Ph. D. thesis

MEASUREMENT ON AEROSOL ABSORPTION ÅNGSTRÖM EPONENT AND SIZE DISTRIBUTION – STUDY OF THE POSSIBILITY OF SOURCE APPORTIONMENT

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Szeged

2012

1. Introduction

Identification of the emission sources of atmospheric aerosol is one of the most dominant topics of environmental science. Numerous international conventions and decisions demonstrate the importance of the problem. The Clean Air for Europe (CAFÉ) Program, which exists within the 6th Environment Action Programme, handles atmospheric aerosols as air pollutants posing the highest health risk. The Program gives opportunity for a Member State to reduce its national pollution amount by the contribution of pollutions which sources are proven to originate from outside of the country's border. At the same time, the Program calls on the Member States to reduce their emission in pursuance of their sources. According to these tasks, also in the aerosol science the emphasis continuously shifts from the qualitative analysis to the quantitative.

The Photoacoustic Research Group of the University of Szeged has performed experiments related to the quantitative analysis of aerosols since 2003. I have joined to this work in 2006 during my graduate work.

The goal of laboratory and field measurements presented in my thesis is the elaboration of the fundamentals of an optically based, real-time aerosol source apportioning method. In the course of my work, I have studied how the wavelength dependence of aerosol optical absorption is changing with varying particle size distribution or chemical composition. I have also studied the possibility of concluding the strength of the emission sources relative to each other from these changes. I have used during my experiments a homemade four-wavelength photoacoustic spectrometer and two types of commercially available particle size distribution measuring instruments (SMPS+OPC).

2. Objectives

Our former results supported, that the in-house developed four-wavelength photoacoustic spectrometer is able to measure the optical absorption of aerosol even under field conditions [11]. We have proved by our laboratory experiments that the instrument, thanks to its extremely wide measuring wavelength coverage, is able to distinguish between carbonaceous aerosols with different chemical compositions [10].

My aim was the elaboration of the basis of a real time, optical aerosol source apportionment method under laboratory and field conditions.

The main subtasks of the presented work are the following:

- Determination of wavelength dependent specific optical absorption coefficients of laser ablation generated pepsin particles having different size distribution but analogous particle shape.
- Study of the relative strength of the main anthropogenic aerosol sources of urban aerosol based on optical absorption measurements during wintry, field conditions.
- Laboratory characterization of red mud and hematite samples in their dispersed state, determination of wavelength dependent optical absorption coefficient, elemental composition and size distribution.
- Validation of the measurement of wavelength dependent optical absorption coefficient by model calculations on known particles based on Mie-theory.
- Determination of wavelength dependent optical absorption coefficient of atmospheric aerosol under special conditions, real-time detection of the presence of red mud dust in ambience.

3. Applied instruments

Four-Wavelength Photoacoustic Spectrometer (4λ-PAS)

I have used an in-house developed four-wavelength photoacoustic spectrometer during my measurements. Technical description of the prototype can be found in our former paper [9]. The speciality of 4λ-PAS is, that it measures the optical absorption of particles in their natural dispersed state at four wavelengths from the near IR to the UV range (1064, 532, 355, 266 nm) at the same time. The special lightsource is based on a frequency converted Q-switched Nd:YAG OEM disc laser (Smaragd5M, JenOptik). All the four generated upper harmonics serve as exciting beams in photoacoustic cells. Frequency conversion occurs in several steps by using three different nonlinear crystals (LBOI, LBOII and BBO). Schematic view of the 4λ-PAS can be seen in figure 1.

