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CONCENTRATION LEVEL AND SURFACE CHEMICAL COMPOSITION OF URBAN AIRBORNE PARTICLES NEAR CROSSROADS IN ZABRZE, POLAND

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STĘŻENIE, STRUKTURA I SKŁAD CHEMICZNY POWIERZCHNIOWEJ WASTWY PYŁU ATMOSFERYCZNEGO W OKOLICY SKRZYŻOWANIA W ZABRZU

W artykule przedstawiono wyniki badań prowadzonych w 2005 r. przy sześciu skrzyżowaniach w Zabrzu. Pomiary dotyczyły określenia natężenia ruchu na skrzyżowaniach, obserwacji parametrów meteorologicznych i przede wszystkim wyznaczenia stężeń pyłu PM2,5 i PM10 we wszystkich badanych punktach. Porównano strukturę aerozolu w okolicy skrzyżowań ze strukturą aerozolu w punkcie odniesienia oddalonym od wpływu komunikacji poprzez wyliczenie udziału PM2,5 w PM10 w każdym punkcie. W jednym z punktów pomiarowych pomiary prowadzono kilkanaście dni, a pobrane próby PM10 poddano analizie składu chemicznego powierzchniowej warstwy pyłu metodą XPS. Zidentyfikowane zostały główne oraz występujące w śladowych ilościach pierwiastki na powierzchni pyłu pobranego przy skrzyżowaniu.

Summary

The paper presents results of investigations carried out in 2005 at six crossroads in Zabrze. The investigations comprised determinations of vehicular traffic intensity, observations of meteorological conditions and, as a main subject, determinations of concentrations of PM2.5 and PM10 at all observed sites. Structure of ambient aerosol in the vicinity of crossroads was compared with the structure of aerosol at a reference measuring point, located beyond effects of vehicular traffic, by determining a share of PM2.5 in PM10 for each site. At a selected crossroad the measurements lasted 11 days and the sampled dust was analyzed for chemical composition of surface of its particles with the use of the X-ray photoelectron spectroscopy (XPS). Both the most abundant and trace elements in the surface layer of dust sampled at the crossroads were identified.

INTRODUCTION

Atmospheric aerosol is a complex disperse system of solid and liquid particles of different size, shape, chemical composition and reactivity. Epidemiologi-

cal studies in the past [3, 17, 23] gave a strong hint on extended morbidity and mortality even due to relatively low burdens of particulate matter. Although a lot of research efforts have been put in within the last years and more recent epidemiological findings basically confirm the earlier results [6, 16, 22], the understanding of the causal chains between the versions parameters describing particulate aerosol and the corresponding health effects are still lacking [6]. For example, elevations in airborne particulates, especially those of aerodynamic diameter less than 2.5 μm (PM2.5) increase the incidence of human cardiac and respiratory diseases but the mechanisms involved are poorly understood. Also, the formation mechanisms of particulates need to be investigated to establish a link between the source and effect of such particles.

Recently, motor vehicles have become a major source of the criteria pollutants and hazardous air pollutants that are ubiquitous to urban areas. Particulate matter originating from mobile sources is thought to be responsible for a myriad of adverse health outcomes, ranging from cancer to cardiopulmonary disease, and environmental problems [1, 3, 18].

Exhaust after treatment, such as catalytic converters and diesel particle filters, has resulted in significant reductions in the masses of both gaseous and particulate pollutants [5]. However, some researchers reported increases in the emissions of particles from vehicles due to particle nucleation occurring downstream of after treatment devices [25]. Some, new studies (example [12]) have determined that a significant fraction of diesel particulate matter is semi-volatile with a mode diameter typically smaller than 50 nm (nucleation mode) whereas a non-volatile (refractory) portion, generally in the 50–200 nm range (accumulation mode), constitutes the bulk of particulate matter mass and consists of particles with an elemental carbon core and low vapor pressure hydrocarbons and sulfur compounds adsorbed on their surface. Therefore, the chemical characterization of the surface of aerosol particles is critical in identifying particulate sources because new species produced from chemical reactions in the atmosphere occur on the particle surface. Also the species present on the surface are critical for health effects because it is the particulate surface which is directly accessible to biological fluids after inhalation. However, for this kind of studies a new surface sensitive method is needed. Such, a very promising, method seems to be X-ray photoelectron spectroscopy (XPS) but during the last thirty years only few studies have addressed the surface chemistry of urban air particulates by using XPS [2, 7, 8, 15, 26–28]. Till now, probably nobody has applied this method to characterize the aerosol particles of traffic origin.

