
Papers

Laser ablation studies of solid aerosols on the Baltic coast

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KEYWORDS

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Abstract

A Berner cascade impactor was used for the separation of solid urban aerosols in two localities of the Baltic coastal macro-region – Słupsk and Hel – in different seasons and weathers. Ten ranges of aerodynamic diameters between 0.009 and 8.11 μm were used. The elementary composition for each diameter was obtained in a complex procedure consisting of laser ablation of deposits, then their successive ionization in an inductively coupled plasma generator, and finally, mass selection in a quadrupole spectrometer. Despite its complexity, the chemical element analysis method proved to be versatile, allowing the identification air pollution from natural and industrial sources, and road traffic.

1. Introduction

Studies of the chemical composition of small atmospheric particles help to understand their transport, deposition and transformation in

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the atmosphere and to quantify their emission from natural and anthropogenic sources (Zieliński & Zieliński 2002). However, the optical and toxicological properties of airborne aerosols depend both on the chemical composition of particles and on their size (Seinfeld 1989). Moreover, the size and chemical composition of aerosol particles can be used to identify sources (incinerators, smelters, power plants, motor vehicles, etc. (Gard et al. 1997, Tai et al. 1999)). Different methods have been used to characterize the elemental composition of airborne aerosols. They include inductively coupled plasma atomic emission spectrometry (ICP–AES) (Seelig & Broekaert 2001), particle-induced X-ray emission (PIXE) (Potocek 1997), Neutron Activation Analysis (NAA), X-ray fluorescence (XRF) (Injuk & Van Grieken 1995, Eltayeb et al. 2001) or voltametry (Khandekar et al. 1981). Unfortunately, many of these instruments cannot measure the aerosol size, an important physical attribute.

On the other hand, with the impactor method (Alonso et al. 1999, Huang & Tsai 2001, Zieliński & Zieliński 2002), measurements of the size distributions of aerosol particles are possible. Recently, the combination of aerosol collection and size separation impact techniques and their mass spectrometry analyses were used to determine the chemical composition of aerosols. For example, Prather et al. (2000) carried out real-time measurements of aerosols in the 0.2–3.0 μm aerodynamic diameter size range and determined their chemical composition with the aid of a transportable aerosol time-of-flight mass spectrometer (ATOFMS).

Generally speaking, material samples must be introduced into the mass spectrometer in the gaseous phase. Solid samples can be dissolved and sprayed, or evaporated into a mass analyzer. In the first case, the solvent is also measured, since its influence on the 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 required for this process, as well as the possibility of 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 ablation (Camata et al. 2000) and electrothermal vaporization (Lüdke et al. 1999) are used. Generally, they come under the heading *Thermal Sample Introduction Methods* (TSI methods), in which vapor is produced from the sample components (Kántor 2001). However, these methods usually produce small particles from solid materials (Camata et al. 2000). They are sporadically used in the chemical analysis of aerosols (Hoffmann et al. 1999) or rock samples, archaeological artifacts (Pereira et al. 2001) and tree rings (Prohaska et al. 1998). Small aerosols in urban areas are emitted principally by road traffic and are composed of carbonaceous and organic

carbon. TSI methods are usually used to study samples of aerosol deposited on graphite targets. Thus, measurements of samples containing carbon are impossible.

In the present work a sensitive method was developed for the size and elemental analysis of particles contained in atmospheric aerosols. The aerosol particles were separated by size on aluminum targets with an eleven-stage Berner cascade impactor. In order to determine the elemental composition of the particles, the aluminum plates were evaporated using laser ablation and analyzed by inductively coupled plasma mass spectrometry (LA ICP-MS).

Measurements were performed in two localities in the Pomeranian macro-region in different seasons and atmospheric conditions: (i) Słupsk – a medium sized city (100 thousand inhabitants) 18 km from the coast but with a heavy transit road traffic, (ii) Hel, 500 inhabitants, a spa locality on the Hel peninsula, Baltic coast. Because emission of anthropogenic gases in an urban area depends on the time of year, aerosols were sampled in autumn, winter, spring and summer. All the measurement points in Hel and Słupsk were of a similar character, far from industry or central heating plants.

