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1 Overview

Measurements of aerosol particles are vital for enforcing EU air quality regulations to protect human health, and for research on climate change effects. Although metrics such as the mass concentration of airborne particulate matter (PM) are currently in use, the level of uncertainty is too high, and the traceability is insufficient. Therefore, the project established reproducible reference methods for PM₁₀ (inhalable particles with diameters of 10 micrometres and smaller) and PM_{2.5} (fine inhalable particles, with diameters of 2.5 micrometres and smaller) by developing a new facility for artificial aerosol generation. In accordance with EU regulation and air quality monitoring networks requirements, the project achieved target uncertainties of below 15 % for aerosol measurements and characterised regulated components in airborne particles for PM instrument calibrations. In addition, the project produced quantification procedures for elemental compositions of airborne particles, based on x-ray analytical techniques that use chemical and physical traceability chains, along with complementary analytical techniques such as ICP-MS, for validation purposes. The partners also engaged with key members of the supply chain; from accredited laboratories to standards developing organisations (such as ISO and CEN), as well as end users (such as the AQUILA network); in order to facilitate the take up of technology and measurement infrastructure developed during the project.

2 Need

Regulatory bodies, air quality networks and atmospheric instrument manufacturers all require the improvement of air quality monitoring; however, there is currently a lack of traceable calibration standards and harmonised calibration procedures for measuring airborne PM. In addition, methods measuring PM_{10} and $PM_{2.5}$ (particle mass concentration) within the EU Air Quality Directive 2008/50/EC need improving, in order to ensure the comparability of local data measured by instruments relying on different working principles (e.g. gravimetric vs. optical measurements). Therefore, reference methods for measuring PM_{10} and $PM_{2.5}$ and calibration methods for the instruments used for such measurements are needed.

The chemistry of aerosols (elemental composition analysis) is also part of the existing regulation and it is necessary to understand their origins, behaviour and environmental fate and impacts (i.e. effects on health and climate). However, current methods for the quantification of regulated aerosol components (e.g. Elemental Carbon and Organic Carbon (EC/OC), metals, anions, and cations) are notoriously inflexible in terms of time, spatial resolution and lack accuracy. Therefore, validated methods for the determination of major components of PM are needed as well as reliable procedures for standard instrumentation such as Mobility Particle Size Spectrometers (MPSS) and Condensation Particle Counters (CPC). Modern x-ray analytical techniques have the potential to enable the quantitative chemical analysis of airborne particles directly at their emission sources, therefore new SI-traceable x-ray techniques is a development desideratum.

3 Objectives

The overall aim of the project was to develop and demonstrate methods for traceability and calibration of different aerosol instruments capable of covering the environmentally relevant size range from several nm up to 10 μ m and the regulatory relevant mass concentrations (0.1 μ g/m³ to 1000 μ g/m³) and number concentrations (10² to 10⁶ particles per cm³). The traceability and calibration considered the above metrics ,as well as mass concentration and chemistry of particle components. The project also focussed on providing the necessary EU wide calibration infrastructure for aerosol instruments. The specific objectives of the project are:

- 1. To develop reproducible reference methods for PM₁₀ and PM_{2.5}, including the design and building of a demonstration aerosol chamber system for calibrating PM₁₀ and PM_{2.5} instruments using representative generated aerosols and to achieve target uncertainties below 15 %.
- 2. To establish traceable validated methods for the determination of major components of particulate matter, such as elemental and organic carbon (EC/OC), total carbon, anions and cations and major metals (e.g. arsenic, cadmium, mercury, nickel) in order to meet the data quality objectives of current regulation.
- To develop calibration procedures for Mobility Particle Size Spectrometers (MPSS) for ambient measurements in the size range up to 1000 nm - in support of standardisation requirements from ISO TC 24 WG 12 and CEN TC 264 WG 32. To provide calibration facilities for measuring particle number concentration using Condensation Particle Counters (CPCs) in ambient air – as required by the standard FprCEN/TS 16976.



- 4. To apply mobile x-ray spectroscopy techniques combined within particle sampling techniques for quantifying particle compositions in the field for real time analysis. Results will be corroborated by a backup lab-based reanalysis of samples. To qualify a synchrotron based GIXRF setup as a traceable reference for a quantitative chemical aerosol analysis with mobile and bench top GIXRF instrumentation. Full traceability will be achieved by the use of fabricated micro and nanostructures and subsequently calibration along a complete traceability chain will be described in standard operation procedures.
- 5. To facilitate the take up of the technology and measurement infrastructure of the project by the measurement supply chain (accredited laboratories), by standards developing organisations (such as ISO TC 24 and CEN TC 264 and those linked to the EU Air Quality Directive 2008/50/EC) and end users (e.g. Network of National Air Quality Reference Laboratories (AQUILA) and the European Monitoring and Evaluation Programme (EMEP).

4 Results

Objective 1: New reproducible reference methods for PM10 and PM2.5

The design, development and validation of an Aerosol Chamber to be used for calibrating PM_{10} and $PM_{2.5}$ instruments using synthetic ambient aerosols has been the most relevant result with respect to the first objective. The aim of the related work was to develop a chamber system for the mixing and homogenisation of the primary aerosols in order to produce so-called synthetic aerosols that are representative of real ambient aerosols. These representative aerosols were to be tunable with respect to particle chemistry, size distribution and mass concentration (between 10 μ g/m³ and 60 μ g/m³). The aim was to achieve an externally/internally mixed homogeneous aerosol comprising the major chemical components found in ambient air (e.g. dust, combustion particles, hygroscopic and volatile substances).

Two kinds of chamber designs were proposed in the project:

- a smaller (<5 m³) 'Sampling Aerosol Chamber' (SAC) where the devices under test are placed outside of the chamber and sample aerosol from multiple outlets of the setup
- a larger (>5 m³) 'Volume Aerosol Chamber" (VAC), where the devices under test are placed inside the chamber.

At the very beginning of the project, a slight modification was proposed based on the following considerations:

- the dimensions of the facility should be such that this fits into a "standard" lab and allows for easy access and operation; this was one of the reasons why the volume limit of the VAC chamber was reduced compared to the one given in the AEROMET proposal
- the sampling heads of the aerosol devices to be tested in the chamber should not be used, so that just
 a sampling line was connected from the chamber to the device; the consortium agreed that this would
 be a good compromise for the AEROMET project.

As a result, the two groups of aerosol chambers were then called as follows:

- a tunnel-like convective chamber, where the flow is flowing on one direction inside the chamber, generally imposing isokinetic conditions (former SAC chamber)
- a ventilated chamber where calm air should be provided in the sampling zone, where isokinetic sampling is not necessary (VAC chamber)

The methodology here was to use numerical calculations to design these chambers. Experimental validations of these simulations were done in two steps:

- by measuring the flow, in order to assess the flow obtained by the simulations
- by assessing the experimental homogeneity for one inert aerosol

Humidity and temperature control were provided in the chamber, but effects such as evaporation/condensation of volatile species have not been calculated since they are expected to be negligible or can be compensated by selecting/tuning the physical properties of the primary aerosols accordingly.



The aerosol homogeneity attained in an aerosol chamber depends on different phenomena occurring in the aerosol. For example, if an aerosol is volatile, its size might change within the mixing chamber, so it will not be diffused and transported as a non-volatile dust aerosol.