To improve the understanding of the influence of emission of particles from the roads on the properties of the atmospheric aerosol, this study was undertaken with the objective to analyze the PM2.5/PM10 ratio and to determine the surface chemical characteristics of aerosol particles near the crossroads.

METHODS

The investigations were performed in 2005; they were carried out in two stages. A site under investigation was the crossing of Bytomska and Stalmacha Streets in Zabrze, numbered "1" in the paper (Fig. 1).

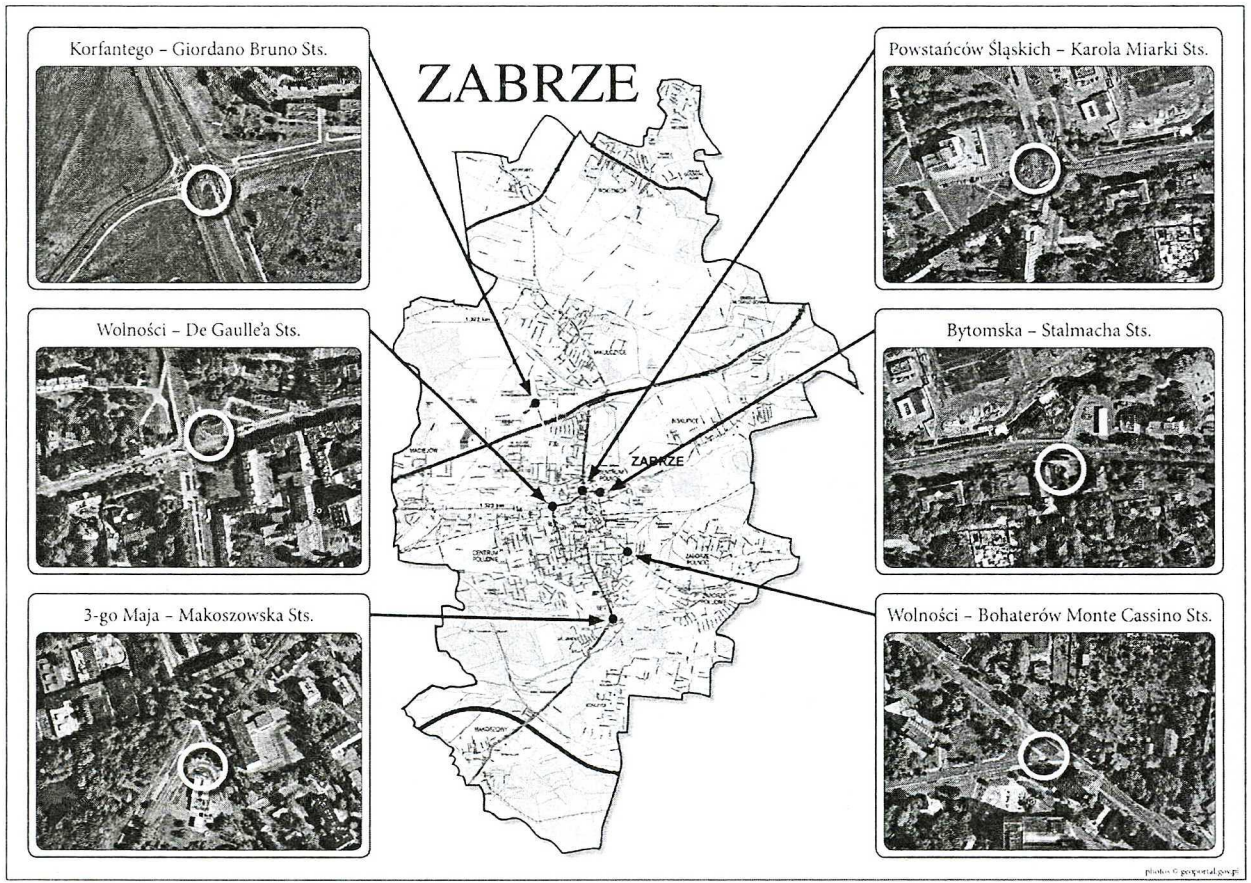

Fig. 1. Locations of measuring sites

The first stage comprised field measurements of traffic intensity and dust concentrations. The PM10 and PM2.5 concentrations were measured simultaneously at the measuring site "1" in the summer (5–18 April). From 3 June to 1 July, further, auxiliary measurements of PM10 and PM2.5 were done at the busiest five crossroads (numbered from "2" to "6") of the city. The measuring sites are characterized in Table 1, their locations – in Figure 1.

Table 1. Measuring sites – crossroads and traffic

Site number	Site description (crossroad)	Minimum traffic intensity		Maximum traffic intensity		Average traffic intensity	
		light vehicles [veh./h]	heavy vehicles [veh./h]	light vehicles [veh./h]	heavy vehicles [veh./h]	light vehicles [veh./h]	heavy vehicles [veh./h]
"1"	Bytomska and Stalmacha Sts.	980	128	2850	300	1350	195
"2"	Wolności and de Gaulle'a Sts.	2580	180	3120	420	2910	315
"3"	Powstańców Śląskich and K. Miarki Sts.	1680	180	2400	600	1980	384
"4"	3-go Maja and Makoszowska Sts.	1680	120	2580	360	1954	257
"5"	Korfantego and Giordano Bruno Sts.	1200	120	2580	360	1820	260
"6"	Wolności and Bohaterów Monte Cassino Sts.	1500	180	1740	300	1605	240

