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AND URBAN AEROSOLS**

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## X-RAY MICROPROBE STUDIES OF HUNGARIAN BACKGROUND AND URBAN AEROSOLS

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### INTRODUCTION

In order to determine the polluting atmospheric sources in urban and background areas source apportionment of the air particulate matter is necessary. Hitherto these studies were mostly based on bulk composition measurements of the aerosol. Source profiles, i.e. the concentrations of several elements for air particulate matter originating from one source, can be deduced from the receptor data using a number of multivariate techniques among which the chemical mass balance. The application is limited by the large number of observations that must be made for each of the variables. Often an elaborated sample preparation is necessary for fractionating the sample into several sub samples, according to the density, particle diameter or other relevant properties. Often this may result in poorly resolved source profiles.

On the other hand, methods for single particle analysis provide direct information on chemical composition and morphology for each individual particle. In case of sufficient lateral resolution and chemical sensitivity this enables a ready fractionation on the basis of some measured or derived parameters, as well as an extraction of source profiles.

Automated electron probe x-ray micro analysis (EPMA) has sufficient spatial resolution (0.1-0.3  $\mu\text{m}$ ) to detect individual particles, and it

has successfully been used to classify atmospheric aerosol particles from urban, remote, continental and marine areas, or suspension particles in estuaries and seas [1,2]. Such method was never before used to analyze aerosol samples from the area of Eastern Europe. In previous work only flyash particles originating from this geographical area were studied by single particle analysis [3]. The emitted stack flyash particles were classified into several chemically and morphologically different groups. The measurement data of summer and winter sampling showed that in the smaller ( $<2\mu\text{m}$ ) particle size fraction two types of unexpected groups are present. One group has high barium content and the other group consists of calcium sulfate particles with high arsenic content. This arsenic is supposed to be on the surface of the particles due to the condensation in the cooled stack gas.

The aim of the present work is to find the relative abundance of the particle types originating from two different background monitoring stations in the middle of the Great Hungarian Plain. In urban areas most pollutants originate from traffic and municipal waste incineration. Since heavy metals play an important role in these samples the highly sensitive x-ray microscope (XRM) of the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory was used. A feasibility study on individual aerosol particles sampled at the above background stations and in the urban area of Budapest is discussed.

## EXPERIMENTAL

### Sampling

Seven samples were taken in the spring of 1990 at the sampling site K-pusztá, which is located nearly at the center of Hungary between the rivers Danube and Tisza, about 70 km south east of Budapest. The closest town of 100 000 inhabitants is about 10 km SE, and an iron work is 50 km from the station. The closest paved road (with very low traffic density) is at least 5 km away. The station is situated on a forest clearing in a pine forest but vineyards are in the neighborhood as well.

Sampling was performed at 2 m above ground level using Nuclepore filters of  $0.4\ \mu\text{m}$  pore size, with  $1.5\ \text{cm}^2$  exposed area. The sampling time was 24 h and the sample volume varied between 3 and  $8\ \text{m}^3$ .

A similar sampling procedure was carried out in the Hortobágy National Park near Nagyiványi about 50 km west from Debrecen, 2 m above ground level. This campaign resulted in six samples taken in August 1990. Several samples were taken in the urban areas of Budapest at ground level, in traffic tunnel ventilation systems and on top of buildings. Only giant particles of this samples were studied by XRM.

### EPMA

The aerosol loaded filters were measured by a JEOL 733 Superprobe equipped with a Tracor Northern particle recognition and characterization program (PRC) that facilitates a fully automated analysis on a preset number of particles. For x-ray micro analysis, 25 keV and 1 nA operating conditions were used. The PRC system operates in the following way. As the beam scans across the field of interest a particle is considered as detected when the digitized backscatter signal exceeds a preset threshold value. The coordinates of the contour points are determined and additional information such as particle diameter, perimeter and shape factor ( $\text{perimeter}^2/4\pi\text{area}$ ) are calculated. Energy dispersive x-ray spectra are collected for 30 seconds with the electron beam positioned in the centroid of the particles. In each sample about 300 particles were measured. Measurement data were stored on floppy disc

for "off-line" data processing on a VAX 11/780. The large data set consists of: net intensities for 18 elements, diameter and shape factor for each particle.