Four case studies (focused on roadside aerosol at winter / summertime during pollution episode or not) have been agreed by the consortium. For each case study, the synthetic aerosol will consist of three types of primary aerosols:

- Type 1: Soot particles (elemental carbon core with organic coating)
- Type 2: Dust particles
- Type 3: Ammonium nitrate and ammonium sulfate particles, either externally or internally mixed.

The physicochemical properties of ambient aerosols depend, among others, on the season (summer/winter) and the pollution levels (pollution episode, non-episode). The following parameters differ therefore for each case study:

- the mass proportion of each primary aerosol type (for example, 40% of type 1, 10% of type 2, 50% of type 3)
- the aerosol size distribution of each aerosol type
- the total mass concentration of all three types together.

Using aerosol chamber numerical simulations, it has been proposed to reach a target aerosol based on these above-mentioned criteria. The important parameters in the simulations are the sizes and the density of the particles. The mass concentration of each type is only important if mass transfer is considered (due to coagulation, evaporation). This point has not been assessed in the calculations here. One argumentation for that was that the aerosol that will be injected in the chamber will already be chemically stable or will reach its chemical stability on a very short time compared to its the residence time in the chamber. This point has not been assessed in this project and constitute a valuable contribution for further work,

The following criteria to qualify a mixing chamber were proposed: stability, spatial homogeneity which is relative to a so-called transfer efficiency, and the sampling zone (so called sampling efficiency). Parameters that can influence the quality of this chamber are of three types:

- Stability: Temporal stability of the inlet and outlet boundary conditions, which involves working under steady state flow conditions.
- Transfer efficiency: it relies on the gas turbulent mixing inside the chamber and on the aerosol deviation from the gas flow: since the behavior of an aerosol is highly dependent on the behavior of the air itself, the verification of the flow homogeneity is a preliminary step; the aerosol concentration homogeneity must be checked.
- Sampling efficiency: which characterize the transfer of the aerosol from the sampling zone to the measurement filter/sensing zone, conventionally defined as the aspiration efficiency and the penetration efficiency.

Assuming a monodisperse spherical inert aerosol, the following ideal quantitative parameters based on these above defined criteria were proposed:

- For stability:
 - o temporal stability of the convective velocity at the main convective inlets by measuring the standard deviation of the maximum mean velocity during a characteristic time.
 - o temporal stability of the mass concentration at a given point by measuring the standard deviation of the mean mass concentration at one point during a characteristic time.
 - Initial discussions recommend several hours of sampling with the reference manual gravimetric method considering the typical aerosol mass concentrations of the atmospheric environment (a few tens of µg/m³).
- For the transfer efficiency:
 - o Gas phase: obviously, since an aerosol consists of particles suspended in the air, the behavior of an aerosol is highly dependent on the behavior of the air itself, so that the verification of the



flow homogeneity should be a preliminary step for characterizing the transfer efficiency (considering the level of aerosol concentration in the atmospheric environment, it is assumed that the particle phase cannot have an influence on the turbulence):

- for a ventilated chamber, a tracer gas (Helium or SF6) mimics well the transfer process of a contamination, and brings some information (presence of a dead zone, i.e. a recirculating zone that can concentration the contamination and leads to homogeneity) : the logarithmic tracer gas concentration decrease by ventilation in the chamber is the parameter used to check this mixing.
- for a channel-like flow, fully developed flat turbulent velocity profile should be obtained to be sure that established turbulence is reached: the ration U/Vc (velocity/ centerline velocity) should follow the standard power law functions.
- o Particle phase: After assessing the gas phase, the particle phase should be checked ; the phenomena that can modify the transfer efficiency of the particle phase are the particle inertia (i.e. size and density of the particles), any mass change (evaporation/condensation or coagulation), turbulent diffusion and all surface losses ; for an inert monodisperse aerosol, the parameter to check the aerosol homogeneity can be the mass concentration at the potential locations where the sampling lines of the measurement devices are planned to be installed ; a proposed parameter to assess this concentration is the mean coefficient of variation at the different locations ; however, as soon the aerosol size distribution has modes of very different regimes (diffusion, intermediate, inertial), or the aerosol is composed of different types (change of density) or if any mass transfer occurs (by phase change or by coagulation), the mass concentration criteria should be supplied by number concentration and size distribution measurements at the different locations where the sampling lines of the aerosol, the residence time of the particle installed; furthermore, in case of any mass change of the aerosol, the residence time of the particle inside the chamber should be a parameter for the design of a chamber,
- For the sampling efficiency: this parameter is assessed by comparing the sampling head of the device with a reference sampler; initial discussions mentioned that the sampling lines and heads of the devices to be tested should not be considered in this work.

A 36 m³ ventilation chamber, built at IRSN in the past for studying sampling heads measurement in working environment, has been evaluated for the purpose of the AEROMET project. Only aerosol measurements have been performed here (no flow measurements but CFD simulations have been performed in the past the flow inside the facility is known) and has oriented the measurement zone: the mass concentration stability has been measured over several hours as well as the coefficient of variation over 10 different locations. Two configurations have been tested, modifying mainly the way the aerosol is injected (and also the references probes location). Some modifications of the facilities were under discussion to improve such results on the homogeneity and perform numerical calculations in that way. However, it appeared more interesting to design a chamber that was easy to construct, so having a lower volume; this chamber does not allow also an easy extension to humidity and temperature tests. As a result, such kind of chamber was not suitable for AEROMET, and has thus not been retained by IRSN as a possible design of a mixing chamber within AEROMET; however, such large scale chamber have the main advantage of allowing to put aerosol analyzers inside the chamber ; it could be interesting to re-evaluate the use of such large-scale chamber by performing more investigations outside the AEROMET project. The use of a ventilator was prohibited in the design of the ventilated aerosol chamber. Even if a ventilator is very useful to mix gases or particles, it generates a level of turbulence that is difficult to characterize and to simulate, in other words, it induces some uncertainty on the boundary conditions of a numerical simulation. In order to use numerical simulations with good confidence, such uncertainty in boundary conditions are to be avoid. As a result, simulations would not have been valuable for the design and further study, including some mass transfer effects, would the not be good to simulate. The objective of the design of a ventilated chamber was thus not to use a ventilator to control the boundary conditions.

Furthermore, the aerosol sampling zone should not be in the convective flow, but in so-called calm (still) air, since in such a volume chamber, isokinetic sampling is out of scope. At least, dead volume should be avoided because they generate a kind of secondary diffusive flow that can only lead to inhomogeneity in gas and aerosol. As a result, to achieve mixing without a ventilator, with a zone of still air, but without dead volume, many different simulations have been performed with different parameters. After considering the simulated flow of all the designed chambers, a few configurations have been selected in order to evaluate their flow homogeneity using so-called tracer gas technique. For this technique, the slope of the decrease of a tracer gas concentration (decrease only due to the ventilation rate of the chamber) is evaluated. If a single slope is



obtained, the configuration indicates no dead zone, which is the minimum requirement before assessing aerosol homogeneity. These results mainly indicate that for such geometrical configurations, no dead zone is obtained. It is also good to notice that the conclusion was the same for several sizes of the volume of the chamber. Since the volume of the chamber did not played a role here, a smaller volume chamber of 1m³ was chosen, in order to reach a steady state more rapidly. In order to avoid the convective flow interacting with the sampling zones of the aerosol devices, the upper inlets configuration was chosen. It was verified by numerical simulations that a calm air, i.e. an air velocity below 0.2 m/s was obtained. This last configuration kept for the AEROMET project is an upper gas injection and a lower facing opening and several aerosol sampling lines that can be connected at a so-called sampling level. An aerosol upper aerosol injection was added at the same level of the main gas flow injection. The results of this design are still under post-processing at this time. However, since the flow is low, and the aspiration effect on the velocity has an impact of a small region, this effect should not be important if only one or two devices are connected. However, numerical simulations will assess this point. Flow velocity has been validated by comparing the velocity values obtained by PIV (Particle Image Velocimetry) and the simulations. This evaluation has been performed in the 1 m³ chamber. A good agreement is observed in the main convective flow. This allows to validate the parameters of the simulations for velocities.