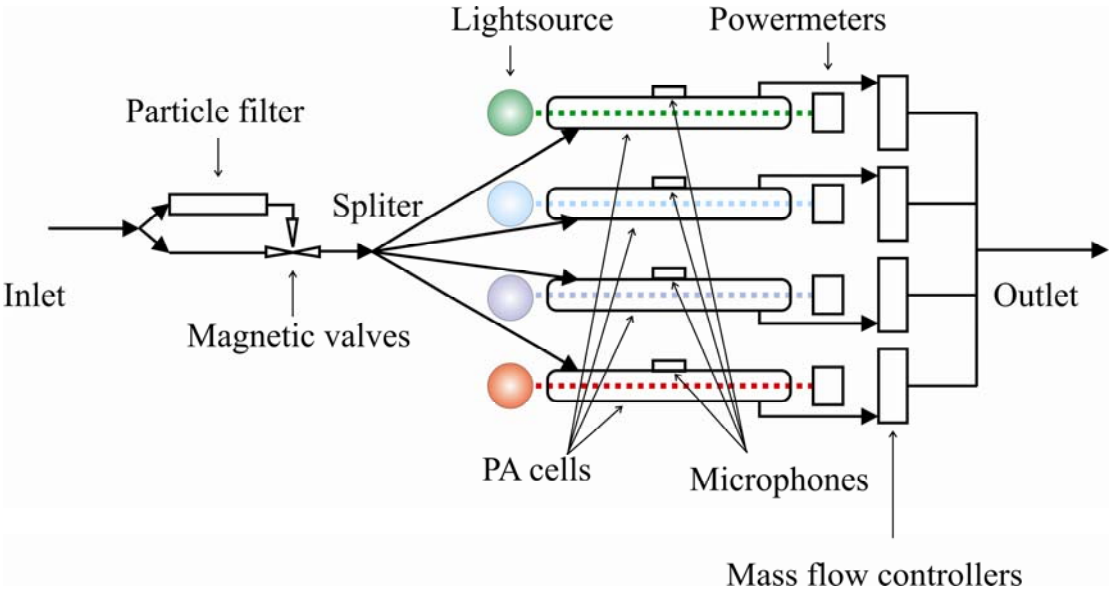

Figure 1: **Schematic view of the four-wavelength photoacoustic spectrometer**

The electronic unit is able to close the flow of the sample gas by a magnetic valve, and direct it to the PA cells through a particlefilter. It is possible by this technique to measure the optical absorption of all non-aerosol components, and substract it from the recorded signal during the data analysis.

Scanning Mobility Particle Sizer

The Scanning Mobility Particle Sizer (SMPS) systems are designed to measure size distribution of ultrafine particles. The two main parts of the instrument are the Differential Mobility Analyzer (DMA) and the Condensation Particle Counter (CPC). The DMA classifies particles according to their electrical mobility. The separation can be achieved by the alteration of the applied voltage. The CPC performs particle counting. I have utilized to my measurements a Grimm 5400 SMPS+C system with Vienna type M-DMA (Grimm Aerosol Technik GMBH), in 44 size ranges between 5.5 and 350 nm. Schematic view of the system can be seen in figure 2.