To determine traffic intensity, vehicles passing a crossroad were counted for 15–20 min between whole hours from 8:00 a.m. to 7:00 p.m. and the results were extrapolated to receive one hour data. All crossroads were equipped with traffic lights that eased car counting by precluding traffic from some directions between light turns. Light (mainly passenger) and heavy (trucks, buses) vehicles were counted separately, the heavy ones assumed (according to [9]) to be diesels. At the sampling point "1", the traffic intensity was determined each third day of the measuring period, starting from the first day.

Concentrations of both suspended dust PM10 and its respirable fraction PM2.5 were determined gravimetrically; for PM10 glass fiber filters and for PM2.5 Teflon membrane filters were used.

The dust was sampled with use of ATMOSERVICE MVS6D aspirators, certified, conforming to the CEN EN 12341 norm. Each aspirator had two heads, one for PM10 and another for PM2.5 measurements, both operating at the air flow 2.3 m^3/h.

All the time the samples were collected the meteorological conditions were observed: wind direction and wind strength (strong, moderate, weak, calm), air temperature, pressure and precipitation.

The second stage of investigations consisted in determining content of particular elements in surface layer of dust by applying the X-ray photoelectron spectroscopy (XPS). Three pairs of samples were analyzed. Both samples in a pair were completed on the same day at the measuring point "1", each pair consisted of a sample of PM10 and a sample PM2.5.

The analysis was accomplished by using a PHI 5700/660 Photoelectron Spectrometer. A monochromatic Al K_α source of X rays (1486 eV) was used. Spectra of energy distribution of photoelectrons were analyzed by a hemispherical analyzer; resolution of the analyzer was approximately 0.3 eV. The area 0.8 × 2 mm of a filter surface was analyzed. Each analysis lasted 12 h. The measurements were performed at ultra high vacuum – under pressure of 10^{-7} Pa. Electric charges on the sample surfaces were neutralized by using a low energy electron gun.