Classification of the particles was carried out by hierarchical cluster analysis based on the Ward's error sum strategy, that has previously been proven to be one of the most advantageous procedure for environmental applications [4]. A second hierarchical clustering was performed on the average composition data of the samples and resulted in a set of training vectors (centroids) that are relevant for the total sampling campaign. Finally a nearest centroid sorting is used to classify all particles from one campaign according to their distances from the centroids of the clusters. The method of Forgy [5] minimizes the sum of squares of the distances to the centroids for a fixed number of clusters. This procedure results in an average composition data set for each sampling site and the abundances of the particle groups in each sample.

### XRM

Synchrotron radiation x-ray analysis has been performed on beam line X26 at the NSLS at Brookhaven National Laboratory. The NSLS source is characterized by the following parameters: electron energy 2.53 GeV, critical energy 5.0 keV, maximum ring current about 200 mA. The experimental methods adopted for this work are very similar to the ones described in [6]. The XRM utilizes the continuous x-ray spectrum produced by the bending magnet. The flux for photon energies about 4 keV is  $2 \times 10^6$  photons/ $\mu\text{m}^{-2} \text{ s}^{-1} \text{ mA}^{-1}$  at 9 m from the x-ray ring. A set of four stepper-motor-driven tantalum slits can be used to produce collimated beams down to about 40  $\mu\text{m}$ . A tantalum collimator placed 3.5 cm from the sample position was used in the present experiments to produce an x-ray beam of 4  $\mu\text{m} \times 7 \mu\text{m}$ .

### RESULTS AND DISCUSSION

Size distribution curves of all samples were calculated. They show that 80 % of the detected particles is smaller than 3  $\mu\text{m}$ . Under certain meteorological conditions as encountered this particle fraction might have long residence time in the atmosphere [7]. Hierarchical clustering of the chemical and morphological data showed that most particles (>0.3  $\mu\text{m}$ ) during this sampling period were of antropogenic origin, mainly from power stations and industrial emissions. Table I gives an overview of the 11 major particle types of the K-pusztá sampling campaign.

The largest group seems to be industrial particles originating from power plants and metallurgy. Silicate particles of industrial origin are different in composition and shape from the soil silicates. They can originate from any type of coal burning. Their abundance did not depend significantly on the wind direction. Very few particles were observed with a relatively high V and Ni content which would indicate oil fired power station as aerosol emission source.

The second group, gypsum, is very common in flyash since often lime is added to reduce gaseous sulphur emission. In some Hungarian power stations (Ajka) alkaline lignite with high Ca content is burned. However, gypsum particles might originate from various sources [8].

Table 1.  
Particle groups in background aerosols sampled in April-May  
in K-pusztá as detected by EPMA

Origin	Abundance (%)	Major components detected by EPMA	Diameter ( $\mu\text{m}$ )	Shape factor
<u>Industrial</u>				
Silicate	24	Si, Al, S, Fe	2.6	1.7
Gypsum	15	Ca, S, Si	2.3	2.2
Iron rich	12	Fe, Si	1.5	1.5
Pyrite	7	Fe, S, Si	1.2	1.6
Metal	1	Al or Ti or As		
<u>Soil dust</u>				
Silicate	22	Si, Al, K, Fe	2.7	2.6
Quartz	10	Si	1.5	2.3
Limestone	1	Ca	1.7	2.5
<u>Sulphate</u>	1.5	S	0.8	1.7
<u>Traffic</u>	1.2	Pb, Cl, Br	0.6	1.3
<u>Biological</u>	3	S, P, K	2.6	2.5

The iron rich particles might originate from various sources like steel smelters, corrosion and coal burning. The abundance of this group depends on the wind direction. The same holds for the iron sulfate group.

Soil dust silicates have rectangular or irregular shape giving shape factor  $>1.5$ . Their Na, Mg and K content is also higher than that of the flyash silicates. However if the measured data have higher statistical error the distinction of the two groups is very difficult. Quartz was present in all samples but the lime particle group was only occasionally observed.

