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| Baltic Coastal Zone<br>No. 10 |  |
| (5-14)<br>2006                | Institute of Biology and Environmental Protection<br>Pomeranian Pedagogical University<br>Słupsk |

## CHEMICAL ANALYSIS OF THE AEROSOL PARTICLE ON THE BALTIC COAST

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### Abstract

Berner cascade impactor was used to study urban aerosols in two localities of the Pomeranian macro-region Słupsk and Hel in autumn at different weather conditions. The range of aerodynamic diameters between 0.009 and 8.11  $\mu\text{m}$  were separated. Elementary composition for each diameter was obtained in a complex procedure consisting of laser ablation of deposits then their successive ionization in inductively coupled plasma generator and finally mass selection in a quadrupole spectrometer. The chemical element analysis method proves to be quick and versatile, allowing to identify different sources of air pollution, natural, industrial and due to the road traffic.

**Key words:** laser ablation, impactor, LA ICP-MS, particle distribution

### INTRODUCTION

Studies of chemical composition of small atmospheric particles help to understand and clarify such processes as their transport, deposition and transformation of particles in the atmosphere and quantification of emission from natural and anthropogenic sources. However, optical and toxicological properties of the air-born aerosols depend both on the chemical composition of particles and on their size (Seinfeld 1989). Besides, the aerosol particles size and chemical composition can be used to identify sources (incinerators, smelters, power plants, motor vehicles, etc.) (Gard et al. 1997). Different methods have been used to characterize elemental composition of airborne aerosols for example inductively coupled plasma atomic emission spectrometry (ICP-AES) (Seeling and Broekaert, 2001), particle-induced X-ray emission (PIXE) (Potocek 1999) or X-ray fluorescence (XRF) (Carlson et al. 1995, Eltayeb et al. 2001). Unfortunately, many of these instruments cannot measure the aerosol size, an important physical attribute.

On the other hand, the impactor method (Alonso et al. 1999, Huang and Tsai 2001) allows to measure the size distributions of aerosol particles. Recently, the combina-

tion of aerosol collection and size separation impact techniques and their mass spectrometry analyses have been used to determinate the chemical composition of aerosols. Generally, material samples must be introduced to the mass spectrometer in the gas phase. Solid samples can be dissolved and sprayed, or evaporated for mass analyzer. In the first case, dissolvent is also measured and its influence on mass spectra can be significant. In the second case the sample is analyzed directly, often without the need for any sample preparation. This reduces or eliminates the time associated with this process as well the chance for sample contamination (Denoyer et al. 1991). Different methods are applied to vaporize the samples. Usually spark (Scheeline et al. 1981), arc (Jones et al. 1971) and laser (Outrige et al. 1996; Denoyer et al. 1991) ablation and electrothermal vaporization (Lüdke et al. 1999) are used in these methods.

Small aerosols at the urban areas are emitted principally by road traffic and are composed of carbonaceous and organic carbon. TSI-methods usually study deposited samples of aerosol on the graphite targets. Thus measurements of samples containing carbon are impossible.

In present work a sensitive method has been developed for the size and element analysis of particles contained in atmospheric aerosols. The air aerosol particles were separated by size on aluminum targets with eleven stages Berner cascade impactor. To determinate the elemental composition of the particles the aluminum plates were evaporated using laser ablation and analyzed by inductively coupled plasma mass spectrometer (LA ICP-MS).

Table 1  
Weather conditions at the collection time of the aerosol particles in autumn

|                             | Słupsk                     |                        | Hel                        |                          |
|-----------------------------|----------------------------|------------------------|----------------------------|--------------------------|
|                             |                            |                        |                            |                          |
| Datum                       | 23.10.2002<br>(wet)        | 4.11.2002<br>(dry)     | 17.10.2002<br>(day)        | 17/18.10.2002<br>(night) |
| Air flow                    | 1400 l/h                   | 1400 l/h               | 1400 l/h                   | 1400 l/h                 |
| Sampling time               | 8h                         | 8h                     | 8h                         | 8h                       |
| Temperature                 | 11°C                       | 4°C                    | 16°C                       | 30°C                     |
| Wind speed<br>and direction | 2.1 m/s<br>N-W             | 1 m/s<br>N             | 5.4 m/s<br>W-S             | 4.6 m/s<br>W-S           |
| Humidity                    | 96%                        | 87%                    | 75%                        | 83%                      |
| Weather<br>conditions       | cloudy, wet,<br>light wind | sunny,<br>without wind | cloudy, dry,<br>light wind | sunny, light<br>wind     |