The selected samples were analyzed qualitatively (identification of elements on dust particle surfaces) and quantitatively (determination of relative amounts of the detected elements from their XPS spectra; the energy range was from 0 to 1400 eV). The results were developed with the use of the Multipak computer program. Bonding energies of particular elements were referred to the C 1s level (284.6 eV). On the surface of the particles of PM10 and PM2.5, mean atomic concentrations of F, C, O, N, Fe, S, Si, Na, Zn, I, Cu, Cl, Al, Ca, K, Mg, Pb, Ti, P, Mn were determined.

The XPS spectra of clean both Teflon and glass filters were also obtained. For filters covered with very thin layer of dust the effect of filter surface on the spectrum lines of proper elements was determined.

RESULTS AND DISCUSSION

The measurements were done in summer on rainless and warm days, when wind speed did not exceed 2 m/s. The days with similar weather conditions were selected, characteristic of the urban summer climate.

Table 2. Analysis of meteorological conditions at sampling sites on measuring days

Site number	Meteorological conditions		
	Temperature °C	Atmospheric pressure hPa	Qualitative analysis of anemometric and actinometric conditions
"1"	10–25*	961–1001*	Wind blowing at various times of day, each day with different strength, usually from one of the streets towards the measuring point, occasional rains from 8 to 11 April
"2"	27–34	988	No clouds; calms, weak east or northeast winds
"3"	29–37	986	Cloudy sky till noon, quite strong south and southeast winds; bright sun, no winds nor clouds in afternoon
"4"	26–37	992	No clouds, calms or weak west, south or southwest winds,
"5"	25–31	986	Cloudy sky till 1 p.m., occasional rain, weak south, southeast or east wind; after 1 p.m. bright sun, no clouds, frequent calms
"6"	25–34	979	Weak southeast wind; after 10 a.m. frequent calms, bright sun, no clouds

* – the highest and the lowest air temperature and pressure observed on measuring days at measuring point "1"

To determine the amount of PM2.5 in PM10, concentrations of both fractions were measured simultaneously at the measuring point "1" during 11 measuring days of summer season. Additionally, the two concentrations were measured at each of the points "2", "3", "4", "5", "6", one day at each point, PM2.5 and PM10 simultaneously. The results are presented in Table 3.

Table 3. Concentrations of PM10 and PM2.5 at measuring points "1" to "6" and proportion PM2.5/PM10 – structure of ambient aerosol in busy crossroads vicinity

"1"			
Date (day of week)	Diurnal concentr. PM10 [μg/m³]	Diurnal concentr. PM2.5 [μg/m³]	PM2.5/PM10
5–6 April (Tue./Wed.)	94.86	32.29	0.34
6–7 April (Wed./Thu.)	93.01	39.93	0.43
7–8 April (Thu./Fri.)	97.15	65.78	0.68
8–9 April (Fri./Sat.)	32.25	24.89	0.77
9–11 April (Sat./Sun./Mon.)	27.67	23.79	0.86
11–12 April (Mon./Tue.)	67.83	50.05	0.74
12–13 April (Tue./Wed.)	58.33	57.84	0.99
13–14 April (Wed./Thu.)	56.07	49.82	0.89
14–15 April (Thu./Fri.)	93.70	32.64	0.35
15–16 April (Fri./Sat.)	96.47	38.12	0.40
16–18 April (Sat./Sun./Mon.)	49.00	24.97	0.51
Mean at "1"	69.67	40.01	0.63
"2"			
3.06.2005	46.3	23.4	0.50
"3"			
14.06.2005	38.6	21.1	0.55
"4"			
16.06.2005	61.1	39.9	0.65
"5"			
22.06.2005	35.0	29.6	0.85
"6"			
1.07.2005	68.4	36.6	0.54
Mean "1"–"6"	49.88	30.12	0.618
Mean urban background	32.0	24.0	0.75

As can be seen from Tables 3 and 4, the decisive factor affecting concentrations is meteorological conditions, especially precipitation and wind speed.