2. Experimental

2.1. 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 the literature (Hinds 1982). We used an eleven-stage multijet Berner cascade impactor. Particles are separated into eleven size classes with the cut-off diameters between 0.009 and 8.11 μm at a flow rate of 24.9 l min^{-1} . Usually, the separation characteristic for the cascade impactor is given for spherical particles of unit density. The diameter of the actual particles, which differ from the ideal, is expressed as the aerodynamic diameter, d_a . Particles of given sizes were collected on aluminum plates (rings of 70 mm external diameter, 30 mm internal diameter, 15 μm thick) arranged in front of the jet-nozzles of the cascade impactor. The elemental identification of the collected aerosol particles requires their sampling on a material which does not interfere with the subsequent analytical procedure. The rough, soft surface of the aluminum rings yielded a sufficient sampling efficiency, which minimizes particle losses as a result of elastic collisions. A special preparation of the deposition target was not required.

The collection time was 8 hours. During this time 11.2 m³ volume of air passed through the impactor. The weather records for the sampling period are given in Table 1.

Table 1. Weather records for the aerosol particle sampling periods

Słupsk					
	autumn		winter	spring	summer
date	Oct. 23 2002 (wet)	Nov. 4 2002 (dry)	Jan. 7 2003	May 6 2003	July 17 2003
temperature [°C]	11	4	-20	20	32
wind speed [m s ⁻¹]	2.1	1	3.5	7.5	2
direction	NW	N	NW	S	N
humidity [%]	96	87	86	56	50
Hel					
	autumn		winter	spring	summer
date	Oct. 17 2002 (day)	Oct. 17/18 2002 (night)	Feb. 25 2003	May 2 2003	July 19 2003
temperature [°C]	16	3	-1	13	23
wind speed [m s ⁻¹]	5.4	4.6	2.4	2.8	3.9
direction	WS	WS	W	N	SE
humidity [%]	75	83	76	75	75

Note: air flow for all measurements – 1400 l h⁻¹ and sampling time – 8 h.

2.2. Laser ablation and mass spectrometer

A Perkin-Elmer SCIEX (Thornhill, Canada) Elan 6000 ICP mass spectrometer was used for the multi-element analysis. The system incorporates a 40 MHz frequency generator as the ionization source coupled with an adiabatic plasma-sampling interface. The efficiency of the ionization process by coupled plasma is about 99% for all the elements in the particles (McCurdy & Potter 2001). The ionized particles were selected and analyzed by quadrupole mass spectrometry. The mass spectrometer was connected to a laser sampler (Model 320, Perkin-Elmer SCIEX) by a 1.5 m elastic tube.

The laser ablation system is based on a Nd:YAG laser, running at 1064 nm wavelength. The a Nd:YAG laser was operated in the Q-switched mode with a first harmonic wavelength 1064 nm giving 29 mJ beam energy per pulse. The laser worked at 10 Hz and only 5 shots were chosen for

the ablation process. This laser condition guarantees that all particles were evaporated and the aluminum plate was not destroyed. Argon carrier gas was passed through the sample chamber at the rate of 1 l min^{-1} . Table 2 gives the technical parameters of the equipment. During the laser ablation process secondary particle formation may take place after vaporization from the aluminum surface. These particles may nucleate and condense, thereby reducing the elemental concentration. Nevertheless, this factor can be neglected because of the low pressure and low vapor concentration.

Table 2. Working conditions of the laser ablation ICP–MS

LA – laser ablation	
wavelength	1064 nm
laser beam energy	29 mJ
laser mode	Q-switched
number of shots	5
frequency of shots	10 Hz
ICP – inductively coupled plasma	
power RF generator	40 MHz
plasma gas flow	15.0 l min^{-1}
auxiliary gas flow	0.8 l min^{-1}
transport gas flow	1.0 l min^{-1}
MS – mass spectrometer	
scanning mode	peak hopping
dwel time	10 ms
replicates	200
determination of isotopes	^{12}C , ^{13}C , ^{28}Si , ^{52}Cr , ^{58}Ni , ^{59}Co , ^{63}Cu , ^{75}As , ^{114}Cd , ^{208}Pb

To determine the concentration of atoms of the sampled element, a calibration procedure was carried out using external standards (graphite tables). The sensitivity of the LA ICP–MS instrument is adequate for determining the elements in the required concentration range.

In order to analyze the impacted particles, strips of the aluminum targets with deposited aerosols were placed on the sample stage in the chamber. The sample chamber was purged with argon during about 3 min. The laser beam focused on the spot evaporated the aerosol particles, which were then analyzed by mass spectrometer. The background signal was determined by evaporating the empty spot of the aluminum target. The total measuring time of one sample was about 30 s.