Measurements have been performed in two places of Pomeranian macroregion in autumn at different atmospheric conditions (Table 1). The emission of anthropogenic gases depends on the urban area, the collection of aerosols was carried out in autumn on Hel (a spa locality on the Baltic seaside peninsula, 500 inhabitants) and Słupsk (a middle size city, 100 thousand inhabitants, but with a heavy transit road traffic). All measurement spots inside the two localities were chosen in places of similar character – suburban for Słupsk, rather far from industry or central heating plants. As said before, road traffic is rather heavy in Słupsk (East-West Europe road E28 passing through the center of the town in Słupsk).

## EXPERIMENTAL

### Sample collection

Many different sampling devices have been developed for the collection of aerosol particles. The method used in our studies is based on inertial deposition and size fractionation by a cascade impactor. The operating principle of a cascade impactor is well described in literature (Hinds 1982). I used an eleven-stage multijet Berner cascade impactor. Particles are separated in eleven size classes with the cut-off diameters between 0.009 and 8.11  $\mu\text{m}$  at the flow rate of 24.9  $\text{l min}^{-1}$ . The cut-off diameters correspond to a 50% collection efficiency and depend not only on the particle size but also on the density and the particle shape (Hinds 1982). Usually, the separation characteristic for cascade impactor is given for spherical particles of the unit density. The diameter of actual particles differing from the ideal one is expressed as an aerodynamic diameter,  $d_a$ . The particles of defined sizes were collected on aluminum plates (rings of 70 mm external diameter, 30 mm internal diameter, 15  $\mu\text{m}$  thick) arranged in front of the jet-nozzles of cascade impactor. The element identification of the collected aerosol particles requires their sampling on a material which does not interfere with the subsequent analytical procedure. The rough and soft surface of aluminum rings yielded a sufficient sampling efficiency, which minimizes losses of particles due to elastic collisions. An especial preparation of deposition target was not required.

The collection time was 8 hours. During this time 11.2  $\text{m}^3$  volume of air came through the impactor.

### Laser ablation and mass spectrometer

For the multi-element analysis, a Perkin-Elmer SCIEX (Thornhill, Canada) Elan 6000 ICP mass spectrometer was used. The system incorporates a 40 MHz frequency generator as the ionization source coupled with an adiabatic plasma-sampling interface. Efficiency of the ionization process by coupled plasma is about 99% for all elements in the particles (McCurdy and Potter 2001, Denoyer et al. 1991). The ionized particles were selected and analyzed by the quadrupole mass

spectrometer. The mass spectrometer was connected with a laser sampler (Model 320 from Perkin-Elmer SCIEX) by 1.5 m elastic tube.

The laser ablation system is based on Nd:YAG laser, running at 1064 nm wavelength. The Nd:YAG laser was operating in the Q-switched mode with a first harmonic wavelength 1064 nm giving 29 mJ beam energy per pulse. Additionally, equipment for higher harmonic generation (532 nm, 355 nm, 266 nm) and wavelength separation is installed in the laser setup. The laser worked at 10 Hz and only 5 shots were chosen for the ablation process. The adjustment all of the laser ablation parameters guarantee that collected particles were evaporated ( $\sim 0.5$  s) and the aluminum target not destroyed.

Inside the sample chamber was installed a small moveable in three dimensions sample stage. The argon gas was transported of  $1 \text{ l min}^{-1}$  flows through the sample chamber. In the Table 2 are given all the technical parameters of the equipment.