Since the detection of the particles is under automatic control, very small aerosol particle groups about a few tenth of microns are not always observed. Moreover, in view of the energy deposited by the electron beam in the EPMA and the vacuum condition, unstable components will disappear. For this reasons the secondary  $(\text{NH}_4)_2\text{SO}_4$  particles are not detected as abundant as they are present in the aerosol [9]. Since the sampling stage was far from paved road the presence of automobile exhaust particles was not significant.

Morphological visualization also confirmed that the samples contained numerous biological particles.

Relative abundances or particle number concentrations (expressed in percent) in each individual sample are given in Figure 1 for the K-pusztá campaign.

The particles originating basically from coal burning have similar tendencies during the sampling period.

The sampling campaign he in Hortobágy showed very similar particle group abundances except for biological particles that were more abundant there due to the summer season. Silicates contained much less sulfur which means that flyash was not as dominant as in the K-pusztá sample, despite that the site is much closer to the northern industrial area.

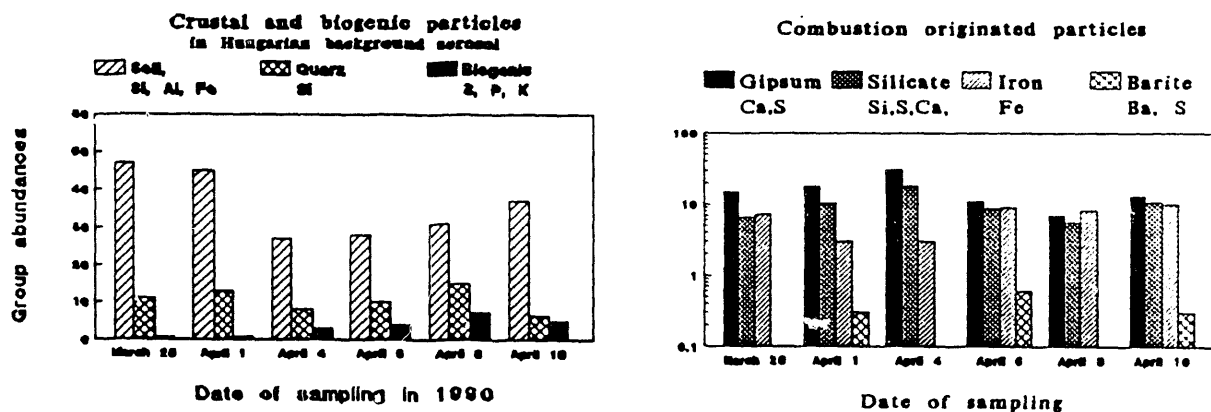
From the EPMA data it can be concluded that antropogenic particles are

present at unexpectedly high abundance in the so called background aerosol. In order to get better source profile a high performance micro chemical technique, XRM was tested to study the detectability of various trace metals in atmospheric particles. Since the beamsize was relatively large compared to the average particle diameter in the aerosol at present only giant particles were measured. Table 2. shows illustrative examples for some elements found in single aerosol particles. The values correspond to 300 s counting time.

Table 2.  
Elements detected by XRM in individual aerosol particles

Particles	diameter ( $\mu\text{m}$ )	Elements above determination limit
<u>Background aerosol</u>		
Soil	5	Si S K Ca Ti Mn Fe Zn
Flyash	3	S K Ca Ti Mn Fe Cu Zn Pb
Pyrite	6	S Ca Ti Cr Mn Fe Cu Pb
<u>Urban</u>		
Rust	4	S Ca Ti Cr Mn Fe Ni Cu Zn Pb Mo
Lead	6	S Ca Ti Cr Mn Fe Cu Zn Pb
Soot	5	S Ca Cr Mn Fe Ni Zn Pb
Agglomerate	20	S Ca Cr Mn Fe Ni Cu Zn Pb

Figure 1.  
Group abundances in % of crustal biogenic and combustion originated particles in the K-puszta campaign



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