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CONCENTRATIONS OF 42 ELEMENTS IN ATMOSPHERIC FINE PARTICLES IN ZABRZE, POLAND

One of the methods of measuring the concentrations of trace elements in atmospheric dust is the X-ray fluorescence spectroscopy (XRF). For the first time in Poland, a high-class X-ray fluorescence spectrometer was used to determine the content of trace elements in atmospheric dust collected on filters. Calibration was performed by measuring thin-layer standards and its correctness was checked. The energy-dispersive X-ray fluorescence spectroscopy (EDXRF) was used to determine 42 elements in PM_{2.5} (ambient particulates with the aerodynamic diameter not greater than 2.5 μm). The presence of some elements in the samples of ambient dust collected in 2003 was revealed and their concentrations were determined.

1. INTRODUCTION

The particles in the air can be characterized by a number of features, including their size, density, shape and composition. In general, the properties and health and environmental effects of particles are related to their size. The smaller the particle, the greater the distance of its transport from the emission source and the deeper and more efficient its penetration into human lungs [1]. The composition of a particle is important because it determine the particle size, density, volatility, reactivity, and toxicity [2], [3].

Atmospheric PM is a complex mixture of elemental carbon, ammonium, nitrates, sulfates, mineral dust, trace elements and water [4]. Especially PM_{2.5} (particulate matter of aerodynamic diameter smaller than 2.5 μm) accumulates considerable amounts of compounds, including trace elements and heavy metals [2]. Detailed investigations of the chemical characteristics of atmospheric PM (especially PM_{2.5}) are important for elucidating the particle toxicity.

Silesian Agglomeration, owing to highly developed industry, advances power engineering, high density of population and high traffic intensity, is the area not

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entirely recognizable in terms of air pollution. No studies on the content of elements in PM_{2.5} have been performed so far (neither in Silesian Agglomeration nor anywhere else in Poland) in the scope that has been broadened for many years in the world [5], [6].

In this study, we determine the concentrations of 42 elements in PM_{2.5} from Silesian Agglomeration – Zabrze and analyze their variations.

2. METHODS

2.1. COLLECTION OF PM_{2.5}

PM_{2.5} samples were collected using Rupprecht & Patashnick (Dichotomus Partisol[®]Plus 2025) sampler equipped with an inlet with a 10- μm cut-point, operating at a nominal flow rate of $16.7 \text{ dm}^3 \cdot \text{min}^{-1}$. Each sampling period lasted approximately 24 hours. The filter media consisted of 46.2 mm diameter Teflon filters (Whatman PTFE 2 μm). The particles entering the sampler were divided into two size fractions by a virtual impactor with a 2.5- μm cut-point. The samples of particles with aerodynamic diameter smaller than 2.5 μm (PM_{2.5}) were chosen for the analyses of elements' content. A total of 24 samples (12 samples from winter season and 12 samples from summer season¹) of PM_{2.5} were collected. The samples were conditioned for 48 hours in a weighing room at $50 \pm 5\%$ relative humidity and 20 ± 2 °C before and after dust collection. Blank filters and filters with dust were weighed with Mettler Toledo microbalance of 2 μm resolution.

2.2. PLACE OF PM_{2.5} SAMPLE COLLECTION

Sampling point was located in Zabrze, an industrial center on of Upper Silesia, Poland, extending over the area of 80.5 km², and densely populated (2,363 persons/km²). The site was located about 1,400 m away at the Institute of the Environmental Engineering of the Polish Academy of Sciences (figure 1), where there is an air quality monitoring station belonging to the regional network. This is an urban background site, although it can be influenced in specific circumstances by emissions from radial motorways and the industrial-urban plume from other parts of the Upper Silesia Industrial Zone.

¹ The seasons were divided assuming the 15th March as the beginning of summer season, and the 15th September as the beginning of winter season (heating season).