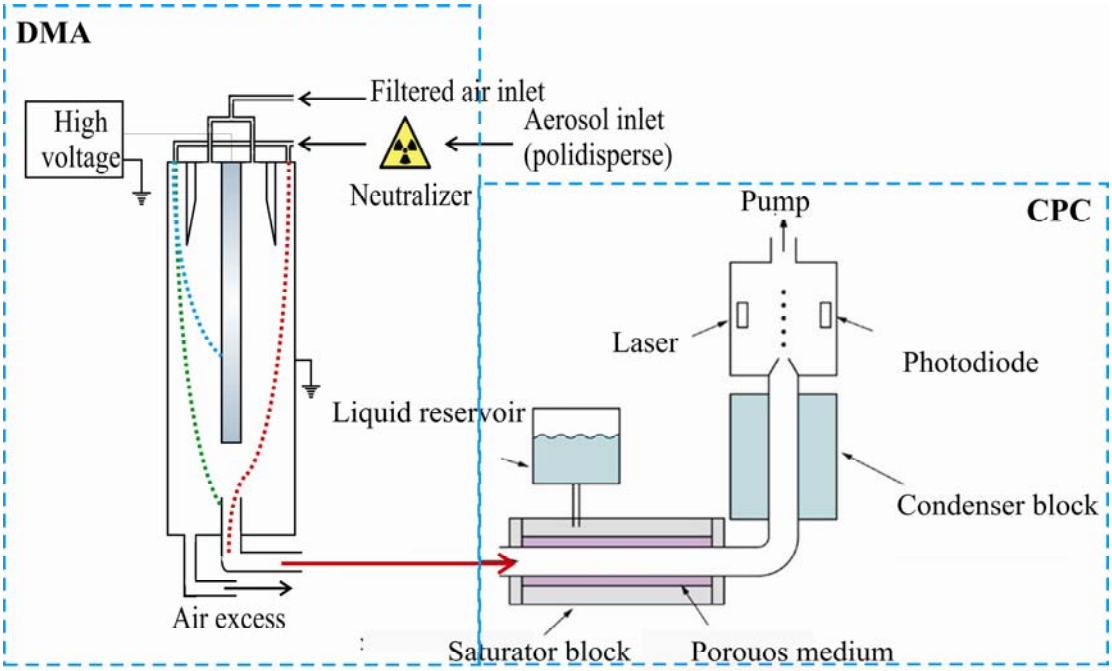

Figure 2: **Schematic view of the Scanning Mobility Particle Sizer**

Optical Particle Counter

Optical Particle Counters (OPC) detect light scattering on an individual particle passing through a laser beam. By known geometry and flow parameters, the optical diameter, the size distribution and the total concentration of particles can be calculated from the intensity of scattered light. Schematic view of the applied OPC (Grimm 1.109) can be seen in figure 3. This instrument counts particles classified into 31 size ranges between 0.25 – 32 μm.

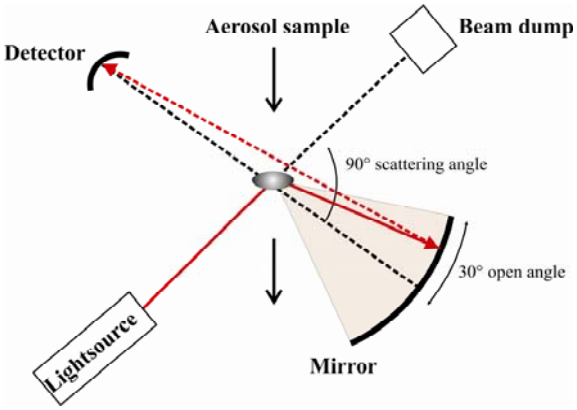

Figure 3: **Schematic view of the applied OPC**

4. New scientific results

1. I have determined the specific optical absorption coefficients of laser ablation generated pepsin particles by using the four-wavelength photoacoustic spectrometer. Shapes of the particles were similar but the size distributions were distinct during the experiments. The particles with different sizes showed significant distinctions under the studied wavelength coverage in optical absorption and in its wavelength dependence, too. The reason of these differences according to my explanation is the particle size dependence on the optical absorption [2].

2. I have determined the shadowing effect originating from the optical absorption of the laser ablation generated particle cloud, based on my photoacoustic measurements. In the first case, I have studied the shadowing effect during the duration of the ablating laser pulse. In this case particles composed a concentrated aerosol cloud directly above the surface of the target, and the reduction of the laser pulse intensity reaching the surface of the target (i.e. the part of the laser pulse arriving later in time) could reach even 10 % according to my calculations. In the second studied case, when the particles already uniformly filled the ablation chamber, the shadowing effect was negligible. I have found that the shadowing effect of an ablation generated aerosol cloud is required to take into consideration (i.e. the incoming power density is reduced by 1 %) if the mass concentration of the aerosol cloud is 5,91 and 7,52 g/m^3 by 440 mJ/cm^2 and 660 mJ/cm^2 ablating power density, respectively [2].

3. I have studied the opportunity of source apportionment of the main anthropogenic aerosol components of urban aerosol based on optical absorption measurements during wintry, field conditions. I have found intermediate correlations (i.e. statistically strong connection) between the absorption Ångström exponents calculated from different wavelength pairs and the source specific ratio derived from number concentration of characteristic modes of number size distribution, the elemental composition of the particles and the mixing ratio of air pollutant gases. The high correlation efficiencies proved that the sources of the studied components were the same, and therefore the applied procedure could serve as the basic of elaboration of an *in-situ* source apportionment method [4, 7].

4. I have performed the laboratory characterization of red mud and hematite samples in their dispersed state. I have determined the elemental composition, particle size distribution, and wavelength dependent optical absorption at the measurement wavelengths of the four-wavelength photoacoustic spectrometer of the two types of aerosols. I have concluded based on the comparison of the measured optical absorption data, that in the absorption spectrum of the red mud at 1064, 532 and 355 nm, the hematite content dominated, which also dominated in mass concentration. Nevertheless, at 266 nm red mud had extremely high absorption coefficient, differing from hematite. This strong UV absorption is very likely caused by other components of red mud besides hematite. I have proved the conclusions drawn from the measurements with model calculations based on Mie-theory [1, 3].

5. I have studied the main anthropogenic aerosol components among the atypical red mud dust during my field measurement carried out at the red mud disaster area. I have found beside the correlations experienced under normal air pollutant conditions, one up to this point not known, strong connection between the amount of particles having larger diameter than 500 nm and the aerosol optical absorption measured at 266 nm. This found connection reveals the presence of red mud dust. This relationship could serve as further principle of an *in-situ* source apportionment method bearing on ambient red mud dust content [3].