The following elements were monitored: ^{12}C , ^{13}C , ^{28}Si , ^{52}Cr , ^{58}Ni , ^{59}Co , ^{63}Cu , ^{75}As , ^{114}Cd , ^{208}Pb . These isotopes were chosen because of their possible sources. For example, the main sources of aerosols containing silicon is soil dust. This dust may originate locally or result from long-range transport by wind. An example of long-range transport of soil dust aerosols was reported recently by Hamonou et al. (1999) for Saharan sand. Coal is produced by vegetation and anthropogenic sources like industry, domestic heating and motor vehicles. Chromium, copper, arsenic, cadmium and lead are produced mainly by industrial sources.

3. Results and discussion

An eleven-stage impactor was used for the separation process. Stages that exhibited no visible particle deposits consistently yielded intensities of element signal in the mass spectrometer near the background value.

Of the two localities, the concentrations of elements of different diameters in Hel were lower than in Słupsk, except for the winter measurements. In this latter case, the concentrations of all the measured elements were about three times higher. Another general observation is that air pollution levels are higher in winter than in autumn and summer.

In Słupsk in cloudy weather (i.e. with slight rain towards the end of the day) the amounts of C, Ni, Cd, Co and Pb are lower than in sunny weather, by a factor of approximately two; for Cu this difference is almost tenfold; for arsenic the cloudy weather causes a rise in concentration by a factor of about seven.

The concentration of the measured elements are the highest for carbon (120 000 ppm), lead (4000 ppm) and silicon (2200 ppm) in the 0.2–0.8 μm range. Other elements are less abundant: in the majority of cases the level of copper does not exceed 1 ppm, nickel 8 ppm, cadmium and arsenic about 200 ppm, and cobalt 18 ppm. A general observation is that the distributions with the maximum in the 0.2–0.8 μm range are lognormal for all elements, except for silicon the distribution of which resembles a bimodal one. This is especially apparent for carbon, lead and arsenic.

Both stable isotopes of carbon ^{12}C and ^{13}C were measured. The carbon distributions for these two isotopes show essentially the same behavior and therefore only the measurements of ^{12}C are given in Fig. 1. This figure shows that for both Słupsk and Hel, the winter carbon concentrations are higher by as much as a factor of seven than in the other seasons of the year.

The suspended particles of carbon are derived from organic sources (for example, pollens), urban traffic and industrial pollution. Note that in the present method it is not possible to determine the chemical formulae of carbon-containing compounds, i.e. complex organic molecules originating

from organic processes, simple hydrocarbon components from road traffic, or soot from domestic heating systems. As can be deduced from Fig. 1, a certain level of carbon aerosols, independent of locality, should be ascribed to anthropogenic sources.

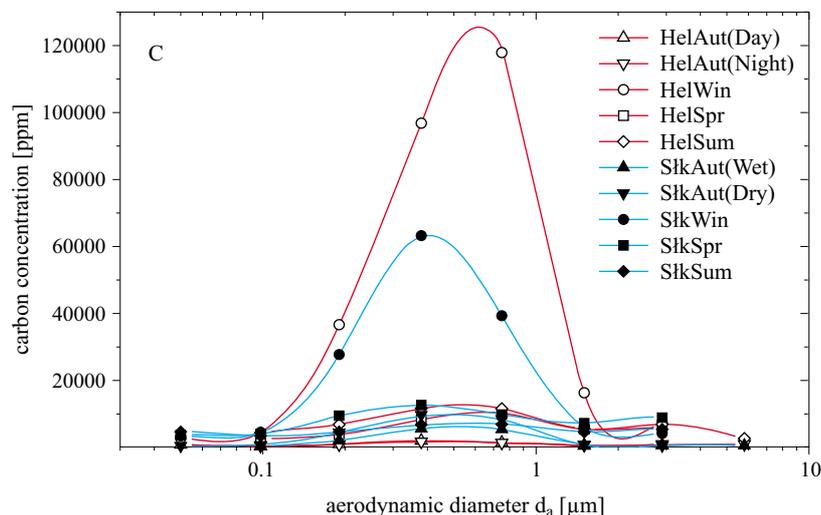


Fig. 1. The distribution of carbon concentration vs. aerosol size in all seasons of year in Hel and Słupsk. The meanings of the abbreviations can be deduced from Table 1

The emission of carbon components in winter is much more intense than in other seasons. An interesting fact is that the winter concentration of carbon in Hel is twice as high as in Słupsk. This trend is also observed for the other elements sampled. The probable explanation for this fact is wind transport of pollution aerosols from large urban areas (from the Tri-City conurbation 25 km to the south).

