

**AEROSOL METROLOGY FOR ATMOSPHERIC SCIENCE AND AIR QUALITY**

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**ABSTRACT**

Measurements of airborne particulate matter are of paramount importance for the protection of human health, the design of the appropriate measures and legislation as well as the investigation of climate change. Usually, the research is focus on PM<sub>10</sub> και PM<sub>2.5</sub> (particulates with aerodynamic diameter less than 10  $\mu\text{m}$  and 2.5  $\mu\text{m}$ , respectively). The problem is that the level of uncertainty is too high and the traceability is insufficient. The project "AEROMET", in the framework of EMPIR (European Metrology Programs for Innovation and Research) project aims to properly address and propose solutions for such issues. Participants in AEROMET project involve 21 entities from 15 E.U. countries, mainly National Metrological Institutes (NMIs) with PTB (Physikalische-Technische Bundesanstalt, Germany) acting as coordinator. Laboratory of Inorganic and Analytical Chemistry of NTUA participates as external funded partner. Specific aims of AEROMET project are as follows in individual work packages (WP, Work Packages):

1. Design and building of a demonstration aerosol mixing chamber delivering stable reference aerosol for long time and large range of flow rates. Using this chamber the calibration of automated instruments for PM<sub>10</sub> and PM<sub>2.5</sub> particulates and the validation of methods for quantification of their composition is in progress (WP1).
2. The application of traceable validated methods for determination of various species of carbon (i.e. elemental (EC), organic (OC) and total carbon (TC)) as well as cations and toxic elements, such as As, Cd, Pb, Ni and Hg (WP2).
3. Development of calibration procedures for Mobility Particle Size Spectrometers (MPSS) and Condensation Particle Counters (CPCs) (WP3).
4. Use of mobile X-ray spectrometers for the real time and on-site quantification of the composition of particulates. These measurements will be compared with the instrumentation usually employed for such analysis (e.g. ICP-MS). Sampling and in-situ measurements using TXRF have been performed in an urban area (Cassino, Italy) and in a suburban background area (Budapest, Hungary) (WP4).
5. Design and construction of substrates using nanomaterials for the measurement of fine and ultrafine particulates (UFP) (WP5).

Laboratory of Inorganic and Analytical Chemistry participates in WP2 και WP4, as well as in the dissemination of results, mainly through the biannual international conferences of modern analytical chemistry "IMA", which were founded in 1999. This year, IMA 2019 will be held in Ioannina (<http://www.conferre.gr/congress/ima2019>).

**INTRODUCTION**

Atmospheric pollution by airborne particles contributes significantly to climate change and has been linked to adverse health effects, such as respiratory, cardiovascular diseases and lung cancer. It has been estimated that only in Europe, more than 500,000 deaths per year can be attributed to PM exposure <sup>[1, 2]</sup>. For the member states of the EU, the Air Quality Directive 2008/50/EC <sup>[3]</sup> is mandatory, comprising quantification of airborne particles and their components. The most important metric to monitor particulates in air constitutes the total mass per unit volume of air of particles with aerodynamic diameter smaller than 10  $\mu\text{m}$  or 2.5  $\mu\text{m}$ , commonly referred to PM<sub>10</sub>