The capacity of the numerical calculations to simulate the general flow configuration and especially the gas mixing rate has been assessed. This point is important, since in a chamber, it is not possible to validate the low at all locations, like in a tunnel type chamber where the flow is mainly only in one direction. So, the values of the velocities in a given zone do not assess completely the kind of flow. Mixing rate was evaluated on the basis of the tracer gas techniques described earlier in the document. A comparison between numerical calculations and experiments was arranged for. These results were obtained with different meshes and different conditions (including an injection pipe for the gas or injecting directly the gas from a whole) and show that the performed simulations are in good agreement with the experiments. Since the simulations do not include any mass transfer (evaporation of a volatile aerosol or coagulation between aerosols), if the flow is homogeneous, there is no real reasons that an inert aerosol in a given size range should not be homogeneous in the so called sampling zone, especially in a long integrated time, which is one of the requirement if the gravimetric method is used in such a chamber. The only reasons could then be the aerosol injection stability. This parameter has thus been checked experimentally before performing aerosol mass concentrations measurements at different locations on the sampling plane. Temporal stability of the gas velocity boundary conditions has been assessed by measuring the velocity field using Particle Image Velocimetry close to the inlet locations at different times during the steady state, over a ten minutes period. Temporal stability of the aerosol concentration directly at the inlet of the chamber is not directly measured here, but the stability at one given point of the chamber was measured experimentally and found to be of less than 5% (calculated over 2 hours). The aerosol mass concentration has been measured at 21 locations on a horizontal plane. The global coefficient of variation is found to be less than 5%.

METAS developed and tested a novel facility to generate a homogeneous mixture of different primary aerosols (salt, dust, soot and aged soot) in a downward pipe flow. This facility consists of a 2.4-m-long pipe with inner diameter of 160 mm. The primary aerosols are injected in the centre of the pipe and are subsequently mixed by three air jets arranged concentrically around the pipe. Details on the design of the facility will be presented below. Isokinetic sampling can be achieved by using differently sized extraction cones that lead the aerosol to the reference gravimetric method and the different devices under test (oscillating microbalances, light scattering instruments etc.).

Measurements of the homogeneity of an aerosol consisting of 500 nm PSL particles showed that 2.3 m downstream of the aerosol injection the distribution was homogeneous within 5%. CFD simulations and Laser velocimetry measurements showed that the flow exhibited a turbulent "flat" velocity profile at the sampling location, although the Reynolds number is around 1800.

Temperature and humidity control were to be realised using Nafion membrane humidifiers (Permapure, USA) which have been successfully used in other aerosol facilities. Flow-controlled air will be delivered through these while the membranes are covered with flowing temperature-controlled water. This leads to a fully saturated airflow at water temperature. The air flow will be subsequently heated up by passing through temperature-controlled pipes. This will allow to simulate typical European winter (5 °C and 80% RH) and summer (20-25 °C at 60% RH) conditions. The two inflows, namely the top main flow and the flow through mixing jets (see figure 20), will be separately controlled with mass flow meters.

The facility consists of a 164 mm inner diameter pipe with 2.3 m total length. 120 l/min of air is delivered from the top through 5 inlets, each having a diameter of 8 mm. One is placed centrally, the other four at equal



distances around the centre. 40 cm downstream of the top, the premixed aerosol is injected through an 8 mm inner diameter pipe. Further 15 cm downstream, 3 axially symmetric pipes with an inner diameter of 4 mm and a downward inclination of 60° are built. Each pipe injects 20 l/min of additional mixing air. Even further down, two 90 cm pipe sections, connected smoothly with flanges, allow the flow to develop. At the bottom, air is iso-kinetically extracted with the use of specially designed sampling probes. Each probe has the shape of a funnel and its dimensions have been selected according to the flow rate of the measurement device. The excess flow is directed to the exhaust system of the lab.

Two different aerosol mixing chambers have been designed by METAS and IRSN, thus following complementary approaches. After consultation with WP1 partner institutes the chamber designed by METAS (SAC chamber) was selected for the calibration of automatic PM monitoring instruments.

This chamber allows for a fast-dynamic change of aerosol properties and fast recovery of equilibrium conditions has a cylindrical form installed vertically to minimise gravitational losses of large particles (>1 µm diameter). It is equipped with inlets for various primary aerosol species, a multiple-stage dilution air injection allowing for turbulent mixing, humidity and temperature control for aerosol processing. This chamber accommodates isokinetic sampling ports and allows for an aerosol homogeneity of better than 1.5 % at the different sampling outlets (see Figure 1).

The dimensions of the chamber are such that it can fit into a standard laboratory. Material costs for its construction do not exceed 2 k€. A schematic representation of the chamber is presented in Figure 1.



Figure 1: Schematic representation of the pipe flow mixing chamber (SAC chamber) to be used for the calibration of automatic PM measuring instruments with synthetic ambient aerosols (left panel). Validation tests with DEHS particles indicated that an aerosol homogeneity of better than 1.5 % can be attained close to the sampling outlets of the chamber (see above panel).

strongly on the humidity.

The second main result of the AEROMET project with respect to the first objective was establishment of a protocol for the equivalence testing of PM10 and PM2.5 instruments, including a new procedure for the comparison of automated methods with the reference gravimetric method using aerosols standardised for humidity, temperature, and composition with a target uncertainty below 15 %.

Atmospheric pollution by airborne particles contributes significantly to adverse health effects, such as respiratory, cardiovascular diseases and lung cancer. It has been estimated that in Europe alone more than 500,000 premature deaths per year can be attributed to particulate matter (PM) exposure, while in pollution hot spots PM is responsible for a loss in statistical life expectancy of up to 36 months. For the member states of the EU, air quality monitoring - as laid down in the Air Quality Directive 2008/50/EC – is mandatory and comprises quantification of airborne particles and their components.

The most important metric for monitoring particulate air pollution is the mass concentration, more specifically the total mass per unit volume of air of particles with aerodynamic diameter smaller than 10 μ m or 2.5 μ m, commonly referred to as PM10 and PM2.5 respectively. Ambient limit values for these metrics have been established in Europe, the USA and elsewhere. All local, national or EU-wide action plans and measures to reduce particulate air pollution rely on air monitoring networks; the quality of data they provide depends on the measurement methods they use.

PM mass concentration was established as the default metric of PM on the basis that mass measurements can be easily made in a traceable manner. However, since then significant challenges have been understood. The gravimetric filter-based reference methods for PM10 and PM2.5 (EN 12341:2014), fall short in areas such as consistency and comparability because:

Many particles are hygroscopic, so that their mass and size depend

• Many particles, such as ammonium nitrate and some organic materials, are semi-volatile, evaporating from the filter during or after collection. The reference procedure is designed to standardize the losses of such materials to give a consistent result.

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• There can be significant sampling issues such as impaction (removing larger particles) and diffusive losses to walls (removing smaller particles) resulting in uncertainty in whether the desired size fraction has been collected.