Domestic heating is also a likely cause of the broad maximum in the winter data of both localities. The most probable source of sub-micronic carbon aerosols in the winter data could be the so-called cold emission from diesel engines. It is known that low ambient temperatures cause a rise in road traffic pollutants (CO, NO_x, volatile hydrocarbons). But while this rise is observed only when engines are cold (initially as much as sevenfold at 0°C for volatile hydrocarbons in catalyzed vehicles), the emission for sub-micronic solid aerosols increases in a permanent way, i.e. does not fall when engines are warm, about threefold at 0°C according to air pollution engineering references TNO (1992).

The relationship with respect to silicon is somewhat different from that of the other elements. The concentration distributions of silicon-containing

aerosols do not show major changes for different atmospheric conditions and localities. As can be seen in Fig. 2, the distributions show two maxima, at $0.8 \mu\text{m}$ and $1.2 \mu\text{m}$. These particular features of the size distributions probably reflect two natural sources of Si-containing aerosols – local and distant ones. The importance of long-range transportation mechanisms, such as the one reported for Saharan dust, is acknowledged by Eltayeb et al. (2001). These small sizes may be transported by wind blowing along the coast of the Hel peninsula.

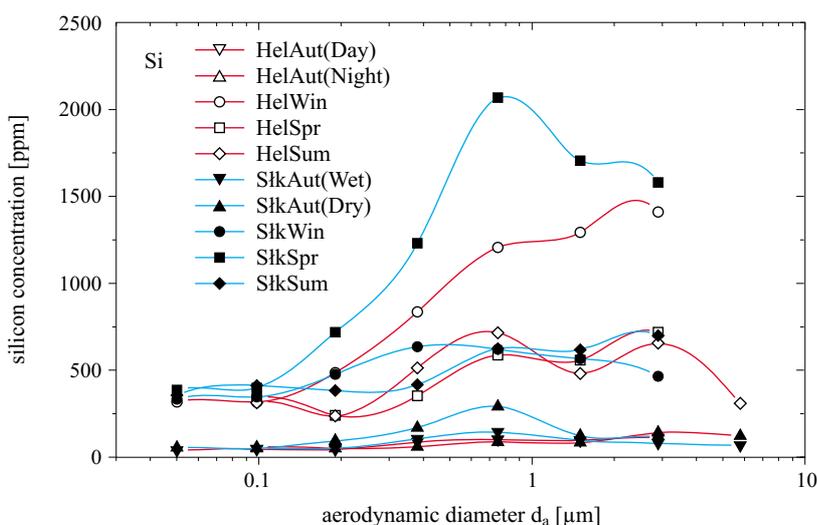


Fig. 2. The distribution of silicon concentration vs. aerosol size in all seasons of year in Hel and Słupsk. The meanings of the abbreviations can be deduced from Table 1

The other elements, like Pb, Cd, Cu, Cr and As are lognormal distributed in aerosol sizes with a maximum at $0.3\text{--}0.7 \mu\text{m}$ aerodynamic diameter. A good example of this distribution is arsenic (Fig. 3). In fact, however, there are some differences. In Słupsk the concentration of arsenic is very high in ‘wet’ (rain three hours before the end of measurements) than in ‘dry’ weather. This seems unnatural because rain washes out aerosol particles from air. The concentration should be less, as is the case with the other for example Cu (Fig. 4).

To explain this peculiarity regarding the high arsenic concentrations in Hel in winter and in Słupsk, two considerations are necessary. Firstly, the combination of coal in individual domestic heating systems may be one of the sources of arsenic. Coal, in particular that from Central Europe, contains substantial quantities of pyrite, arsenopyrite (FeAsS) being the main admixture. Secondly, in sunny weather in Słupsk, the overall arsenic

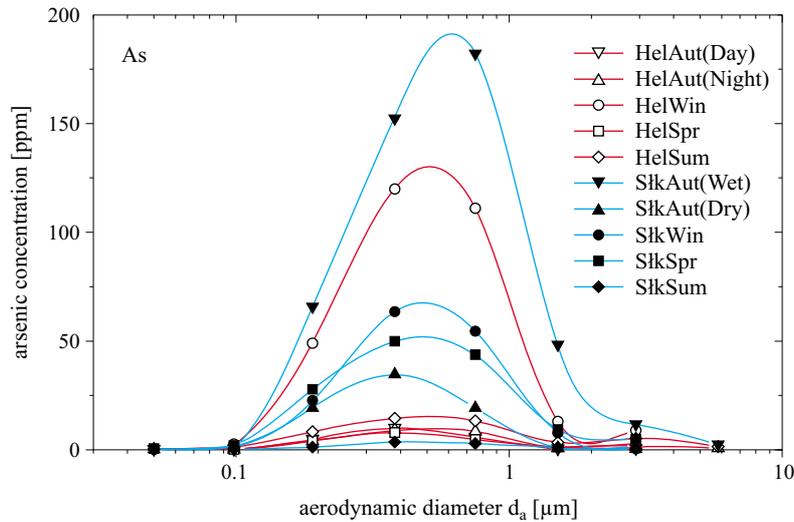


Fig. 3. The distribution of arsenic concentration vs. aerosol size in all seasons of year in Hel and Słupsk. The meanings of the abbreviations can be deduced from Table 1