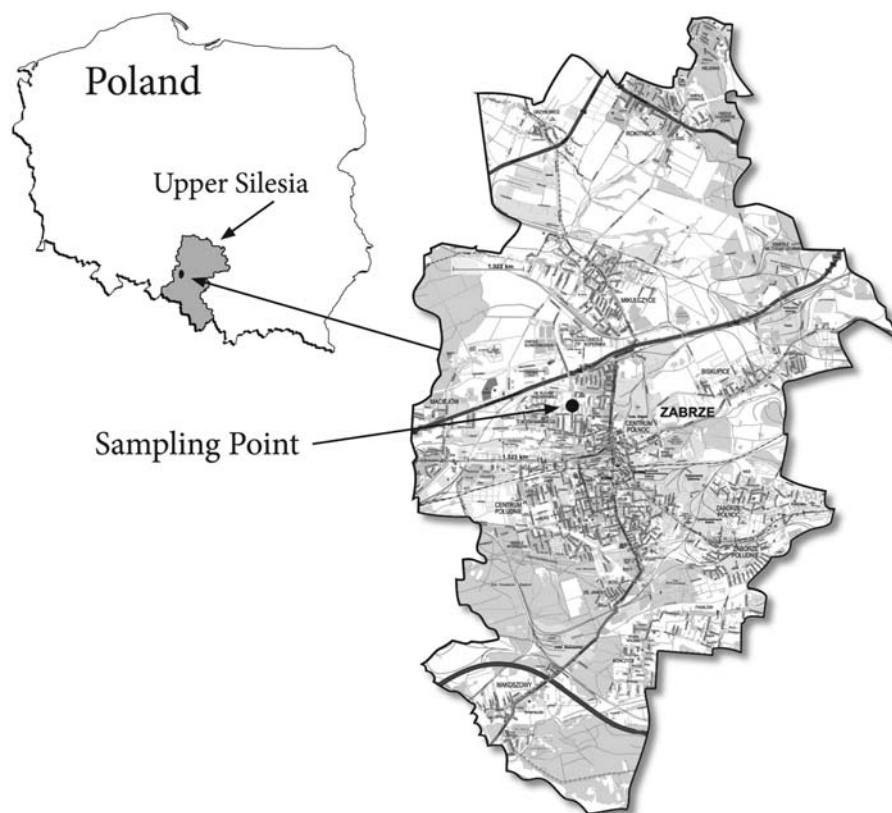


Fig. 1. Location of sampling point

The vicinity was constituted of the national road no. 88 (DK 88) to the north within about 500 m, residential blocks and flats to the east, the center of Zabrze to the south and south-east with the residential buildings and commercial buildings, and housing estate and the allotment gardens to the west.

2.3. EDXRF ANALYSIS

The concentration of 42 elements (Na–Pb, excluding Zr, Nb, Tc, Ru, In, Hf, Ta, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Os, Ir, Pt, Hg) in PM_{2.5} was determined using the technique of Energy Dispersive X-Ray Fluorescence (EDXRF) [7]–[10]. PANalytical ED Spectrometer (Epsilon 5) was used for measurements. Epsilon 5 is equipped with X-ray water-cooled tube with side glass (gadolinium anode, the measuring range of 25–100 kV, 150 μm thick beryllium window), the system of nine secondary targets (Al, Ti, Fe, Ge, Zr, Mo, Ag, Ce₂O₃,

Al₂O₃) and Ge(Li) detector (the resolution of 140 eV, the power range of 0.7–100 keV, 30 mm² of working space, 8- μ m thick beryllium window).

The filters with PM2.5 samples were placed in the measuring cups (Epsilon equipment) for regular tests, and then placed on the trays, in the sequence determined earlier and introduced to the software together with other information about the samples analyzed. The instrument is ready for measurement when an appropriate analytical program is attributed to each sample, and the tray with samples is located in the relevant place of the automatic sample changer. Owing to the thin layer of the sample analyzed, the radiation (especially during the analysis of heavy elements of higher energy) can penetrate into it and interact with the material of the measuring cup. This problem was solved due to the application of specially prepared aluminum inserts. The aluminum of which the inserts are made does not interact with X-ray radiation, which penetrates into the filter or the standard under the measurement conditions.