Automatic PM monitoring systems, which were developed to enable time resolutions below 24 hours, and to allow remote real-time data collection, must demonstrate their equivalency to the reference manual gravimetric method. The demonstration of equivalence takes the form of long field comparisons using ambient air as the measured substance.

Four comparisons, each lasting at least 6 weeks, must be carried out at a minimum of two monitoring sites. This is intended to ensure variable composition and concentration of the PM fraction, with high and low fractions of semi-volatiles, high and low air temperature and humidity, and variations of wind speed to cover the impact on sampling inlet performance. However, this is an aspiration that depends on the details of the sites and the weather conditions at the time of the comparisons, even with the long times involved.

Automatic PM measuring instruments use several very different physical principles (e.g. Tapered Element Oscillating Microbalance (TEOM), beta attenuation monitors and optical scattering-based instruments). The equivalence process is therefore problematic due to the fact that the different working principles are affected by the particle properties in different ways, and may give unrepresentatively good or bad results, depending on the ambient aerosol at the time of the trial. The field trials are also long and expensive.

The proposed solution within AEROMET is a procedure for using traceable reference methods for the harmonized laboratory evaluation of equivalence, and for the calibration of automatic PM measuring instruments. A key element of the procedure is that several different test aerosols, with varying hygroscopic and semi-volatile components, for example, must be used. The use of a single test aerosol would not evaluate the accuracy of automatic instruments for all expected aerosol types, and would risk instruments being declared accurate, when in fact they had been "tuned" to a specific aerosol type.

The methodology for equivalence testing and calibration of automatic PM instruments in the laboratory is, in principle, straightforward. Automatic instruments monitor a laboratory-generated aerosol, whose PM mass concentration is known, either by parallel measurement with the reference method, from a calibrated automatic instrument, or from the parameters of the aerosol generation system.

There are two aspects of the measurement that need to be addressed: the particle size selection that determines that the correct size fraction, PM10 or PM2.5, has been made; and the mass determination, which, as mentioned above, is sensitive to the hygroscopicity and volatility of the aerosol particles. The size selection is not explicitly dealt with in this document, whose focus is on mass determination. This is because the potential errors in mass determination are generally much larger than those from size selection, unless there are many aerosol particles with a size close to the 10 μ m or 2.5 μ m cut-off, which is unusual in normal circumstances, away from quarries, for example. The extension of the procedure to cover size selection is described in the Conclusions section.

For the mass determination aspect, the required facilities consist of:

- stable aerosol generation facilities for a mixture of non-volatile, semi-volatile, hygroscopic and nonhygroscopic particles, with realistic particle sizes (especially important for optical instruments)
- aerosol conditioning facilities for stable, controlled, temperature and humidity
- a chamber suitable for exposing PM instruments to a well-mixed, uniform aerosol of the desired type, stable over the required test duration.

There are several aspects to a working protocol for declaring automatic PM instruments equivalent, or for calibrating them. The questions are similar to those that are addressed by the Equivalence document. Detailed specifications for the laboratory facilities needed for the experimental work, and procedures for demonstrating both that the facilities are suitable for doing the work and that the specifications are being met during the tests.

A general set of parameters for the experimental work, which will depend on whether it is an equivalence trial, in which case two reference samplers would need to be present, a primary calibration, in which case one reference would be needed, or a secondary calibration, against one or more calibrated automatic instruments.

The duration of each parallel measurement would depend strongly on the requirement for reference samplers, which would typically need at least 8 hours of sampling. Without reference samplers, durations of one or two hours would be sufficient;



The number of different test aerosols would depend on the purpose of the tests. If the aim was to demonstrate equivalence of the instrument across Europe, at all types of site, then test aerosols and conditions spanning typical roadside, industrial and background pollution climates would be needed. There could be (let us say) 12 distinct test aerosols in such cases, requiring 12 test days, but this would still be a considerable improvement on the current 160 test days, which may not, in practice, cover the full set of conditions. Instruments intended for use in more limited circumstances could be given a smaller number of tests.

A set of detailed specifications for each test aerosol, including components, particle sizes, concentration of each component, total concentration, temperature, humidity etc, together with procedures for verifying that they have been met. An example set of specifications is given in table 1 below.

A description of how the generated data would be processed and used to decide on equivalence or used to calculate calibration factor(s). It would be essential that the protocol was agreed at a European level, for example through CEN TC 264 WG 15 (the working group for PM).

Table 1: An example set of test aerosol specifications. Volatility and hygroscopicity would be defined in terms of the proportions of semi-volatile and hygroscopic components.

Property	Roadside, winter episode	Roadside, winter, non-episode	Roadside, summer episode	Roadside summer non-episode		
Particle size at low sizes	Median >300 nm	Median >300 nm	Median >300 nm	Median >300 nm		
Particle volatility	high	low	high	low		
Particle hygroscopicity	high	low	high	low		
Particle mass	PM2.5: 40 µg/m ³	20 µg/m³	40 µg/m³	20 µg/m³		
concentration	PM10: 70 µg/m ³	40 µg/m³	70 µg/m³	40 µg/m³		
Temperature	~10°C	~10°C	~30°C	~30°C		
Relative humidity	80%	80%	40%	40%		

Key outputs and conclusions (Objective 1)

Overall, this objective was fully achieved. The procedures described in this document outline a proposed set of tests that could be used to demonstrate equivalence of automatic PM instruments with the reference method, or to calibrate them routinely. The essential elements of the procedure have been demonstrated experimentally. Moreover, the expanded uncertainty in the determination of the reference PM mass concentration remains well below 15 %. This experimental work has shown, for the first time, that it is practical to assess automatic PM instruments with aerosols that are representative of ambient air with controlled properties of the kind that affect different instrument types in different ways. The procedures are currently focused entirely on the mass determination part of the measurement. Extension of the procedure to include the particle size selection part could be accomplished relatively easily, by adding larger sized particles to the generated aerosol, and enlarging the chamber so that the full sampling heads can be accommodated.

With further development work, there is a realistic prospect for PM measurement to be made traceable to standardized aerosols with known properties, rather than to a standard method with uncontrolled deficiencies. This would greatly improve the accuracy and practicality of PM10 and PM2.5 measurements, with consequent benefits both to monitoring compliance with regulation and to evaluating health effects.

Objective 2: Methods for the analysis of major components of particulate matter and metals.

A key result of the project with respect to the second objective has been the successful validation for traceable methods for the determination of major components of particulate matter such as elemental and organic carbon (EC/OC), anions, cations and major metals in order to meet the data quality objectives of current regulation. This work intended to establish or improve traceable validated methods for the analysis of the major regulated components of particulate matter, which are elemental and organic carbon (EC and OC), total carbon, anions and cations, together with regulated metals (arsenic, cadmium, mercury, nickel), in order to meet the data



quality objectives of current regulation within Directive 2008/50/EC (on ambient air quality) and 2004/107/EC (on metals and polycyclic aromatic hydrocarbons).

The value of these monitoring activities to the protection of human health and environmental sustainability is crucially dependent on the traceability of the measurements, ensuring stability over time so that trends can be evaluated, on the comparability between locations so that spatial variation can be properly assessed, and should in overall be regardless of the measurement method used, which themselves need to have uncertainties to be rigorously determined and kept as low as possible. Measurements of OC and EC, ions, and metals in PM are three areas where full traceability is not straightforward, and where the currently used methods are not always comparable to other monitoring systems (such as EMEP). The work within AEROMET improved SI traceability for these important measurements, generating robust measurement uncertainties and helping reduce them from their present levels. The Directive's data quality objective for metals measurements, for example, is 40 %, and by applying the knowledge gained in the project, the uncertainty of measurements should be reduced to 30 %.