and PM<sub>2.5</sub>. Ambient limit values have established in Europe in Directive 2008/50/EC<sup>[3]</sup>. Analogous legislation has been imposed to USA (National Ambient Air Quality Standards, E.P.A.)<sup>[4]</sup>. All local, national or EU action plans and measures to reduce particulate air pollution rely on air monitoring networks<sup>[5]</sup>, the quality of data they provide and the methods in use<sup>[6, 7]</sup>. It is recognised that the regulated metrics for particulate air pollution suffer from severe methodological deficiencies. PM mass concentration was established as the default metric of PM allowing mass measurements in a traceable manner. The gravimetric filter based reference methods for PM<sub>10</sub> and PM<sub>2.5</sub> (EN 12341:2014; EN 14907:2005), however, fall short in areas such as sensitivity and ongoing Quality Assurance and Quality Control due to the following reasons: Many particles are hygroscopic, so that their mass and size depends strongly on the humidity. There can be significant sampling issues such as impaction (removing larger particles) and diffusive losses to walls (removing smaller particles) resulting in uncertainties of the total mass determination of up to several 10 %. Collecting particles on filters for subsequent chemical analysis can give rise to additional sampling issues relating to chemical interactions and differing effects of different filter materials. Moreover, automatic PM monitoring systems, which were developed in order to avoid these disadvantages and enable time resolutions below 24 h, must demonstrate their equivalency to the reference manual gravimetric method. This is problematic due to both the inconsistency in the automatic instruments based on different working principles and the ambiguity within the aerosols used for comparison. PM<sub>10</sub> and PM<sub>2.5</sub> methods are being revised within CEN TC 264 WG 15, where it is recognized that further research is needed to bring the reliability of measurements in line with that for other regulated air quality metrics. The proposed solution in AEROMET project is the implementation of traceable reference methods for the harmonized lab based calibration of automatic PM measuring instruments. It is evident that mass concentration is too crude a metric regarding spatial and temporal resolution and sensitivity to characterize ambient aerosol particles for the purposes of understanding their sources, health effects and possible effects on climate. Additional metrics with high time resolution such as particle number concentration and size distribution need to be integrated into air quality networks in order to make variations in time and space measurable, and to better identify sources, primary particles and peak concentrations. This is especially necessary for the fraction of ultrafine particles (UFP), as their mass is negligible in comparison to PM<sub>2.5</sub> and PM<sub>10</sub>. Current metrics for UFP are not as harmonized as those for PM<sub>10</sub>, PM<sub>2.5</sub> or black carbon and the reliability of the existing data is not ensured. General calibration concepts for the measurement of particle number concentration and particle size (with CPCs and MPSS) are already described in fundamental standards (ISO 15900:2009 and ISO 27891:2012). A CEN working group is adapting them to the needs of ambient air quality monitoring networks (FprCEN/TS 16976). These calibrated “network”-CPCs should have an upper limit of 10<sup>5</sup> per cm<sup>3</sup> in particle number concentration in ambient air; lower and upper particle size limits should be 7 nm and a few micrometres, respectively. Consequently, monitoring networks need reliable calibration services. The project AEROMET is aiming at providing the necessary independent calibration facilities.

Anions and cations constitute important parameters for understanding secondary inorganic aerosol formation and also for measuring primary ionic PM such as sea salt<sup>[8-11]</sup>. Manual reference methods for anions and cations, and EC/OC are close to being completed in CEN TC 264 WGs 34 and 35, respectively, but a deeper understanding of potential measurement biases such as on filter artefact and the loss of volatile ionic PM is required before the SI traceability can be put in place<sup>[12]</sup>.

As conventional methods for quantitative elemental analysis of environmental aerosols – in field filter sampling and lab based analysis – show substantial reliability and sensitivity restrictions there is a strong need to develop new flexible approaches with increased accuracy, time resolution and speed of analysis. In field XRF in combination with appropriate sampling could - within the

framework of SI traceability and calibration at NMIs and DIs - bring regulatory measurements of PM composition to the required high quality level. A definition of the spatial representativeness of measuring points in air quality networks is still missing in the legislation and the knowledge gap has to be filled by individual temporary measurement campaigns for which in field XRF in combination with appropriate sampling is a suitable candidate method. XRF based aerosol analysis offers additional analytical tools for a more reliable analysis of particulate components which corresponds to the needs from atmospheric sciences <sup>[13]</sup>.

The overall aim of the current project AEROMET is to develop and demonstrate methods for traceability and calibration of different aerosol instruments covering the environmentally relevant size range from several nm up to at least 10  $\mu\text{m}$  and the regulatory relevant mass concentrations (0.1 to 1000  $\mu\text{g}/\text{m}^3$ ) and number concentrations (0.1 to 10<sup>7</sup> particles per  $\text{cm}^3$ ).

## AIMS AND METHODOLOGY

The structure of the AEROMET project is demonstrated in Table 1, reporting the individual Work Packages (WP) with the corresponding Work Package Leaders (WPLs) from several European NMIs (National Metrological Institutes).