Traffic intensity was almost the same at all the crossroads. Proportion of maximum to minimum average traffic intensity was only 2.1, while significant differences of immissions might occur when traffic intensities differ by no less than one order of magnitude (or at least the proportion is 5). Thus, the results reflect only the influence of the crossroad traffic on aerosol concentrations in areas adjacent to crossroads and may be used to determine the structure (contribution of PM2.5 to PM10) of aerosol near crossroads.

Some values of the proportion PM2.5/PM10 considerably differed from its mean values (minimum – 0.34, maximum – 0.99), but its mean for April (0.63) and for whole summer (0.618) was close to its mean for European agglomerations and Zabrze [4, 11, 13, 14, 19].

Concentrations of PM2.5 and PM10 at the crossroads were much higher than concentrations reported by the automatic monitoring station measuring concentrations at the "urban background" site [10]. Except weekends, the summer PM2.5 and PM10 crossroad concentrations were considerably higher (by about 40%) than those at the "urban background site" [20, 21, 24]. The augmentation concerns especially the coarse fraction – the proportion PM2.5/PM10 from 0.75 at the "background site" dropped to 0.618 at the crossroads. This seems to be a specifically Polish phenomenon: it is probably due to a great number of old diesel cars with inefficient engines and great amount of dust on street surface. The deposited on streets and roadsides dust, raised into air by passing cars, is reemitted into the atmosphere.

In Figures 2–7, XPS spectra for PM10 and PM2.5 from the site "1" are presented.

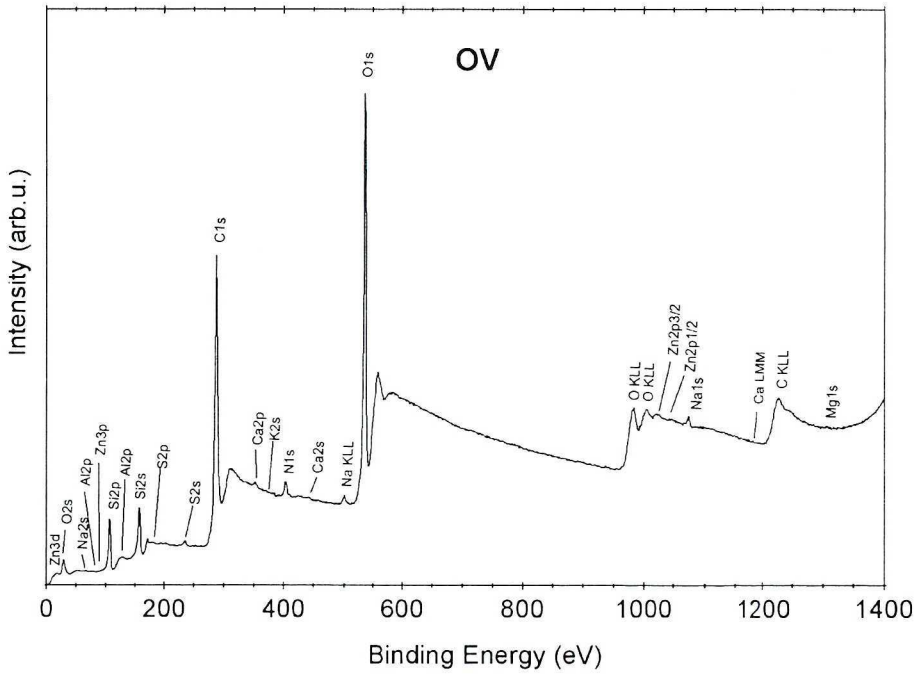

Fig. 2. XPS spectrum for PM2.5 – crossroad "1" (14 – 15 April)