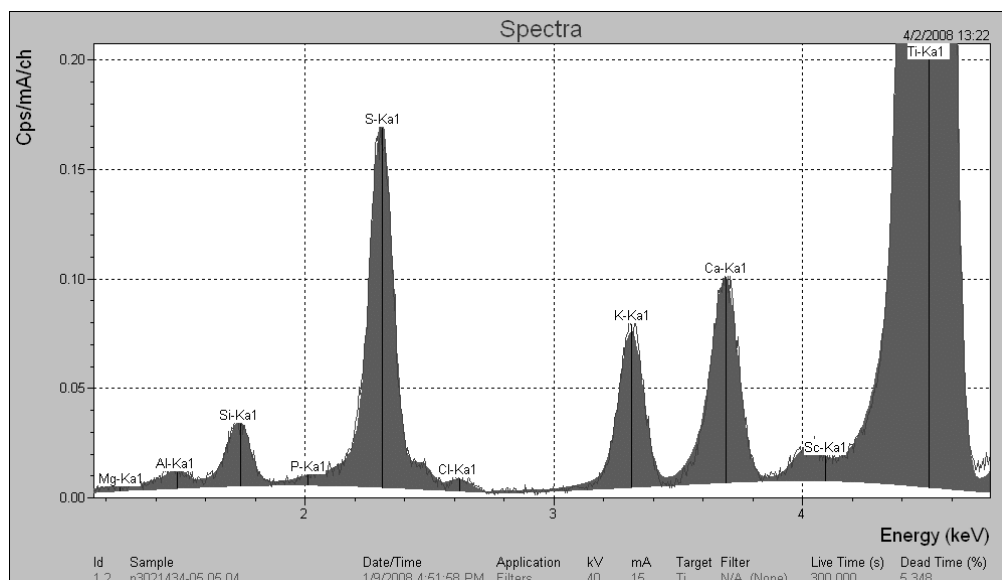


Fig. 2. Example of spectrum of PM2.5 sample

The measurements were carried out in vacuum, the time of analysis was 4800 seconds (it is the total measurement time for the analytical program, in which the secondary Al, Ti, Fe, Ge, Zr, Al₂O₃ targets were used). The settings of X-ray tube depended on the currently used secondary tube and looked the following way: Al/25 keV, 25mA; Ti/40 keV, 15 mA; Fe/40 keV, 15 mA; Ge/75 keV, 8 mA; Zr/100 keV, 6 mA; Al₂O₃/100 keV, 6mA. The concentration of each element depends on its peak intensity representing both the actual sample (figure 2) and the blank filter (background was removed). Epsilon 5 software was used for calculations. The concentra-

tions of the individual analytes were determined by comparing the data obtained with the calibration curves. These curves were determined according to the recommendations of the reference method [7], by measuring the set of thin-layer standards (Micromatter, Inc). Correction coefficients for possible interelement effects were determined for the curves obtained.

2.3.1. QUALITY CONTROL

Daily energy calibration (automatic, done by an instrument), weekly measurements of the NIST 2873 sample (the recovery of each element should be between 90% and 110% of the certified value) and monthly measurements of the monitor are routinely performed to control the quality of this analytical procedure.

The detection limits for the procedure are determined by using two blanks (Teflon filters). Each of the blanks undergoes the whole EDXRF procedure, designed for actual samples, 30 times. The detection limit for each element is computed as a standard deviation from the 60 results obtained for this element by measuring the blanks [7]. For most elements, the detection limits obtained are lower than those required by [7]; for all of them the limits are within the allowable range [7].

3. RESULTS AND DISCUSSION

42 elements determined in the PM_{2.5} samples constitute merely several per cent of the particulate mass (5.7% in winter and 8.3% in summer, the table). It can be concluded that most of the PM_{2.5} mass consisted of carbon compounds, elemental carbon, nitrates, and water [11], [12].

The sulphur has the greatest concentrations in the air and the share in PM_{2.5} mass (the table). Its concentration in the air in winter season is two times higher than that in summer season; however, its share in PM_{2.5} mass was lower in winter than in summer (the table). Na, Mg, Al, Si, Cl, K and Ca also occurred in relatively high concentrations in the air.