**Table 1:** Structure of the AEROMET project

Work package (WP)	WP1	WP2	WP3	WP4	WP5	WP6	WP7
Title	New reference methods for $\text{PM}_{10}$ and $\text{PM}_{2.5}$	Methods for the analysis of major components	Calibration of MPSS and CPC	Quantifying airborne particle composition in the field	Development of reliable XRF techniques	Creating impact	Management and coordination
Leader	METAS	NPL	TROPOS	BAM	INRIM	NPL	PTB

ETAS: Eidgenoessisches Institut fuer Metrologie (Swiss); NPL: National Physical Laboratory (UK); TROPOS: Leibniz Institute for Tropospheric Research (Germany); BAM: Bundesanstalt fuer Materialforschung und Pruefung (Germany); INRIM: Istituto Nazionale di Ricerca Metrologica (Italy); PTB: Physikalisch-Technische Bundesanstalt (Germany)

More specifically, the tasks undertaken in different work packages (WP) are:

In **WP1** the design and construction of a demonstration aerosol chamber system for the lab-based calibration of PM-measuring instruments is under investigation by using synthetic ambient aerosols.

**WP2** investigates the establishment of traceable validated methods for the analysis of major components of particulate matter, such as elemental (EC)-, organic (OC)- and total carbon (TC), anions and cations, toxic trace elements (As, Cd, Hg, Ni) in order to meet the data quality of current regulation (EC Directives on ambient air quality).

**WP3** deals with the improvement of the quality of number-based aerosol measurements in order to meet regulatory needs and to make environmental aerosol data more reliable and comparable.

**WP4** applies mobile and on-site X-Ray spectroscopy techniques combined with mobile on-site particle sampling techniques for real-time mass concentration measurements of EC-regulated elements (As, Cd, Hg, Ni) in ambient aerosols. Re-analysis of the samples with conventional lab-based techniques (ICP-MS) will be carried out.

**WP5** develops traceable and reliable X-Ray analytical methods to measure the elemental mass deposition per unit area, elemental composition and the chemical binding state (speciation) of airborne particles deposited on flat homemade nanostructured substrates, which will be used in cascade impactors for size discriminating of coarse and ultrafine fractions.

**WP6** comprises knowledge transfer via stakeholder meetings, conferences, publications in open access journals, workshops, training and exploitation to the benefit of the end users (calibration services, reference materials and interaction with instrument manufacturers).

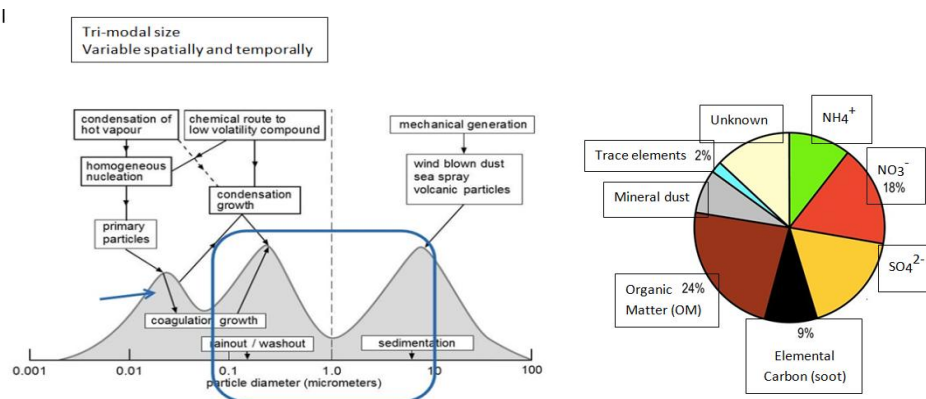
**WP7** aims to the management and coordination of AEROMET project through meetings and project reporting.

## RESULTS AND DISCUSSION

In Fig. 1 (a) the tri-modal size distribution of ambient aerosols and a representative aerosol composition Fig.1 (b) are demonstrated. Aerosols or Particulate Matter (PM) have not a distinct chemical composition, but they consist from variable combustion particles salts, metal oxides, organic substances and other materials. Several factors affect the measured PM weight, as humidity on filter material and on hygroscopic PM, loss of filter material, temperature during sampling, storage and transport on semi-volatile material, weather conditions in general, chemical reactions on the filter, static electricity, balance drift etc. Therefore a suitable standard calibration aerosol for calibrating commercial PM-measuring instruments does not exist.