Regarding elemental and organic Carbon (EC and OC) large Inter-laboratory comparisons have been arranged for as AQUILA/ACTRIS comparisons. NPL took part in two inter-laboratory comparisons (ILCs), organised jointly by AQUILA and ACTRIS for EU air quality reference laboratories, in 2017 and 2019. The ILCs were ran by ECAC (The European Centre for Aerosol Calibration) under ACTRIS-2 for the measurement of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filters. Upon successful registration acceptance by ECAC, METAS also took part in the 2019 exercise after setting up its instrumentation and procedures.

The aims of these intercomparisons were to evaluate the performances of the measurement method (i.e. reproducibility and repeatability) and of individual laboratories (bias and variability). Ambient PM2.5 aerosol samples were collected on quartz fibre filters at a regional background site in Italy (Ispra) and at an urban background site in Spain (Barcelona) for the 2017 exercise, and in 2019 at a regional background site in Ispra, Italy.

Participants were asked to report TC and EC concentration, in μ g C cm⁻², from three replicates of test ambient PM samples. Aliquots of approximately 3.6 cm x 1.8 cm randomly punched out from the test filter samples were distributed to participants. The homogeneity of the test samples was investigated prior and was assessed to be better than 4 and 3% for TC and EC/TC, respectively. It could be reliably assumed that the remaining test samples had similar homogeneities. Additionally, participants were asked to report the OC content of a phthalic acid solution (μ g/10 μ l), which had been precisely prepared and traceable to primary measurements at JRC-ERLAP (the inter-laboratory comparison exercise coordinator). This was carried out by analysing samples prepared by spiking a pre-cleaned filter punch with the 10 μ l solution. This is the procedure normally used by laboratories to determine and verify the FID calibration constant. And the purpose was to assess the uncertainty of the instrument calibration constant determination. Since each phthalic acid solution flask was not checked individually, contaminations cannot be completely excluded.

The assigned values for TC loadings and EC/TC ratios in the test samples were calculated as the robust average values among all participants for TC and among all participants applying the European standard protocol EUSAAR_2 for EC/TC ratio. The assigned value for the concentration of phthalic acid was determined from primary gravimetric and volumetric measurements.

Laboratory performances were assessed for both TC loadings and EC/TC ratio determinations based on zscores, applying as assigned values and standard deviation for proficiency assessment the ones calculated from data obtained in a round of a proficiency testing scheme. Participants showing large (i.e. z-scores > 2) and/or systematic biases were advised to carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. An ILC thus proves to be an invaluable tool by which issues can be identified and explored.

Overall, a few participants showed the systematic tendency (larger than \pm 5% on average) of overestimating or underestimating the assigned TC concentrations. A more accurate determination of the instrument's calibration constant (e.g. implementing CO2 calibration where possible) is believed to be able to correct this tendency. Regarding EC/TC ratios, 47% of all entries were within 10% of the assigned value and 79% were within the 25% of the assigned value. More than half of outliers were by laboratories applying a QUARTZ/NIOSH-like thermal–optical protocol as opposed to the EUSAAR2 protocol. A more solid and stable in time instrument set-up in terms of i) laser stability; ii) FID response in He and He/O2 phases; iii) temperature calibration and iv) transit time would correct this behaviour and reduce the observed variability in EC/TC ratio



The 2019 exercise was similarly organised, with samples based on ambient PM2.5 aerosol samples collected on quartz fibre filters at a regional background site in Ispra, Italy. For TC loadings in 2019, 77% of all entries were within 10% from the assigned TC concentration value. As seen in the 2017 comparison, a few participants showed the systematic tendency (i.e., for all test samples and larger than ± 5% on average) of overestimating or underestimating the assigned TC concentrations. Regarding EC/TC ratios, 55% of all entries were within 10% of the assigned value and 91% were within the 25% of the assigned value.

DTI characterized specific sources of carbonaceous particles, especially focusing on relationship between OC/EC and correlation with online BC monitors. Within a candle campaign finished in 2019 quartz filters were analyzed by DTI and compared with BC measurements obtained with AE51/AE33 BC instruments.

For the phthalic acid solutions, this exercise did not aim to identify systematic tendencies of a laboratory to underestimate or overestimate the carbon content of analysed samples but rather to highlight the potential uncertainty (and variability) that can affect carbon determination, when the spiking procedure is applied to determine the FID calibration constant. It is recommended to implement the calibration with CO2 injections where possible, or to carefully revise the accuracy of all steps involved in the external solution spiking procedure (calibration of the pipette volume, complete deposition of the volume onto a punch filter, drying etc.).

In summary, participating in the ACTRIS/AQUILA inter-laboratory comparison proves to be a robust exercise in TC measurements, particularly useful for a newly set up facility.

NPL and METAS also each took part in a proficiency test in 2019 organised by LGC Standards Proficiency Testing (UK). This "AIR" proficiency test scheme runs annually and is designed to provide external quality assurance for laboratories carrying out chemical analysis of workplace air samples. Fourteen laboratories took part each were sent four x 25 mm diameter quartz filters spiked with diesel fume plus two x blank filters. The primary aim of the testing was to enable laboratories performing the analysis of air sampling media (filters in this case) to monitor their performance and compare it with that of their peers. It also aims to provide information to participants on technical issues and methodologies relating to testing of these test materials. Both NPL and METAS performed well for each of the four samples NPL has taken part in the scheme in the past and through working together as part of this AEROMET project, METAS was introduced to it for future inclusions.

Regarding the TC optimisation corresponding works were carried out at NPL and METAS on optimizing the TC calibration, demonstrating the benefit of weighing the calibration solution in addition to using a standard pipette and comparing different certified solutions. There are currently no OC or EC carbonaceous aerosol standards available for instrument calibration. Calibration materials used for Total Carbon (TC) measurements are homogenous solutions containing a known concentration of a soluble organic compound. Sucrose is the compound used by one of the manufacturers of instruments in this type of analysis: Sunset Laboratory. Sunset recommends using 5-20µl of sucrose solution onto a punch sample of a filter; when using less than 5µl small pipetting errors are expected to lead to substantial differences in carbon deposited on the filter. The current calibration material used in EC/OC analysis by NPL is a solution of potassium phthalate monobasic (KPH) in distilled water that is added to blank filter material before daily analysis of samples begins. NPL replaced their use of sucrose with the compound KPH in 2014 following research into obtaining a carbon compound that was a traceable calibration standard. Previously, lab grade sucrose was used to prepare a standard solution and no equivalent sucrose with traceability appeared to exist on the market at that time. TC calibration carried out by NPL is performed by taking the punch sub-sample of a blank filter on a calibrated balance with 1 µg resolution and using a micropipette with clean tip to drop approximately 10 mg (10µl) of the KPH solution on to the filter punch. The value (to 0.1 mg) is taken as soon as it is stable and is recorded, before any subsequent evaporation, though this is a recognised challenge. Following analysis of the spiked filter, the mass-corrected values of the spiked OC is compared with the expected gravitational value and those from previous calibration runs using a control chart. The check of 10µl is carried out daily before any sample analysis is performed that day. Approximately each week, additional 20µl and 30µl calibrations are carried out in this gravimetric way. NPL currently uses an Eppendorf research pipette which is set to 10µl, thus, to achieve 20µl and 30µl calibrations, two and three drops are required to be delivered onto a blank filter, respectively.