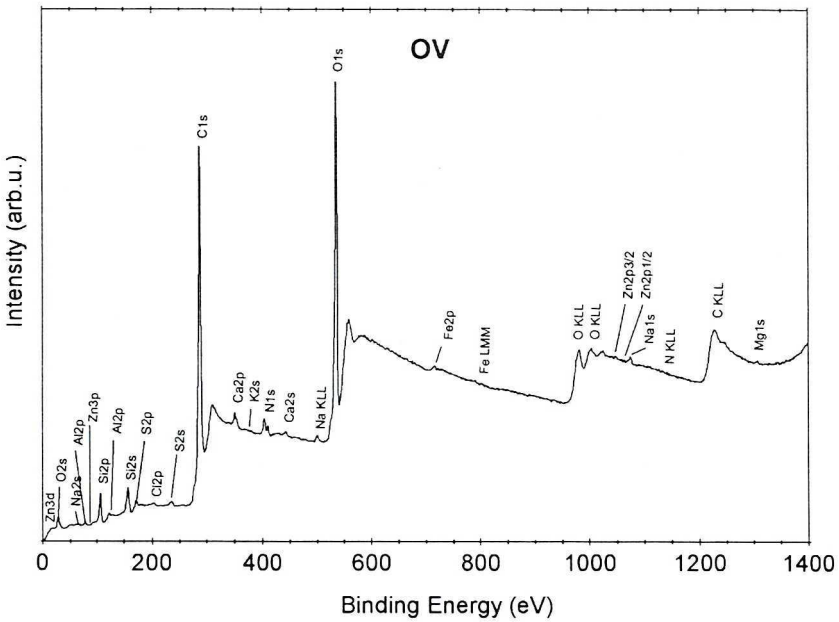

Fig. 3. XPS spectrum for PM10 – crossroad "1" (14 – 15 April)

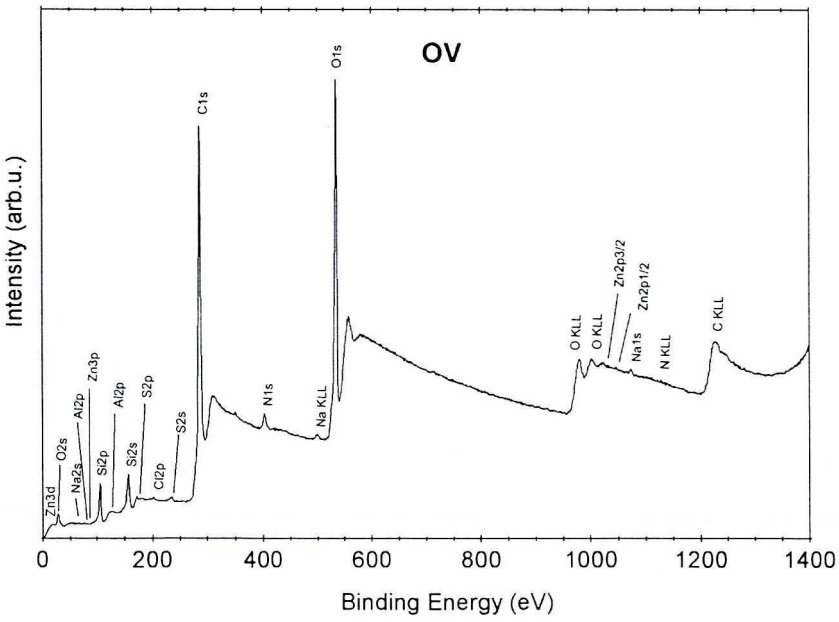

Fig. 4. XPS spectrum for PM2.5 – crossroad "1" (15 – 16 April)