Most elements appeared in much higher concentrations in the air in winter than in summer. It is related to higher concentration of PM_{2.5} over this area in winter [13] and to the domination of the anthropogenic sources of dust emission in Poland (also in this area) [14]. Si, Ca, Mn, As, Te, Cs, La, Au were found to have higher concentrations in summer than in winter, while Al, Ti, Fe, Se, Sr, Sn, Rh occurred in comparable concentrations in winter and summer (the table). This may indicate that these elements are emitted from natural sources (Si) or can be related to the combustion of liquid fuels. Some of the elements listed above originate from traffic-related emission, partly from combustion of fuels in car engines, e.g. petrol-containing all types of additives (e.g. Mn, V, Ni, Fe and others) [15], and partly

from the operation of catalytic converters (Mo, Pd, Rh) [16]. Such elements as: Sn [17], La [18], Pd, Pt, Rh [19]–[23] are related to car traffic and are determined as “traffic-related elements”, and their appearance in the air of urban areas is related to traffic emission.

Table

Concentrations of 42 elements in atmospheric fine particles in Zabrze, Poland, in 2003

Element	Winter season		Summer season		Element	Winter season		Summer season	
	ng/mg PM _{2.5}	ng/m ³	ng/mg PM _{2.5}	ng/m ³		ng/mg PM _{2.5}	ng/m ³	ng/mg PM _{2.5}	ng/m ³
Concentrations > 1ng/m ³					Concentrations < 1ng/m ³				
Na	4956.89	360.79	2345.66	58.92	Sc	2.96	0.04	0.00	0.00
Mg	126.99	11.65	325.18	8.75	Co	2.91	0.27	6.39	0.15
Al	1254.61	66.92	2755.60	57.17	Ga	9.74	0.64	19.22	0.21
Si	1191.23	86.57	5518.02	111.16	Ge	24.96	0.83	20.10	0.41
S	33364.46	2391.63	52715.41	1144.73	As	6.71	0.66	76.75	0.83
Cl	1766.90	133.21	142.11	3.11	Se	4.10	0.41	14.96	0.33
K	6501.27	447.20	6282.03	137.15	Rb	12.73	0.87	25.91	0.33
Ca	262.09	17.54	883.59	18.49	Sr	17.70	0.58	16.64	0.46
Ti	50.28	3.32	163.12	3.23	Rh	33.05	0.58	14.55	0.41
V	15.76	1.29	22.78	0.37	Ag	38.71	0.70	29.41	0.54
Cr	21.27	1.45	39.25	0.95	Cs	9.35	0.46	69.13	0.87
Mn	155.03	11.44	713.91	15.55	W	0.00	0.00	0.00	0.00
Fe	1810.46	135.00	5689.98	132.80	Au	0.96	0.04	15.90	0.25
Ni	27.11	1.58	43.64	0.81					
Cu	162.00	10.32	285.30	6.01					
Zn	3275.69	236.08	3134.71	72.31					
Br	254.03	20.61	52.44	1.02					
Y	81.73	2.78	167.81	2.82					
Mo	20.86	1.41	43.72	0.73					
Pd	48.16	1.78	53.24	0.79					
Cd	39.64	2.18	33.66	0.73					
Sn	67.40	3.36	133.42	2.99					
Sb	174.72	10.32	155.01	3.11					
Te	32.67	0.97	57.36	1.22					
I	90.01	6.05	106.47	2.40					
Ba	88.35	3.69	67.09	1.62	Winter season		Summer season		
La	41.73	2.32	139.26	4.69		$\Sigma_{42\text{Elements}}$		$\Sigma_{42\text{Elements}}$	
Pb	1020.98	74.46	1048.73	26.45		= 5.7% PM _{2.5}		= 8.3% PM _{2.5}	

The proportion of the individual elements in PM_{2.5} mass was higher in summer than in winter. Na, Cl, Sc, Br, Rh were the only elements that had higher proportions in PM_{2.5} mass in winter than in summer (the table). Some metals (for example iron) occurred in PM_{2.5} in similar concentrations in both seasons, and others (for example lead) assumed definitely higher concentrations in the air in winter. This testifies to their relation to the municipal emission.

It is also worth mentioning that some metals presented in the table were found in 2003 in the concentrations considerably higher than those reported from the other parts of the urbanized Europe, or outside Europe [24], [25]. This is surely related to the fact that in the area of interest the production activity was conducted for many years, including intensive production of steel and coke as well as of zinc and lead.

The sequences of the average monthly concentrations of the 16 elements selected are given in figure 3. The PM_{2.5} samples were collected in January, February, March, May, July, August and September. Thus, figure 3 shows the permanent values of the concentrations of 16 elements in 2003 in the periods: March–May and May–July.