The respective works included various activities: A preliminary short study by NPL investigated whether improvements could be made in TC calibration if the number of drops of the calibration standard solution being delivered onto a blank filter would influence the calibration. As stated above, NPL routinely carries out a daily 10µl calibration prior to sample analyses and, typically, further weekly calibrations of 20µl and 30µl. The KPH solution aliquots were applied to a (pre-cleaned) 1.5 cm2 filter (quartz) punch. These calibrations are performed using a fixed 10µl Eppendorf research pipette and thus this involves having to deliver two separate drops to achieve 20µl and three separate drops to achieve 30µl. To investigate the impact of number of drops,



a pipette with a greater range was obtained; Scipette 5-50µl, to achieve delivery of differing drops of different volumes e.g. two drops of 5µl vs one drop of 10µl.

Further work by NPL concentrated on whether the 'type' of pipette used would be critical if relying solely on the stated pipette volume, rather than by gravimetry. This is essential as measurement laboratories will either use gravimetry or volumetric values in order to assess the TC calibration. This is important because it is expected that, inevitably, different laboratories across Europe and beyond will have purchased/will purchase different pipettes depending on what is available on the market or may utilise existing equipment within their laboratory. Whilst it is appreciated that a lab will carry out its own in-house tests on a pipette prior to use, it is important to consider whether there are clear differences in the type of pipette used.

Firstly, the repeatability of masses of drops of KPH solution delivered onto a blank filter was investigated using three different branded pipettes: a) a fixed 10µl Eppendorf research pipette, b) a Scipette 5-50ul and c) a Thermoscientific Finnpipette F2 10-100µl.

A total of 20 repeat weightings were recorded for each at 10µl, 20µl and 30µl, and the mean and standard deviations were calculated.

Secondly, variation between "old" and "new" pipettes was investigated. Three new versions of the above pipettes were obtained, and the weightings repeated.

METAS investigated a different calibration material to NPL and were able to source sucrose now available to the market from NIST that had traceability status. The first part of this work involved carrying out measurements using the "pipette only" method, which is routine at METAS. Five different concentrations of sucrose standard solutions were prepared. A volume of 10µl was deposited onto the filter. The pipette used in the work was a Socorex Acura 825 adjustable volume micropipette (1-10µl), which firstly underwent in-house reproducibility tests. Each concentration of sucrose solution was measured six times.

The second part of this work involved measurements of three of the above sucrose standard solutions but using the gravimetry technique.

Summary of findings. The number of drops being delivered onto a blank filter did not overall affect the accuracy of the TC calibration; for instance, two drops of 5µl vs one drop of 10µl did not result in any significant effect. However, it was apparent during the testing of this technique that four drops of the standard solution was problematic. This is understood to be due to the likely evaporation of the solution causing the mass reading on the balance to be unstable. This meant that the mass recorded from the balance which was recorded was questionable. Therefore, it is advisable to limit the number of drops to three as a maximum.

NPL found that if TC calibration is be carried out using the pipette-only method then the type of pipette (i.e. namely its specified range) needs to be considered, along with appreciating that an 'aged' pipette should be considered for replacement. For the fixed 10µl Eppendorf research pipette it was found that there was improved accuracy and reproducibility when using a newer 'version' (New P1) compared to the existing 'older' pipette. This may be explained by wear and tear of the spring mechanism over time. The age of this pipette was over eight years old. However, since its only intended purposes to date has been used for gravimetry purposes and the exact volume not relied upon, it continues to be used. For Pipette 2, the Scipette 5-50ul model, there was no overall difference in reproducibility when using two models at 30µl, but some overall improved reproducibility for 10 and 20 µl using the more recently purchased version of the pipette. It must be noted that both pipettes were fairly new, both purchased specifically for this project task, and only purchased a few months apart from each other, unlike the 8+ years between the Eppendorf research pipettes mentioned above. For the greater range pipette, the Thermoscientific Finnpipette F2 10-100ul, the reproducibility improved for the second purchased pipette for all three volumes; 10, 20 and 30 µl. As the 'age' of the two pipettes were similar, wear and tear are unlikely to have been a reason for the difference. This shows then that even similar aged pipettes of the same model can, and do, vary in their reproducibility. The only obvious difference to that of the Scipette pipette mentioned above is the increased range that the pipette can measure to.

Overall conclusions. Both NPL and METAS have demonstrated that there are several important factors when trying to achieve an accurate measurement of TC:

Both sucrose and potassium phthalate monobasic (KPH) are suitable traceable compounds to use for TC calibration on the Sunset laboratory Analyser. Furthermore, both are readily available compounds at comparably similar costs. TC calibration can be carried out either by gravimetry or by volume but there are considerations needed for both which are mentioned below. The pipette used needs to be of suitable range and have good reproducibility if going by the volume-only method. An appreciation that the age of a pipette



may affect its ability to dispense an accurate volume, most likely due to increased wear and tear on the spring mechanism. At low concentrations of solution, there may be an issue of evaporation from the filter which will affect the value that is being read on the balance if relying on the gravimetry method.

It was found that there was a variation of methods to calculate uncertainty. In some cases, laboratories use software provided by the manufacturer of their Ion Chromatography analysis equipment to automatically generate a calibration curve and calculate the uncertainty during analysis. In most of these cases the calculation is not transparent, and the manufacturer is unwilling to give details, or provides a fixed uncertainty (e.g. 5%).

In BS EN 16913:2017 and CEN-TR 16269:2011, the uncertainty calculation refers to the full formula for calculating the mass concentration of the ion in ambient air (ug/m3), whereas the results reported in the proficiency tests below only go as far as calculating the mass of the ion on the filter (ug). We found this led to some confusion about how to calculate uncertainty for this component of the full formula. In some cases, laboratories were overestimating by using more uncertainty components then necessary, or underestimating by only using a singular uncertainty component, e.g. repeatability.

NPL use the BIPM standard "Guide to the expression of uncertainty in measurement" (JCGM 100:2008) to create an uncertainty budget, including using specialist software created by NPL to calculate the calibration curve and propagate the uncertainty using complex inverse evaluation. Based on the Ion Chromatography analysis software we use, we allocate a fixed 5% uncertainty to the peaks produced, which propagates to 10-15% uncertainty on the final result.

Several comparison studies were performed regarding both anion and cations. NPL, METAS and UPO signed up for an inter-laboratory Proficiency Test (PT) scheme for "Anions on filters", run every 6 months by LGC in conjunction with HSL. An appropriate cation comparison was not commercially available so NPL ran one with 6 participants. For the first round of the above anion PT, NPL tested the extracted solutions for a suite of cations (Ammonium, Calcium, Lithium, Magnesium, Potassium and Sodium), in addition to the anions, to see if these samples could be used for a comparison study for cations as well. Unfortunately, the blank and spiked filters all had a very high concentration of Sodium, and very low concentrations (below the limit of detection) of Ammonium, Lithium, and Potassium. All the blank and spiked filters had the same concentrations for all the cation analytes, so the blank corrected results were zero for all, so this anion PT was deemed unsuitable for us to use for cations as well. NPL based this cation interlaboratory comparison on the same format as the above anion PTs:

Different types of filters were tested to confirm which yielded the lowest blank results.