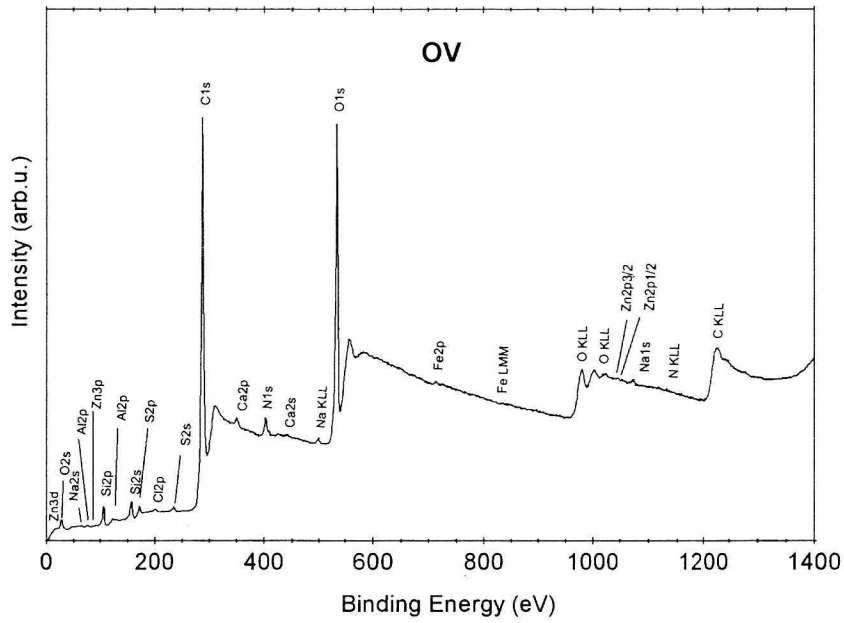

Fig. 5. XPS spectrum for PM10 – crossroad "1" (15 – 16 April)

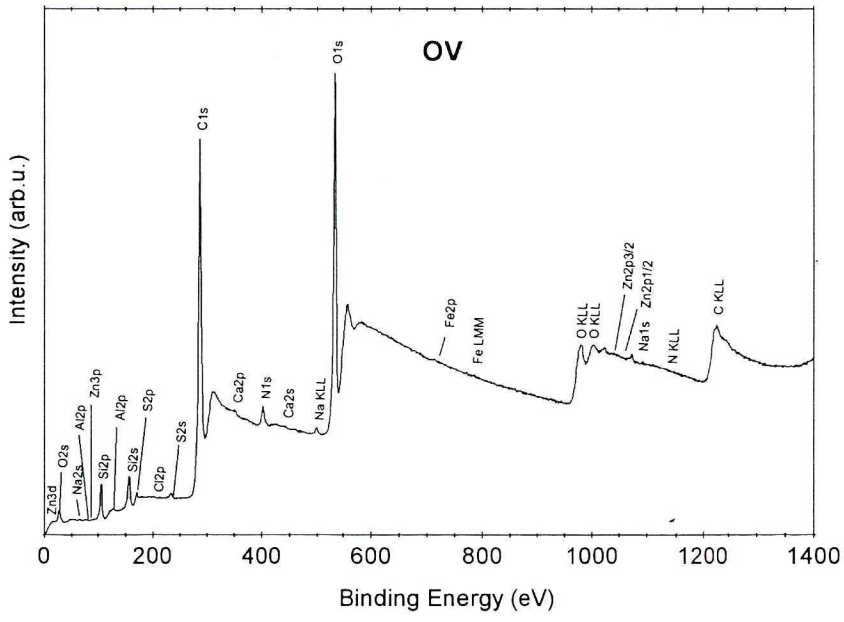

Fig. 6. XPS spectrum for PM2.5 – crossroad "1" (16 – 18 April)

