maximum concentration is above 300 [mg/kg]. The average concentrations of Ba, Cu and Sr are often at the level above 3 [mg/kg], whereas average concentrations of other analyzed elements (Cd, Cr) are below 1 [mg/kg]. The results of metals concentration for exemplary samples are presented in Table 3. The highest concentrations of studied elements were measured for samples of combustion products of medical wastes and coming from domestic fireplaces. Considerable lower metal concentrations were determined for ash fly from a large-scale power plant. These results can be easily explained by the fact that in the hospital combustion installation a large variety of materials (plastics, rubber, biological tissue, cotton-wool, plaster dressings, bandages, chemicals, expired drugs, paper, board) are burned. Lower concentrations of studied elements recorded for fly ash from power plants may be

a consequence of the fact that fly ash samples were collected after passing through electro-filters, which are the last stage of ash removal devices. The combustion process performed in large-scale installations is characterized by appropriate oxygen concentration and favorable combustion conditions, which strongly influence the composition and morphology (size and shape) of its final products emitted directly into the atmosphere.

In this work we applied additionally SEM-EDS and ToF-SIMS methods to study such properties of particles as their size, morphology and chemical composition. Figs. 1 and 2 present SEM-EDS maps of distribution of chosen elements in bottom ash from power plant in the Łódź region and a fraction of fly ash below 10 μm collected from the large-scale power plant in Łódź. Fig. 1. indicates relatively high content of Al, Na, K, P, Si and Ca. Obtained images show that Ca, O, S and P are homogeneously distributed over a surface of the bottom ash. Contrary to this, en-

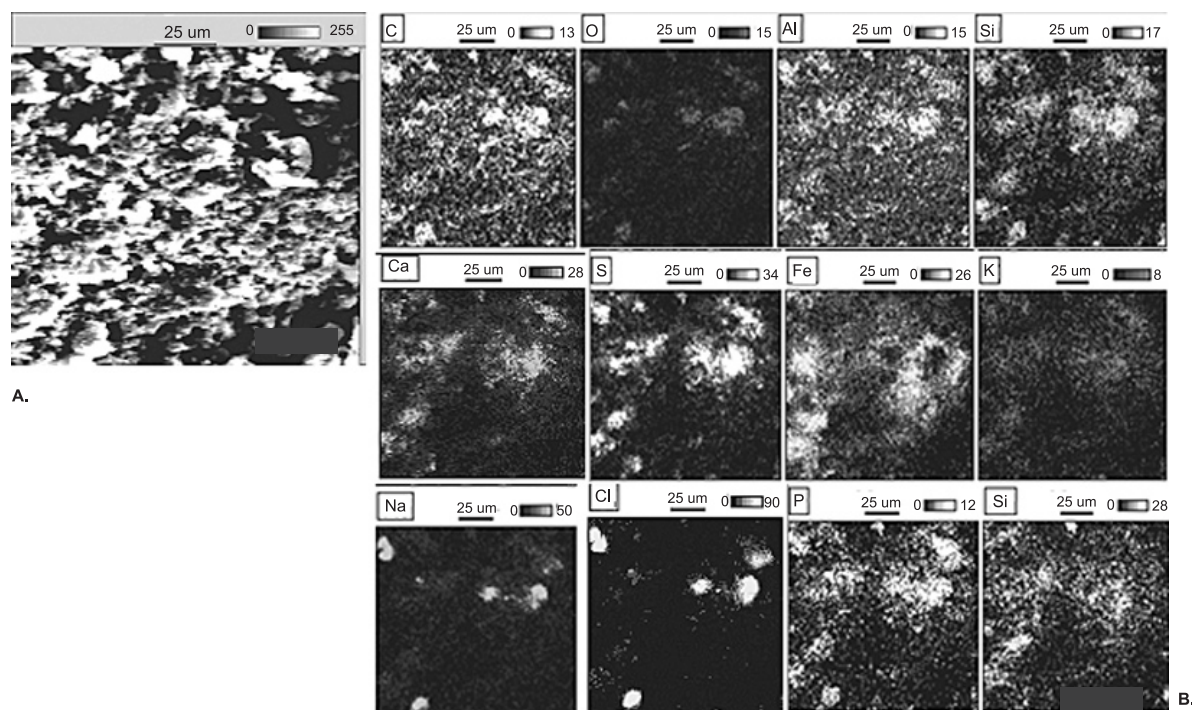


Fig. 6. SEM micrograph (a) and corresponding EDS map of distribution of chosen elements (b) showing the composition of particles generated during a small-scale combustion process of medical wastes; $\times 1.000$.