In order to analyze the impacted particles, stripes of the aluminum targets with deposited aerosols were transferred on the sample stage into the chamber. The sample chamber was cleaned up by transport of argon during about 3 min. Focused laser

Table 2

Working conditions of the laser ablation ICP-MS

| <b>LA</b>                 |   |
|---------------------------|---|
| Wavelength                | 1064 nm   |
| Laser beam energy         | 29 mJ   |
| Laser mode                | Q-switched  |
| Number of shots           | 5   |
| Frequency of shots        | 10 Hz   |
| <b>ICP</b>                |   |
| Power RF generator        | 40 MHz  |
| Plasma gas flow           | $15.0 \text{ l min}^{-1}$   |
| Auxiliary gas flow        | $0.8 \text{ l min}^{-1}$  |
| Transport gas flow        | $1.0 \text{ l min}^{-1}$  |
| <b>MS</b>                 |   |
| Scanning mode             | Peak hopping  |
| Dwell time                | 10 ms   |
| Replicates                | 200   |
| Determination of isotopes | $^{12}\text{C}$ , $^{13}\text{C}$ , $^{28}\text{Si}$ , $^{52}\text{Cr}$ , $^{58}\text{Ni}$ , $^{59}\text{Co}$ , $^{63}\text{Cu}$ , $^{75}\text{As}$ , $^{114}\text{Cd}$ , $^{208}\text{Pb}$ |

beam on the spot evaporated the collected particles of aerosol. The background signal was determined by evaporating the empty spot of aluminum target. The total measuring time of one sample was about 30 s. The Elan instrument allows also to monitor the intensity of given isotopes as a function of time. The intensity-time files of each run were evaluated by self-developed computer program, which permits set up the integration limit for each element individually. The integration time amounts between 2 and 30 s for the detected elements.

The following elements  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{28}\text{Si}$ ,  $^{52}\text{Cr}$ ,  $^{58}\text{Ni}$ ,  $^{59}\text{Co}$ ,  $^{63}\text{Cu}$ ,  $^{75}\text{As}$ ,  $^{114}\text{Cd}$ ,  $^{208}\text{Pb}$  were monitored in present work. These isotopes have been chosen because of their possible sources. For example the main sources of silicon-containing aerosols is the dust from soil. For coal, both vegetation and anthropogenic sources are present – industry, residential heating and motor vehicles. Chromium, copper, arsenic, cadmium or lead are produced mainly by industry sources.

## RESULTS AND DISCUSSIONS

For all measurements the eleven-stage impactor was used but not in all stages on aluminum plate the aerosol particles were detectable. Particles from other stages were not visible and the measured intensity of element signal was near background value.

Out of the two localities, in Hel, the air pollution were lower comparing to Słupsk. In Słupsk in “cloudy” conditions (i.e. with slight rain towards the end of day) the concentrations of all elements at different diameters are lower than in “sunny” weather condition except arsenic. The biggest differences between the highest and lowest levels are observable for copper (up to 9 times for 0.4  $\mu\text{m}$  particle diameter) another elements about 2 times of magnitude. The one probable explanation is that the rain wash out the solid state aerosol from the air. In Hel case the distributions of the elements are very similar without any different between measurements made in day and night. In marine aerosol environmental the concentration of pollution is constant in short period of time.

Another general observation is that the maximum concentration of all measured elements is in 0.3÷0.7  $\mu\text{m}$  range of aerodynamic diameter and they are log-normal distributed.

The good example are measurements of carbon. The distributions (Fig. 1) shows uniform log-normal distribution in size especially in Słupsk. The Hel data distribution is similar in shape but much lower. The maximum concentration is the same and wide range of diameter at around 0.2÷1.0  $\mu\text{m}$  (for all conditions).

The origin of carbon suspended particles is from organic sources (for example pollen) and from urban pollution. Note that in the present method it is not possible to determine the chemical formulae for carbon-containing compounds – complex organic molecules originating due to organic processes, simple hydrocarbon components from road traffic or sooth from resident (heating for example). As can be deduced from fig.1 a certain, rather dependent from the locality, level of carbon aerosols should be ascribed to not natural sources. The most probable source of sub-