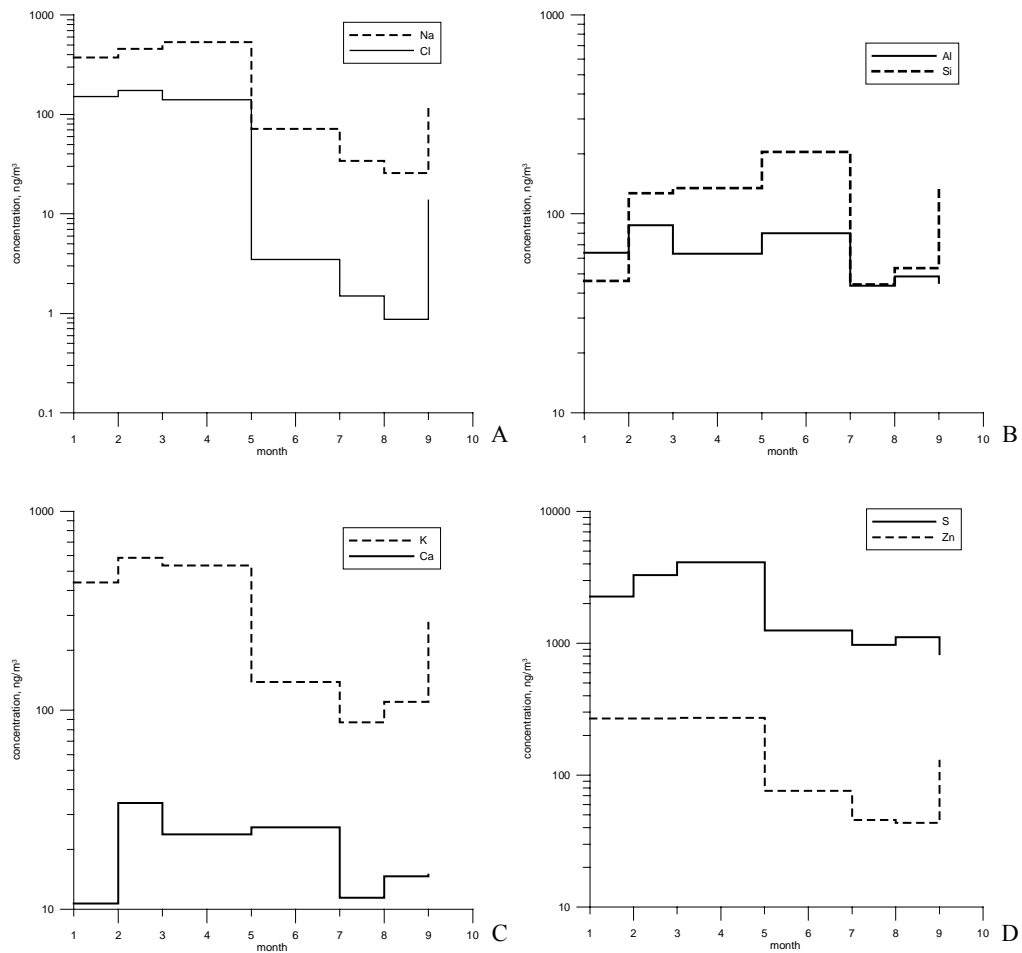


Fig. 3. To be continued

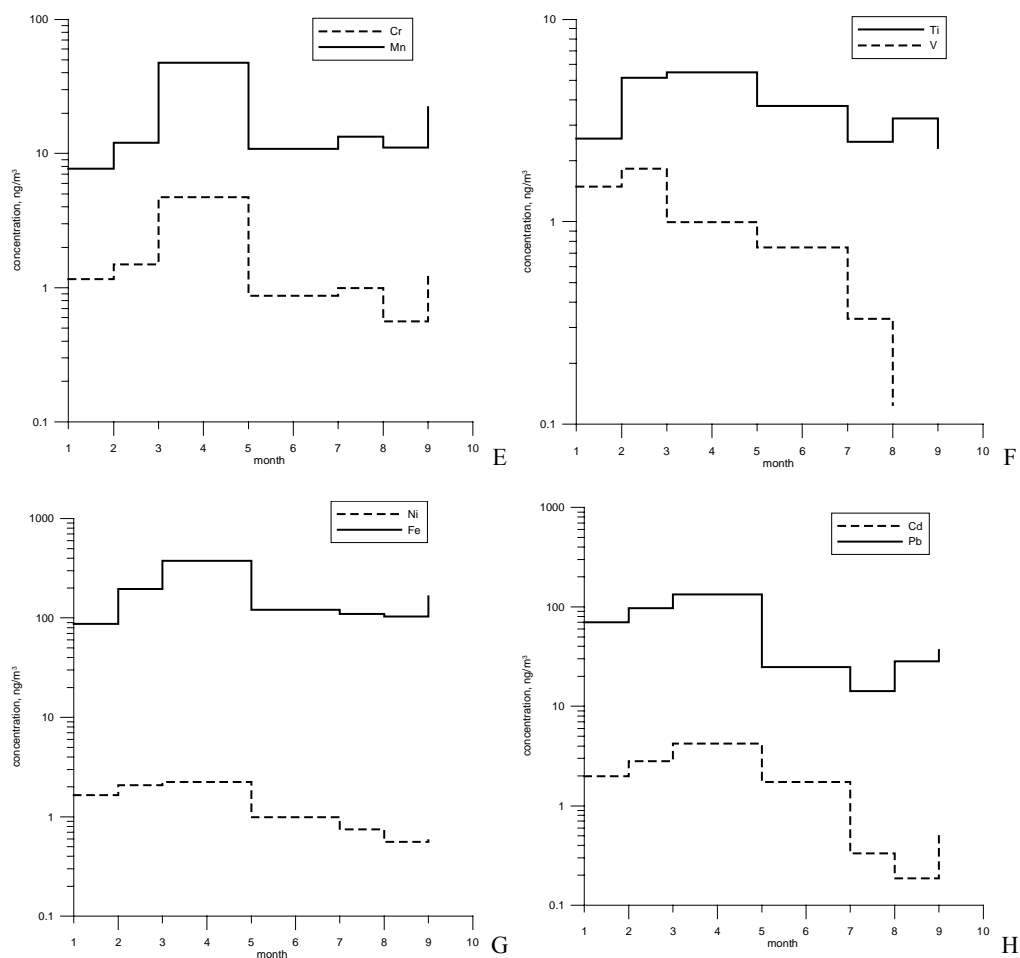


Fig. 3. Average monthly concentrations of 16 elements in atmospheric fine particles in Zabrze, Poland in 2003

Some pairs of the elements indicated in diagrams A–H had similar average monthly sequences in the year 2003. Sodium and chlorine (A) assumed the highest concentrations in the cold season (January, February, March, September), and the lowest – in August. The concentrations of chlorine indicated, however, higher monthly variability compared to these of sodium. The average monthly chlorine concentrations had similar sequences in 2003 (C). Diagrams A and C confirm that the concentrations of chromium, potassium and sodium in the urbanized area are related mainly to the anthropogenic sources of their emission [26]. While the concentration of calcium (C) in the air of the urbanized area can depend both on the emission from the anthropogenic sources (e.g. the combustion of fuel-containing calcium – the maxi-

imum concentration of calcium (C) in February), and on the emission from the natural sources, which is confirmed by its high average monthly concentration in the air within the period from March to July.

The concentrations of aluminum and silicon, the main components of the lithosphere, were higher in summer. At the same time the natural sources of their emission (erosion of rocks and soil) or the secondary emission could be responsible for their concentrations. This tendency is particularly characteristic of silicon (the maximum concentration from May to July); the average monthly concentration of aluminum showed a narrower range compared to that of silicon.

Sulphur (occurring in PM, as SO_4^{2-} anion [12]) is emitted into the atmosphere mainly as a result of different combustion processes (especially of fossil fuels). This confirms the changes of its average monthly concentration (D) – it reached the highest concentration in the period from January to May; from May to September the sulphur concentration was constant and lower than in winter. A similar sequence of average monthly concentration was also found for zinc (D) in 2003.

Almost identical sequences of the average monthly concentrations of chromium and manganese were revealed in 2003 (E), with the maxima of concentrations falling in the period from March to May.