A set of spiking solutions were prepared using Certified Reference Materials (CRMs) with a variety of concentrations of each analyte. Filters were spiked and analysed over a 30-day period to confirm stability.

A new set of spiking solution was prepared for the actual comparison. Filters were spiked and sent out to 5 laboratories, with one set retained by NPL for a blind test.

NPL, together with LNE was to develop capabilities for analysis of metals on PM10 using ICP-MS and following the standard method EN 14902. NPL, LNE and UPO disseminated the traceability to the regulatory community and ensure that these capabilities contribute to the regulatory measurement providers through participation in comparisons already either organised independently of the project, such as by AQUILA, or dedicated comparisons to be organised by NPL:

<u>Intercomparison 1 – AQUILA</u>. NPL took part in the AQUILA metals intercomparison in 2018. The partner labs at LNE and UPO received samples from their national AQUILA representatives and proved their results to NPL for comparison (although LNE and UPO could not officially take part in the AQUILA intercomparison exercise). The analytes were nickel (Ni), arsenic (As), cadmium (Cd) and lead (Pb) reported in ng m⁻³.

Results summary and conclusions. There was generally good correlation between the partner results, but the sample concentrations were very low. The blank filters (quartz fibre, Whatman QMA) were found to be unsuitable for trace metals sampling due to containing high levels of all metals of interest. Therefore, this intercomparison exercise was not considered successful for the purposes of the AEROMET project. A second intercomparison was organised by NPL, using filter samples collected for the UK Metals Network (see Intercomparison 2).

<u>Intercomparison 2</u> - <u>UK Metals Monitoring Network</u>. NPL sent filters sampled with PM10 for the UK Metals Monitoring Network to the partners. The filters used were cellulose, with very low metals content. The concentration range present on the filters was representative of ambient concentrations at a variety of UK site



locations (Rural, Urban, Industrial). The analytes were nickel (Ni), arsenic (As), cadmium (Cd) and lead (Pb), with the option to provide results for additional metals if available. Results were reported in ng m⁻³.

Filter Digestion and ICP-MS analysis. All partners used comparable digestion methods based on the protocol outlined in EN14902. The filters were prepared by microwave digestion with similar temperature/pressure programs in nitric acid (HNO3) and hydrogen peroxide (H2O2). LNE also used hydrofluoric acid (HF), a variation included in EN14902. NPL and UPO used conventional quadrupole ICP-MS determination for all metals analysed. The NPL instrument was an Agilent 8900. The NPL method used helium for the determination of iron (Fe) to remove interference from ArO. UPO used a ThermoFisher X Series II ICP-MS. Their method used no interference correction. LNE used quadrupole ICP-MS (Thermo iCAPQ) for lead (Pb) and ICP-MS-SF (magnetic sector field high resolution ICP-MS, Thermo Element) for analysis of nickel (Ni), arsenic (As) and cadmium (Cd).

Uncertainty budget. All partners calculated full expanded uncertainties (k=2) in accordance with the Guide to the expression of uncertainty in measurement (GUM) (JCGM, 2008). The standard deviation of 3 repeated measurements of the samples was combined with the uncertainty associated with the preparation of the calibration standards, sample dilutions and the calibration curve regression model to give the standard uncertainty (k=1) for the sample result. This was doubled to give the expanded uncertainty (k=2).

Results summary and discussion. The lead results from LNE agreed well with the other partners, but the other metals were typically lower. The first set of results supplied by UPO were very low. The results were checked, and it was discovered that a dilution stage had not been accounted for. The dilution stages were clarified, and the results were re-calculated. Extended discussions were conducted with all partners clarifying the methods for Ni, As and Cd. All these metals have the potential to be impacted by interferences formed in the plasma of the ICP-MS. LNE used a Sector Field ICP-MS because the higher resolution achievable should reduce any signal from such interferences. NPL and UPO had used no interference reduction techniques on the expectation that formation of interfering compounds would be minimal. With no access to a Sector Field instrument, an alternative method available with quadrupole ICP-MS is to use helium gas in the reaction cell to act as a filter to remove polyatomic interferences, e.g. ArCl interfering on arsenic. It was noted that the use of cell gases results in some analyte loss as well as reducing the signal from interferences, so it is a trade-off to optimise the best gas flow rate. NPL re-analysed the samples with helium gas. NPL also spiked two samples with 1 % hydrochloric acid, to confirm if an ArCl interference was forming and influencing the signal for arsenic. Using helium, all results for Ni, As, Cd and Pb slightly reduced, but all within the analytical uncertainty (~ 10 %, k = 2) of the original results achieved without interference removal (and still significantly higher than most of LNE's results). Lead results should not have reduced when using helium, because it is not subject to polyatomic interferences. This suggests the use of helium caused analyte signal loss, possibly for all analytes. The samples spiked with 1 % hydrochloric acid showed no increase in arsenic results compared to the unspiked samples, with or without helium gas. This strongly suggests that polyatomic interferences are not forming at significant concentrations. On the basis of these findings, LNE re-analysed the samples using conventional quadrupole ICP-MS with no interference removal, the method most comparable to those used by NPL and UPO.

Key outputs and conclusions (Objective 2)

This objective has been fully achieved. With UPO results reprocessed for the dilution factor and LNE analysis by quadrupole ICP-MS with no interference removal, partner results generally agreed within the uncertainty of measurement. The exception was nickel, where LNE results were slightly high for some of the samples relative to NPL and UPO results. The overall assessment was that this provides a successful intercomparison for the purposes of the AEROMET project. Partner results showed generally good agreement (reproducibility expectations) and some lessons were learned. Potential for future projects includes investigating the differences between High Resolution Sector Field and conventional quadrupole ICP-MS, with the aim to provide explanations for discrepancies and gain a better understanding of interferences.

Intercomparison 3 - NPL and NTUA. Three samples from the UK metals network were also used for a bilateral comparison between NPL and NTUA. NTUA's digestion procedure followed EN 14902:2005 (microwave, HNO3 / H2O2) without HF due to glass parts within the ICP-MS. Their ICP-MS analysis used 7700xseries AGILENT and Icap Qc THERMO. The elements analysed by both laboratories were: Cd, As, Pb, Ni (regulatory), V, Mn, Cu, Cr, and Zn. Most results agreed within the measurement uncertainties, which are typically 10 – 15% at 95% confidence. However, Cd, Ni, Zn, As and Cr showed significant differences in some samples.



LNE, supported by NPL, PTB, BAM, NTUA, JSI and Bruker, was to develop measurement setups for analysis of aerosols collected with different size fractions, and carry out comparative evaluation of the reference (ICP-MS) and XRF methods. NTUA used ICP-MS for the comparative measurements of the 4 toxic metals (i.e. arsenic, cadmium, mercury and nickel) on the aerosol loaded filters. LNE used ICP-MS and an appropriate calibration technique to determine the total elemental composition of the aerosols collected on either substrates of different cascade impactor stages or aerosol loaded filters for ultrafine, PM2.5 or PM10 fractions. The measurement uncertainty was to be determined for each measurand, aiming to achieve an uncertainty ≤ 10 %. Complementary XRF analyses by PTB based upon independent traceability chains such as internal /external standards (chemical traceability) or reference-free XRF (radiometrically calibrated instrumentation and atomic fundamental parameters) were performed.

Objective 3: Establishment of specific calibration procedures for MPSS for ambient measurements and the provision of calibration facilities for CPCs to the CEN standard FprCEN/TS 16976.