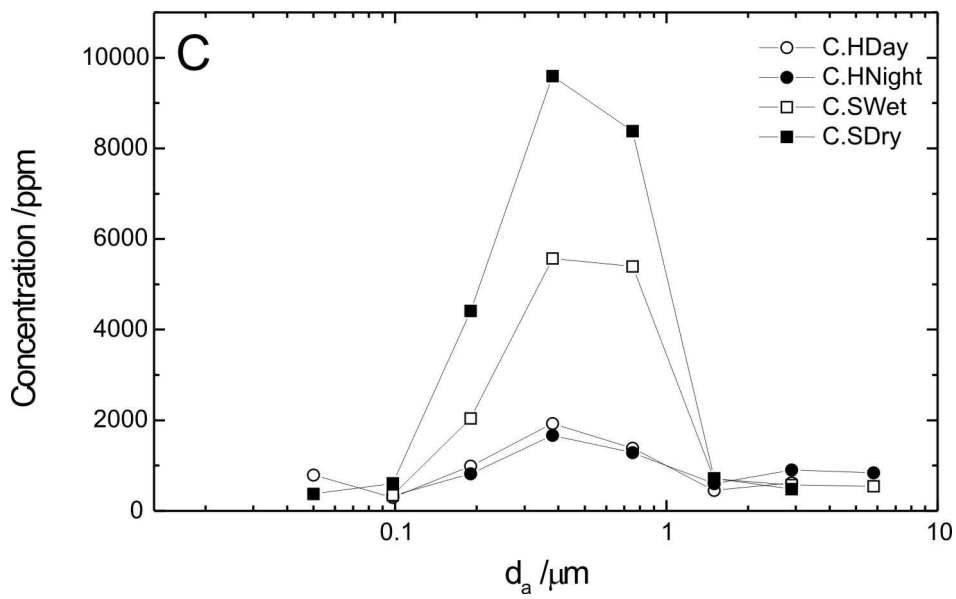


Fig. 1. The distribution of C concentration vs. aerosol size in autumn in Hel and Słupsk

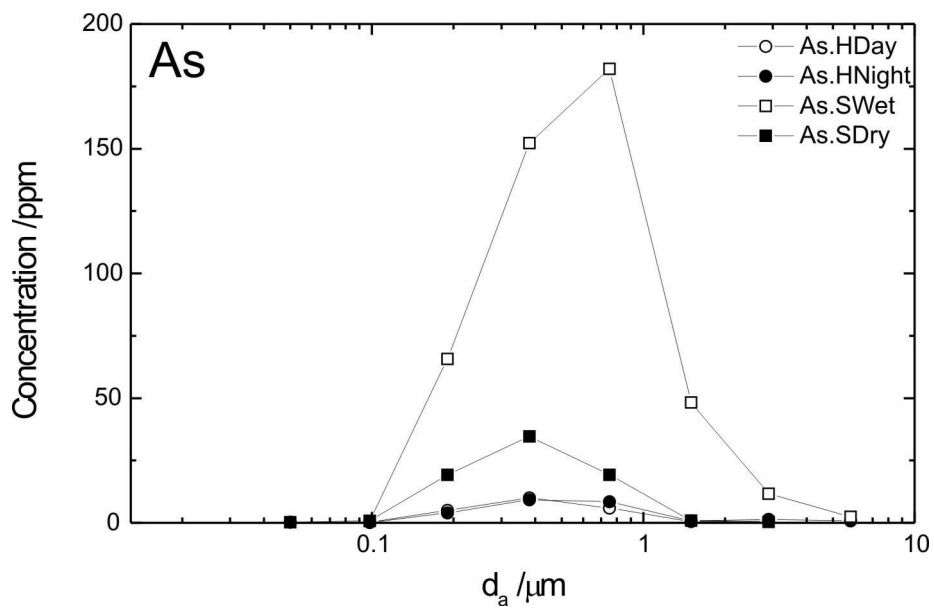


Fig. 2. The distribution of As concentration vs. aerosol size in autumn in Hel and Słupsk