The concentrations of titanium, iron and nickel (G, F) changed monthly within a narrow range. Their maximum monthly average concentrations occurred from March to May. While the concentration of vanadium was the highest in January and February (F).

Lead and cadmium had similar sequences of the average monthly concentrations (H), while the biggest drop in cadmium concentration was found in July, and in lead – in May. Both metals appeared in the highest concentrations at the beginning of the year (the maximum in March), and in the lowest concentrations – in July and August.

4. CONCLUSIONS

The analysis of the concentrations of 42 elements occurring in the atmospheric PM_{2.5} in Zabrze shows that most of them arise from the anthropogenic sources in the urbanized area, including in particular the municipal and traffic-related sources. The majority of the elements being analysed occurred in the air in the concentrations higher than 1 ng/m^3 , and those occurring in lower concentrations were mainly trace elements and precious metals (the table). Particularly the common elements were found to occur in higher concentrations in winter than in summer. However, some elements were also found to occur in higher concentrations in summer season (e.g. Si) than in winter season, since they arose from the natural sources. The concentrations of some other elements in summer and in winter were remarkably similar, since they arose from the sources that did not depend on the season (e.g. traffic). These rela-

tions were especially noticeable in the sequences of the average monthly concentrations of elements in 2003 (figure 3).

Based on the comparison of the concentrations of some metals in the air of Zabrze in the year 2003 with their concentrations in other regions of urbanized Europe and other regions of the world it can be concluded that in the area of Upper Silesian Agglomeration the concentrations of some metals (particularly lead, zinc and cadmium) proved to be exceptionally high due to many-year industrial activity. This translates directly into the exposure of the people living there to a real health hazard.

REFERENCES

- [1] ENGLERT N., *Fine particles and human health – a review of epidemiological studies*, Toxicology Letters, 2004, 149, 235.
- [2] NIEBOER E., RICHARDSON D.H.S., *The replacement of the nondescript term “heavy metals” by a biologically and chemically significant classification of metal ions*, Environmental Pollution, 1980, B1, 3–26.
- [3] *Air Quality Guidelines*, second edition, WHO Regional Office for Europe, Copenhagen, Denmark, 2000.
- [4] BONI C., CARUSO E., CETEDA E., LOMBARDO G., BRAGA MARCAZZAN G.M., REDAELLI P., *Particulate matter elemental characterization in urban areas: pollution and source identification*, Journal of Aerosol Science, 1988, 7, 1271.
- [5] HUEGLIN CH., GEHRIG R., BALTENSPERGER U., GYSEL M., MONN CH., VONMONT H., *Chemical characterization of PM_{2.5}, PM₁₀ and coarse particles at urban, near-city and rural sites in Switzerland*, Atmospheric Environment, 2005, 39, 637–651.
- [6] *Air Quality Criteria for Particulate Matter*, Volume I and II, National Center for Environmental Assessment-RTP Office of Research and Development, U.S. Environmental Protection Agency Research, Triangle Park, NC, October 2004.
- [7] *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium Method IO-3.3 Determination of metals in ambient particulate matter using X-Ray Fluorescence (XRF) Spectroscopy*, U.S. Environmental Protection Agency, Cincinnati, June 1999.
- [8] BERTIN E.P., *Principles and practice of X-Ray Spectrometric Analysis*, Plenum Press, NY, 1975.
- [9] JENKINS R., GOULD R.W., *Quantitative X-Ray Spectrometry*, second edition, Dekker, Inc., NY, 1995.
- [10] JENKINS R., *X-Ray Fluorescence Spectrometry*, second edition, John Wiley, Inc., NY, 1999.
- [11] PASTUSZKA J.S., WAWROŚ A., TALIK E., PAW K.T., *Optical and chemical characteristics of the atmospheric aerosol in four towns in southern Poland*, The Science of the Total Environment, 2003, 309, 237.
- [12] PALEOTTI L., DE BERARDIS B., ARRIZZA L., PASSCANTANDO M., INGLESSIS M., MOSCA M., *Seasonal effects on the physico-chemical characteristics of PM_{2.1} in Rome: study by SEM and XPS*, Atmospheric Environment, 2003, 37, 4869–4879.
- [13] KLEJNOWSKI K., KRASA A., ROGULA W., *Seasonal variability of concentrations of total suspended particles (TSP) as well as PM₁₀, PM_{2.5} and PM₁ modes in Zabrze, Poland*, Archives of Environmental Protection, 2007, 3, 15–29.
- [14] KLEJNOWSKI K., *Stan formalno-prawny zagadnień związanych z ochroną i monitoringiem powietrza. Ocena jakości powietrza w województwie śląskim w latach 20002–2006*, WIOŚ Katowice, ISBN 978-83-7217-311-9
- [15] *Ropa naftowa a środowisko przyrodnicze*, edited by Jan Surygała, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 2001.