Results already obtained, together with future actions for the different WPs are as follows:

In **WP1** a synthetic ambient aerosol was produced using a test dust having a representative aerosol composition (Fig. 1 b) and different atomizer systems tested with dry and wet processes. Furthermore, the design and construction of a mixing aerosol chamber based on computational simulations was developed for the generation of representative ambient aerosols. Finally, the lab-based calibration of automatic PM instruments is in progress using this validated aerosol chamber.

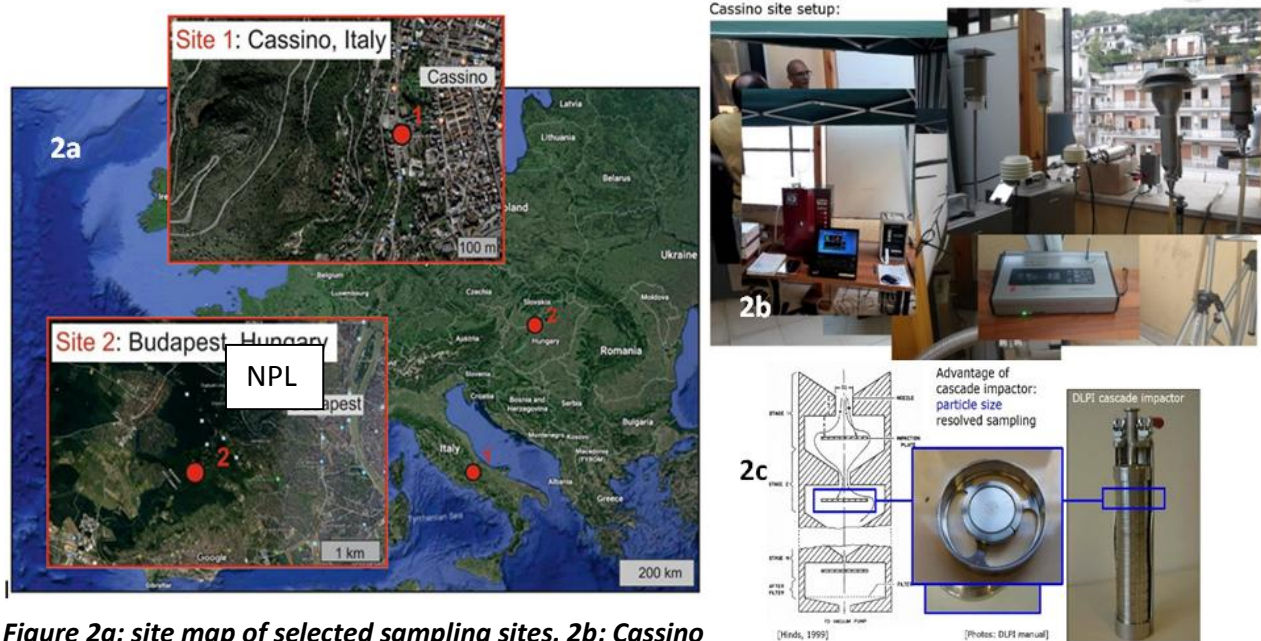


**Figure 1:** Tri-modal size distribution of ambient aerosols (a) and a representative aerosol composition (b)

The leader of **WP2** (NPL) has already successfully participated in ACTRIS/AQUILA inter-laboratory comparison exercises for TC and EC measurements using conventional methods. The results were within the z-scores in a related Proficiency Testing Scheme (PTS). NTUA determined the different carbon species on some quartz filters obtained from NPL using thermal-optical methods according to EN 16909:2017. A deviation of only 5% resulted in comparison to the data of NPL. For the analysis of the required cations (As, Cd, Hg, Ni, Pb) except from the participation in relevant PT schemes using ICP-MS, a new TXRF (Total X-ray Fluorescence) instrument based on internal standardization was tested for its capability to provide independent chemical and physical traceability chains and to extend the range of metals analyzed beyond those required for regulation (see WP4).