hanced concentration of Cl, Si, K and Al can be observed within particles of diameter less than 25 μm . Particles with high concentrations of Si also are enriched with Al. SEM-EDS image of fly ash from a large-scale power plant in Łódź made at higher magnification ($\times 3500$) revealed that a typical diameter of emitted particulates is less than 10 μm and with a round shape (Fig. 2). Particles with such a small dimension have a negative effect on human health and the inhalatory system of plants because they can easily block perspirant apparatus. Data presented in Fig. 2 are in accordance with the fact that fly ash particles emitted from coal-fired power plants mainly consist of Ca, Mg and Na silico-alluminates or mixed iron oxides [10, 11]. Additionally, we were able to observe Fe-rich particulates, which are spherical and very small, generally less than a few micrometers in diameter and most commonly formed during high temperature combustion processes. Further particle analysis with the use of SEM (Fig. 2.c.) showed that part of small particulates can aggregate or exist as an individual bigger particle carrying several smaller ones attached, the so-called complex particulates. Particulates similar to these characterized above were earlier observed on the surface of various plant species and recognized as emitted from anthropogenic sources [10, 11].

Fig. 3 presents the positive and negative ToF-SIMS ion images obtained for fly ash surface from a large-scale power plant in Łódź. The analyzed surface contains relatively high amounts of elemental Ca, Mg, Al (Fig. 3.a.) and C, Cl (Fig. 3.b.). Fe, Si, Na, K, Ba and F are present mainly in small particles irregularly distributed on the studied surface. It is worth noting that

relatively high emissions of CF_2^+ ion are observed. The presence of this ion can be related to highly toxic fluoro-organic compounds.

A different situation was observed for the material formed as a result of small-scale combustion processes carried out in domestic fireplaces (Fig. 4., Fig. 5.) and in the case of incinerating plants of medical waste (Fig. 6). Based on SEM-EDS maps (Fig. 4.) we can distinguish not-round particles with dimensions over 25 μm containing Ca and S as main components, some smaller Al, Si-rich particles with various shapes and the smallest spherical ones containing Fe and Ca.

Generally, the above results are in accordance with ToF-SIMS images (Fig. 5.), which show high intensity of the signal corresponding to H, CH_3 , Na, K, Al, Ca (positive mode) and H, C, CH, O, OH, F, CN, CNO, Cl, S, SO_2 , SO_3 , and SO_4 (negative mode). Moreover, the size of observed particles of soot seem to be more diversified in contrast to fly ash from power plant. Positive ion images show non-homogeneous distribution of individual particles with enhanced concentration of Ca, Pb, Mg, Si, Co, Mn and Fe. The size of these particles ranged from a few μm (Mn, Fe and Mg rich particulates) to about 70–80 μm (Ca, Si, Co particulates). Additionally, in negative mode some separate particles rich in F and Cl with diameters from 10–80 μm were observed.

Fig. 6 shows SEM-EDS maps of elemental distribution within the surface of the product of medical waste combustion. Ca, Al, Si, Fe, S, P, Ba and K are main components of the sample. Na and Cl are present on the surface mainly in the form of particles with diameter around

25 μm . Comparison of the maps obtained for bottom ash from a small-scale power plant (Fig. 1.) and ash from medical waste burning clearly shows different morphology. In the first case we observe homogeneously distributed elements while in the second one they tend to aggregate in grains with diameter smaller than 40 μm .

Conclusions

1. ICP-AES and ICP-MS results show that maximum Al, Fe and Mn concentrations in studied samples are above 300 [mg/kg], average concentrations of Ba, Cu and Sr are at the level above 3 [mg/kg]. The lowest average concentrations below 1 [mg/kg] were determined for Cd and Cr.
2. ICP-AES and ICP-MS results indicate that the highest concentrations of studied metals were measured for samples of combustion products of medical wastes and from domestic fireplaces, while the lowest concentrations were determined for fly ash from large-scale power plants.
3. SEM- EDS and ToF-SIMS proved to be valuable techniques in characterization of chemical composition, surface distribution of elements and/or compounds and morphology of different fractions of solid products of combustion.
4. Chemical composition of combustion products depends on the kind of used fuel and the scale of installation and control devices applied (e.g. filters).

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