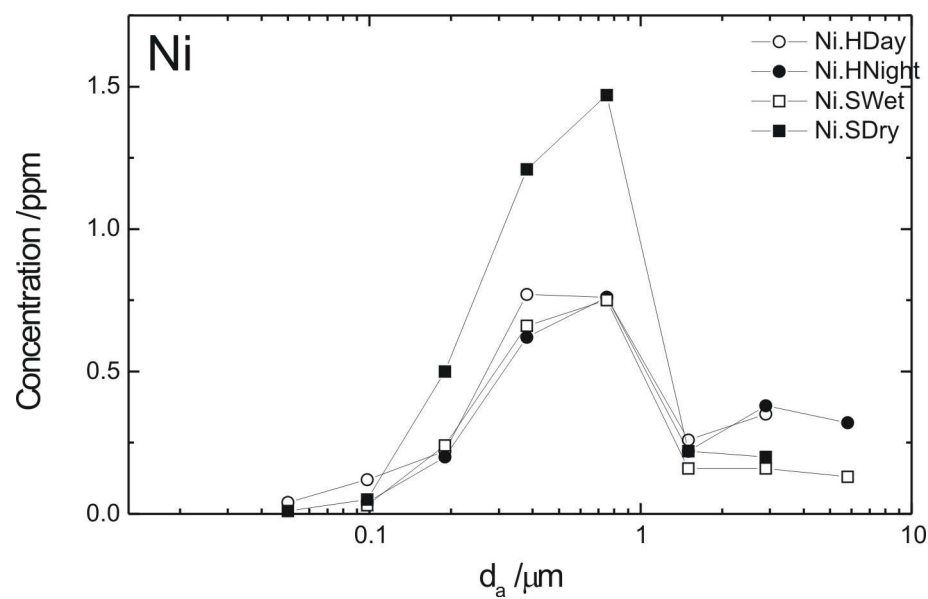


Fig. 3. The distribution of Ni concentration vs. aerosol size in autumn in Hel and Słupsk

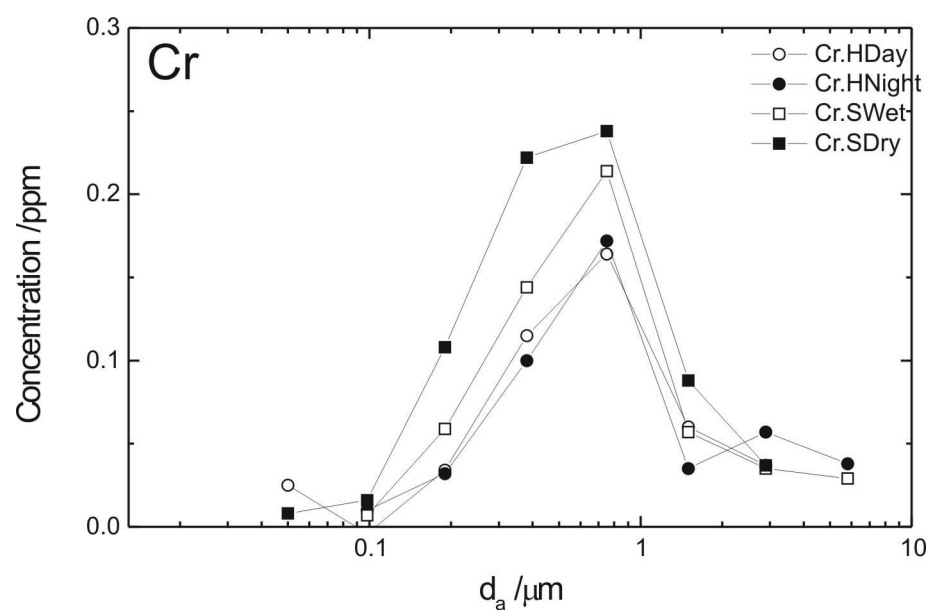


Fig. 4. The distribution of Cr concentration vs. aerosol size in autumn in Hel and Słupsk

-micron carbon aerosols could be so called “cold emission” from diesel engines. The diesel engines in cold atmospheric conditions can emit up to ten times more carbon sub-micron dust than fully operational ones. The lead distribution is very similar to carbon one.