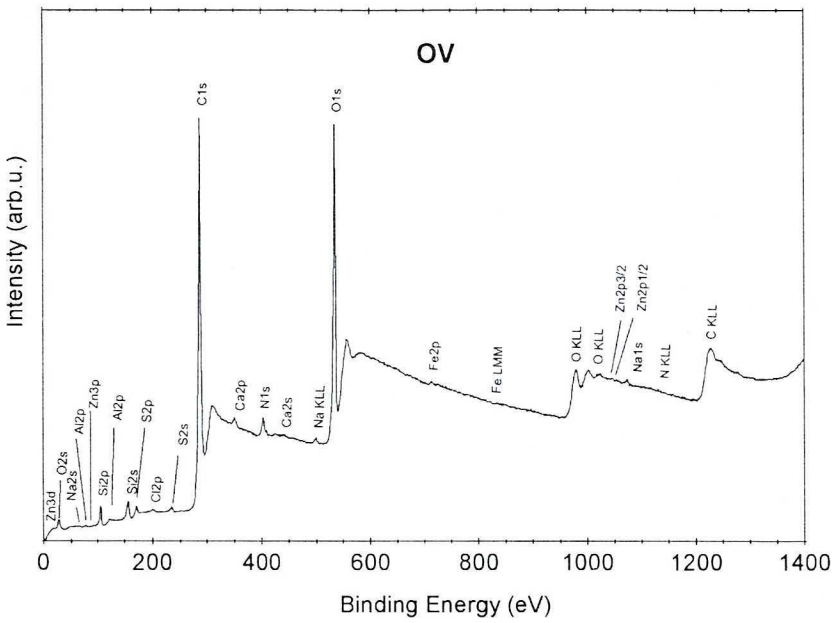

Fig. 7. XPS spectrum for PM10 – crossroad "1" (16 – 18 April)

It can be seen from Figures 2–7 that in the surface layer of particles of PM10 from the crossroad carbon prevails; oxygen, hydrogen, nitrogen and sulphur have lower shares. It is also shown in Table 4, where, computed from all received XPS spectra, mean relative content of elements identified in particles of PM10 and PM2.5 from the site "1" are presented.

Table 4. XPS results for PM10 and PM2.5 from measuring point „1"

Sample	C1s	N1s	O1s	Na1s	Mg1s	Al2p	P2s	Si2p	S2p	K2s	Cl2p	Zn2p1/2	Pb4f	Ca2p	Fe2p3/2
PM2.5															
14–15 April	65.33	1.81	29.73	0.42	0.07	0.21	–	0.98	1.02	0.19	–	0.22	–	0.02	–
15–16 April	71.19	2.11	24.83	0.30	–	0.34	–	0.50	0.47	–	0.13	0.13	–	–	–
16–18 April	68.20	2.64	27.20	0.28	–	0.25	–	0.45	0.74	–	0.05	0.14	–	0.01	0.04
PM10															
14–15 April	70.51	1.68	24.70	0.41	0.27	0.79	–	0.33	0.58	0.08	0.20	0.16	–	0.04	0.25
15–16 April	68.35	2.83	25.55	0.33	0.21	1.04	–	0.13	0.45	0.17	0.60	0.14	0.01	0.02	0.17
16–18 April	69.48	2.69	25.98	0.18	–	0.41	–	0.13	0.67	–	0.22	0.09	–	0.02	0.13

The main components of the surface layer of the dust particles are: carbon, nitrogen, oxygen, sodium, silicon, zinc, calcium. The highest content is of carbon, oxygen and nitrogen.

CONCLUSIONS

- Compared with the urban background in Zabrze, the PM10 and PM2.5 concentrations near the studied crossroads were significantly higher.
- The increase of the aerosol concentrations near the crossroads was higher for the coarse than for the fine particles – it indicates the importance of the resuspension of dust deposited on roadsides to the total traffic generated emission of airborne particles in Zabrze.
- Carbon- and oxygen-containing species prevailed in the surface layer of the airborne particles near the crossroads; traces of N, S, Si, Cl, Na, Al, Zn, Fe, Mg, Ca and Fe were present.

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