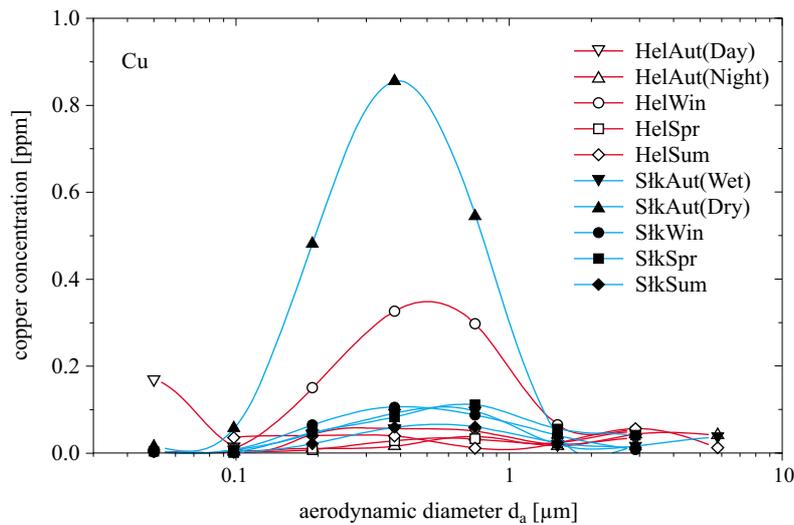


Fig. 4. The distribution of copper concentration vs. aerosol size in all seasons of year in Hel and Słupsk. The meanings of the abbreviations can be deduced from Table 1

content falls more than tenfold. This should be attributed to vertical mixing conditions in the atmosphere.

We estimate that sunny weather in Słupsk corresponds to the ‘B’ class of the Pasquill-Gilford atmosphere stability class (Neiburger et al. 1973),

which would correspond to a vertical mixing height of 1500 m. Cloudy weather in Słupsk corresponds to stability class 'E', and winter weather in Hel to class 'D' (vertical mixing not below 10 000 m). Note, as we can see in Photo 1 taken near Słupsk in winter, that the unfavorable vertical mixing conditions like class 'E' can lead to the injection of carbon smoke into the atmosphere at chimney height and its successive accumulation in a narrow layer a few tens of meters above ground level.



Photo 1. Smoke near Słupsk, due to domestic heating. The photo was taken in March, before sunrise

Chromium, nickel and cobalt 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. Generally, the concentration of these elements in our deposits is very low, about 1–10 ppm. Rather surprising are the relatively high concentrations of Ni and Cr in the data from Hel, both during the day and at night. Note that there is no industry along the Hel peninsula, apart from fishing harbors along it (i.e. upwind of the predominant wind directions).

The source of Cr, Co and Ni pollution in the localities investigated is not quite clear. The relatively high concentrations along the Hel peninsula, and the minimal dependence on the weather (slightly higher in Słupsk 'sunny' data) would indicate a non-local, probably industrial origin.

4. Conclusions

It has been shown that the combination of laser ablation and mass spectrometry methods is useful in the chemical analysis of aerosol particles. In this paper the concentration of ten isotopes in air aerosol particles in urban environments was analyzed. The use of aluminum plates as a collecting target for aerosols enables the measurement of carbon isotopes in addition to other elements. This makes the essential difference between the present measurements and other methods, in which aerosols are collected on

graphite disks and electrothermal evaporation from its surfaces is applied. The present measurements have revealed a correlation between carbon aerosols and other elements, such as As and Pb.

The concentrations of particular elements in the aerosols depend on particle size and season. The data obtained may be important in modeling atmospheric phenomena, and quantifying emissions from anthropogenic and natural sources of pollutant gases, because the transport mechanisms of elements in different size aerosol particles are not well known. Moreover, absorption of aerosols by the Baltic Sea plays a significant part in marine chemistry and has an influence on this ecosystem.

Such measurements will be continued in other areas, e.g. coastal zones, non-industrial towns etc. Finally, the accuracy of absolute determinations will be improved, measuring average values of concentrations over several days in similar atmospheric conditions.

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