5. Summary

It has been already demonstrated by several research groups, that the previously studied aerosol properties (optical absorption coefficient, Ångström exponent and particle size distribution) refer to the emission source, nevertheless, the ratios suggested in present work are not present in the literature. The high correlations which were identified under both laboratory and field conditions confirm that the suggested method can serve as the basis of the elaboration of an *in-situ* source apportionment method.

Referred papers related to the present thesis

1. D. Czövek, Z. Novák, Cs. Somlai, T. Asztalos, L. Tiszlavicz, Z. Bozóki, T. Ajtai, N. Utry, **Á. Filep**, F. Bari, F. Peták (2011). Respiratory consequences of red sludge dust inhalation in rats.
   Toxicology Letters 209, 113-120.
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2. B. Hopp, G. Kecskeméti, T. Smausz, T. Ajtai, **Á. Filep**, N. Utry, A. Kohut, Z. Bozóki, G. Szabó (2012). Characterization of excimer laser ablation generated pepsin particles using multi-wavelength photoacoustic instrument.
   Applied physics A, 107, 2, 429-435.
   IF: 1,76
3. **Á. Filep**, T. Ajtai, N. Utry, M. D. Pintér, T. Nyilas, Sz. Takács, Zs. Máté, A. Gelencsér, A. Hoffer, M. Schnaiter, Z. Bozóki, G. Szabó (2012). Absorption spectrum of ambient aerosol and its correlation with size distribution in specific atmospheric condition after the red mud accident.
   Aerosol and Air Quality Research, accepted for publication
   IF: 2,827

Presentations and posters related to the present thesis

4. T. Ajtai, M. Schnaiter, C. Linke, **Á. Filep**, N. Utry, Z. Bozóki, G. Szabó: Wavelength dependent Ångström exponent based source apportionment and its correlation with aerosol size distribution. EAC 2011, Manchester.
5. T. Ajtai, M. Schnaiter, C. Linke, **Á. Filep**, N. Utry, Z. Bozóki, G. Szabó: In-situ spectral characterisation of atmospheric aerosols after the red sludge disaster in Hungary during the autumn of 2010 based on our novel multi-wavelength photoacoustic instrument. EAC 2011, Manchester.
6. T. Ajtai, **Á. Filep**, N. Utry, M. Pintér, Z. Bozóki, G. Szabó: On the possibilities of on-line identification of red mud particle through its absorption spectrum. DKMT 2012, Szeged
7. T. Ajtai, **Á. Filep**, N. Utry, M. Pintér, Z. Bozóki, G. Szabó: Absorption Ångström exponent, and its correlation with other aerosol variables such asnumber size distribution, gas phase- and trace elements of the atmosphere. A field study. EAC

2012 Granada

Other referred papers

8. T. Ajtai, **Á. Filep**, A. Varga, G. Motika, Z. Bozóki and G. Szabó (2010). Ozone concentration monitoring photoacoustic system based on a frequency quadrupled Nd:YAG laser.
   Applied Physics B: Lasers and Optics DOI: 10.1007/s00340-010-4174-8

   IF: 2,24

9. T. Ajtai, **Á. Filep**, M. Schnaiter, C. Linke, M.Vragel, Z. Bozóki, G. Szabó, T. Leisner (2010) A novel multi-wavelength photoacoustic spectrometer for the measurement of the UV–vis-NIR spectral absorption coefficient of atmospheric aerosols.
   Journal of Aerosol Science, 41, 1020–1029.

   IF: 2,447

10. T. Ajtai, **Á. Filep**, G. Kecskeméti, B. Hopp, Z. Bozóki, G. Szabó (2010) Wavelength dependent mass specific optical absorption coefficients of laser generated coal aerosols determined from multi-wavelength photoacoustic measurements.
    Applied Physics A, DOI 10.1007/s00339-010-6068-3

    IF: 1,76

11. T. Ajtai, **Á. Filep**, N. Utry, M. Schnaiter, C. Linke, Z. Bozóki, G. Szabó, T. Leisner (2011) Inter-comparison of optical absorption coefficients of atmospheric aerosols determined by a multi-wavelength photoacoustic spectrometer and an Aethalometer under sub-urban wintry conditions.
    Journal of Aerosol Science, 42, 859-866.

    IF: 2,447

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