From **WP3**, the establishment of specific calibration procedures for Mobility Particle Size Spectrometers (MPSS) is already carried out<sup>[14]</sup>. Furthermore, the provision of calibration facilities for Condensation Particle Counters (CPCs) to the CEN standard FprCEN/TS 16976 are in progress, as well as the investigation of particle losses as function of flow rate and particle diameter (sub-

10nm). Continuous feedback of findings will be delivered to standardization committees (CEN & ISO) and observational networks (ACTRIS & GAW).



Within WP4 the selection of two representative sampling sites (Fig.2a) (Site1, urban: Cassino, Italy (Fig.2b) and Site 2, suburban background: Budapest, Hungary) were selected and the field campaigns were conducted in May and September 2018. At these two sites, real time in-situ measurements on element mass concentration were carried out by using mobile and semi-automated devices (multi- stage cascade impactors) (Fig.2c). The filters obtained from the different particle size fractions (from 10  $\mu\text{m}$  down to several nm) were measured for the regulated elements in aerosol samples as As, Cd, Hg, Ni, Pb and the main elements of the filters by non destructive in-situ mobile TXRF (Fig. 3a). In Fig.3b the TXRF analysis patterns for different daily time periods are demonstrated. A backup analysis of the same filters by conventional techniques (ICP-MS, lab-based calibrated XRF) is in progress for the comparison of the results.



Fig. 3a: TXRF spectrometer S2 Picofox, Bruker

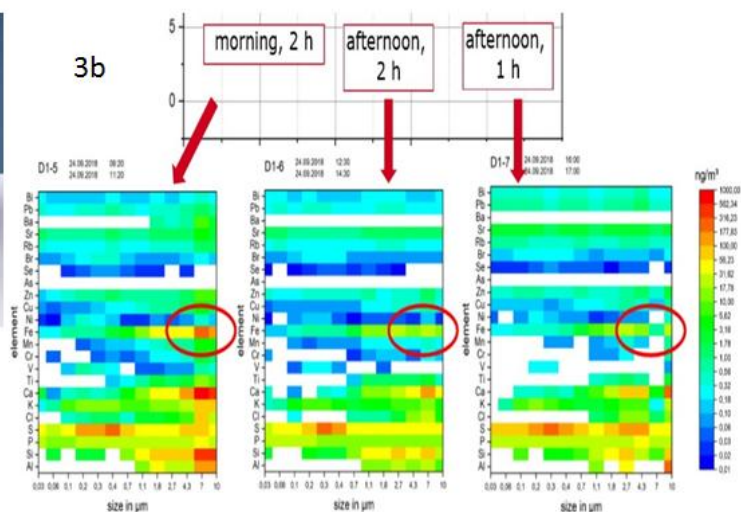


Fig. 3b: Analysis of the elements on the sampled filters by TXRF

In WP5 the design and production by different lithographic approaches of artificial micro- and nanostructured reference samples that are suited for the qualification of calibration standards for



TXRF and GIXRF (Grazing Incidence X-Ray Fluorescence) quantitative and size dependent analysis of aerosols are already in progress. In this framework the fabrication of some micro and nanostructured substrates and some micro and nanoparticles samples, as flat and patterned Si/Ge substrates with disordered and ordered nanoparticles from Fe<sub>3</sub>O<sub>4</sub> seeds, core-shell nanoparticles (silica core and polystyrene shell with different sizes), gold-coated silicon pillars etc. is ongoing or completed.

## CONCLUSIONS

The AEROMET project will have impact on metrological, scientific and industrial communities, as well as on relevant standards. Especially, the new lab-based calibration procedure of PM-measuring instruments will have direct impact on the revision of standards and national air quality monitoring networks. The novel particle chamber test facilities for the generation of synthetic ambient aerosols can be applied in the performance assessment of air filters contributing to the related standards. The novel XRF methodologies enhance the quality of aerosol component analysis in air quality monitoring networks by providing flexible in-situ multi element analysis.

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