- [16] DA SILVA L.I.D., DE SOUZA SARIS J.E., ZOSIN F.M.Z., CARNEIRO M.C., NETO A.A., DA SILVA A.S.A., CARDOSO M.J.B., MONTEIRO M.I.C., *Traffic and catalytic converter-related atmospheric contamination in the metropolitan region of the city of Rio de Janeiro, Brazil*, *Chemosphere*, 2008, 71, 677–684.
- [17] VIANA M., QUEROL X., ALASTUEY A., *Chemical characterisation of PM episodes in NE Spain*, *Chemosphere*, 2006, 62, 947–956.
- [18] GANDHI H.S., GRAHAM G.W., MCCABE R.W., *Automotive exhaust catalysis*, *Journal of Catalysis*, 2003, 216, 433–442.
- [19] BALDANZA M.A.S., MELLO L.F., VANNICE A., NORONHA F.B., SCHMAL M., *Adsorptive and catalytic properties of alumina-supported Pd-Mo catalysts*, *Journal of Catalysis*, 2000, 192, 64–76.
- [20] GOMEZ B., GOMEZ M., SANCHEZ J.L., FERNANDEZ R., PALACIOS M.A., *Platinum and rhodium distribution in airborne particulate matter and road dust*, *Science of Total Environment*, 2001, 269, 131–144.
- [21] RAUCH S., LU M., MORRISON G.M., *Heterogeneity of platinum group metals in airborne particles*, *Science of Total Environment*, 2001, 35, 595–599.
- [22] BOCCA B., CAIMI S., MICHOWSKI P., GOMEZ D., CAROLI S., *Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina*, *Science of Total Environment*, 2006, 358, 255–264.
- [23] ZOTIN F.M.Z., GOMEZ O.F.M., OLIVEIRA C.H., ALCOVER N.A., CARDOSO M.J.B., *Automotive catalyst deactivation: Case studies*, *Catalysis Today*, 2005, (107/108), 157–167.
- [24] SALVADOR P., ARTINANO B., QUEROL X., ALASTUEY A., COSTOYA M., *Characterisation of local and external contributions of atmospheric particulate matter at a background coastal site*, *Atmospheric Environment*, 2007, 41, 1–17.
- [25] KARAR K., GUPTA A.K., KUMAR A., BISWAS A.K., *Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM10 particulates at the two sites of Kolkata, India*, *Environmental Monitoring and Assessment*, 2006, 120, 347–360.
- [26] OOKI A., UEMATSU O., MIURA K., NAKAE S., *Sources of sodium in atmospheric fine particles*, *Atmospheric Environment*, 2002, 36, 4367–4374.

STĘŻENIA 42. PIERWIĄSTKÓW ZWIĄZANYCH Z PM_{2.5} W POWIETRZU ATMOSFERYCZNYM W ZABRZU

Jedną z metod pomiaru stężenia pierwiastków śladowych w pyłe atmosferycznym jest fluorescencja rentgenowska. Po raz pierwszy w Polsce wykorzystano wysokiej klasy spektrometr fluorescencji rentgenowskiej do oznaczeń zawartości pierwiastków śladowych w pyłach atmosferycznych osadzonych na filtrach. Przeprowadzono kalibrację opartą na pomiarze cienkwarstwowych wzorców i sprawdzono poprawność jej działania. Zastosowano technikę EDXRF do oznaczania 42. wybranych pierwiastków we frakcji *fine* pyłu zawieszzonego w powietrzu. Stwierdzono obecność poszczególnych pierwiastków w pyłe PM_{2,5} oraz rozpoznano wstępnie stężenia, w jakich one występują w próbkach z 2003 roku.