Arsenic presents a somewhat different dependence than other elements, see fig. 2. Its concentration is very high under particular weather conditions (wet in Słupsk). In Hel measurements of the arsenic concentration are not so high. The burning coal at heating systems can be one of the sources of arsenic. Coal, in particular that one in Central Europe, contains substantial quantities of pyrite, and the arsenopyrite (FeAsS) is its main admixture. A “natural” background of arsenic, as seen Hel “day” and “night” conditions is by a factor of 10 times less than “Słupsk cloudy” conditions. This should be attributed to vertical mixing conditions in atmosphere. I evaluate that “Słupsk sunny” conditions correspond to the “B” class of Pasquill-Gilford atmosphere stability class (see Neiburger et al. 1973) what would correspond to vertical mixing height, while Słupsk cloudy to “E” and “Berlin winter” to “D” class stability (vertical mixing not below 1000 m). Note, as shown on photo 1 taken near to Słupsk in winter, that the unfavorable vertical mixing conditions, like the “E” class, can lead to “injection” of carbon-burning smoke just to the chimneys height and its successive accumulation in a narrow layer a few tens of meters above the ground level.

Chromium and nickel are constituents of high-quality steels. For example AISI 304 stainless steel contains nickel (8%) and higher levels of chromium (18%). Chromium and cobalt are also commonly used in pigments. The source of Cr and Ni pollution on examined spots is not quite clear. Low concentrations and little dependence on weather conditions (slightly higher in Słupsk “sunny” data) would indicate non-local, probably industrial origin of the pollution (Fig. 3 and 4).

## CONCLUSIONS

It has been shown that the combination of laser ablation and mass spectrometry methods is very useful in chemical analysis of aerosol particles. In this paper contents of ten isotopes in air aerosol particles in urban environment were analyzed. The use of aluminum plates, as collecting target for aerosols, enables to measure contents the carbon isotopes in addition to other particles. This makes the essential difference between present measurements and other methods in which the aerosols are collected on graphite disks and electrothermal evaporation from its surfaces is applied. I note that the contents of particular elements in aerosols depend on their size (volume) and on the weather condition. The obtained data can be important in modeling of the atmospheric phenomenon, quantification of emission from anthropogenic and natural sources of pollutant gases because transport of elements in different size aerosol particles is not well known. Such measurements will be continued for other areas, e.g., see said, road crossing, non-industrial towns etc.



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## ANALIZA CHEMICZNA CZĄSTECZEK AEROZOLI NA WYBRZEŻU BAŁTYKU

### Streszczenie

Do zbierania i selekcji aerozoli został użyty kaskadowy separator aerozoli (cascade impactor), model Berner. Pomiaru obejmowały swym zasięgiem dwa rejonu: peryferie Słupska (20 km od Morza Bałtyckiego) oraz lotniskową miejscowość Hel, położoną na półwyspie Hel nad samym morzem. Odbywały się one jesienią. Dla porównania wykonano pomiary w dzień i w nocy (Hel) oraz podczas ładnej i deszczowej pogody (Słupsk). Separator kaskadowy umożliwiał zbieranie i selekcję aerozoli nadmorskich w jedenastu różnych klasach wielkości, w zakresie od 0,009 do 8,11  $\mu\text{m}$  średnicy aerodynamicznej. Analiza składu chemicznego aerozoli, zebranych na cienkich, aluminiowych foliach, odbywała się metodą odparowania ich zogniskowaną wiązką impulsowego lasera neodymowego Nd:YAG (laser ablation LA) i metoda pomiaru pojedynczych izotopów za pomocą kwadropolowego spektrometru masowego ICP MS firmy Perkin Elmer. Do analizy wybrano izotopy pierwiastków odpowiedzialnych za zanieczyszczenie atmosfery:  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{28}\text{Si}$ ,  $^{52}\text{Cr}$ ,  $^{58}\text{Ni}$ ,  $^{59}\text{Co}$ ,  $^{63}\text{Cu}$ ,  $^{75}\text{As}$ ,  $^{114}\text{Cd}$  i  $^{208}\text{Pb}$ . Ilościowe określenie poszczególnych pierwiastków możliwe było dzięki wcześniejszej kalibracji przyrządu i zastosowaniu zewnętrznych standardów kalibracyjnych. Zastosowana metoda umożliwia precyzyjne określenie składu chemicznego interesujących nas pierwiastków rzędu ppm, a co ważniejsze, dodatkowo uzyskujemy informację o ich zawartości w poszczególnych frakcjach ich wielkości.