A key result with reference to this objective is the development and the evaluation of harmonised calibration procedures for MPSS used for ambient particle number, and size distribution measurements in the size range up to 1000 nm to comply with the requirements from EU standardisation in terms of particle size determination. Mobility Particle Size Spectrometers (MPSS) belong to the essential instruments in aerosol science that determine the particle number size distribution (PNSD) in the submicrometer size range. Following calibration procedures and target uncertainties against standards and reference instruments are suggested for a complete MPSS quality assurance program:

- Calibration of the CPC counting efficiency curve (within 5% for the plateau counting efficiency; within 1 nm for the 50% detection efficiency diameter).
- Sizing calibration of the MPSS, using a certified polystyrene latex (PSL) particle size standard at 203 nm (within 3%).
- Intercomparison of the PNSD of the MPSS (within 10% and 20% of the dN/dlogDP concentration for the particle size range 20 200 nm and 200 to 800 nm, respectively).
- Intercomparison of the integral particle number concentration (PNC) derived from MPSS measurements and number concentration determined by a reference CPC.

Traceability of the parameters is provided according to the scheme shown in Figure 2.



Figure 2: Traceability scheme for MPSS calibrations (Aerosol Sci. Techn. 52, 146, 2018).

This document summarizes step by step recommended quality assurance procedures for MPSS based on the above requirements. A detailed description by TROPOS with underlying physical properties and estimated uncertainties are given in Aerosol Sci. Techn. 52, 146 (2018). CIEMAT and LUND provided consultation on



the standard operation procedures for MPSS calibrations based on their expertise with certified particle size standards and reference instruments for particle counting.

A complete calibration of a candidate MPSS requires the following steps:

- Set-up of the candidate MPSS to the configuration as it is usually operated at the observatory or laboratory, set-up of the reference MPSS and CPC parallel to the candidate MPSS.
- Initial check of flow rates, DMA high voltage and particle sizing.
- Initial intercomparison run of the candidate MPSS and the reference MPSS against the reference CPC for the total particle number concentration for at least 8 hours. Intercomparison of the PNSDs (candidate MPSS vs reference MPSS) and PNC (integrated candidate MPSS vs reference CPC).
- Evaluation of the results of the intercomparison of the PNSDs and the intercomparison of PNCs.
- Calibration of the candidate CPC of the MPSS against the reference aerosol electrometer or reference CPC.
- If necessary, solving technical problems of the candidate MPSS, which cause deviations from the reference instruments larger than the target uncertainty values.
- Final sizing and flow check.
- Final intercomparison run of the candidate MPSS and the reference MPSS against the reference CPC for the total particle number concentration for at least 8 hours. Intercomparison of the PNSDs (candidate MPSS vs reference MPSS) and PNC (integrated candidate MPSS vs reference CPC).
- Confirmation of a successful or a non-successful calibration in terms of a detailed report.

Initial checks of the MPSS system upon arrival at the calibration facility allow for limited correction of previous data obtained by the candidate system at their measurement sites. Flow rates and high voltage accuracy are checked according to manufacturer specifications. Flow rates should not deviate more than 3% from their nominal value. PSL (polystyrene latex) particles (spheres) with a certified diameter of 203 nm are used for the sizing calibration. The initial calibration is successful, if the geometric mean diameter of the main peak recorded by the candidate MPSS operated as normal, is within 3% of the certified PSL particle size (197 to 209 nm). During the intercomparison of the candidate MPSS against the reference MPSS and reference CPC, the instruments are connected to a common manifold, sampling ambient aerosol. In order to obtain sufficient counting statistic, runs last at least 8 hours. To avoid misinterpretations, periods with a clear nucleation mode are excluded from the analysis. The intercomparison of the PNSD of the candidate MPSS is successful if results are within 10% and 20% of the dN/dlogDP concentration of the reference MPSS for the particle size range 20 – 200 nm and 200 to 800 nm, respectively.

In a second step, the PNC of the reference CPC is intercompared against the integrated PNC of the reference and candidate MPSS. For a successful intercomparison, the slope (with forced zero) of each concentration plotted against each other needs to be in the target range from 0.9 to 1.1.

The calibration of Condensation Particle Counters (CPC) is based upon the traceability of a reference particle counter. The CPC used to measure the PNC is calibrated against a reference Faraday cup aerosol electrometer (FCAE). FCAEs measure very small electrical currents down to the femto Ampere range, or respectively, electrical charge densities as small as 10 -15 Coulomb/cm³ and the signal to noise ratio is the limiting factor.

FCAEs used for calibration purposes must - according to ISO 27891:2015 - have a stable zero baseline, i.e., the zero-corrected absolute arithmetic mean electric current when no particles are present must be less than 1 fA (femto-Ampere) with a standard deviation < 0.5 fA. If for example singly charged particles with a PNC of 1000 cm-3 are measured, the corresponding electrical current reading of an FCAE at 1 l/min sample flow would then be 2.67 fA with a relative uncertainty of at least \pm 20% (according to an absolute uncertainty of at least \pm 0.5 fA).

The reference FCAE must be SI-calibrated against a certified fA source (e.g., by a national metrological institute). The flow of the FCAE must be calibrated using a certified traceable flowmeter.

The reference CPC concentration linearity is calibrated against the certified FCAE using 40 nm single charged monodisperse silver particles.



A successful CPC calibration in terms of the CPC counting efficiency curve and the DP50 is a prerequisite for evaluating the performance of an MPSS. The following steps have to be considered:

- Initial status check without any maintenance to obtain the status of the candidate CPC.
 - Measuring the exact CPC aerosol flow rate, which is allowed to deviate up to 3% from the nominal flow rate. The exact flow rate should be used in the calculation of the counting efficiency
 - Checking the CPC counting efficiency curve. If necessary, the candidate instrument will then go through maintenance
- Maintenance of the candidate CPC:
 - Cleaning of the saturator wick or, alternatively, replacing it with a new one (this can be done by the user on a regular schedule)
 - Cleaning of the aerosol nozzle that focuses the droplet flow into the optics (this can be done by the user on a regular schedule)
 - Cleaning of the critical orifice that ensures a constant aerosol flow rate (this can be done by the user on a regular schedule)
 - Cleaning the optics, if necessary (this can be only done by an experienced person)
 - Measuring the actual flow rate again
- Final calibration after maintenance of the candidate CPC

For the CPC calibration of the detection efficiency curve, the particle number concentration of the monodisperse silver particles should be in the range of 1000 to 5000 cm⁻³ to avoid coincidence in the measuring volume of the CPC optics, and to reach a sufficient number concentration for the aerosol electrometer measurement. Monodisperse particles are generated in the range 5 to 40 nm and the counting efficiency is calculated, taking into account:

- the measured aerosol flow rate
- the number of particles counts at the digital CPC pulse out
- the counting time
- the PNC derived from the electrometer

To evaluate the calibration results, following targets are considered.

- The plateau efficiency should not deviate more than 5% from the reference CPC (manufacturers normally indicate an uncertainty up to 10%).
- The lower counting efficiency diameter of the CPC for silver particles should be according to manufacturer specifications.

The performance of a CPC can be evaluated by using a best fit to a function that describes the steep part of the detection efficiency curve. The theoretical fit function is used for data interpretation. The fit parameters are the plateau efficiency A [dimensionless], the lower detection limit B [nm] and DP50, C [nm]; the particle diameter is denoted by x.

After CPC calibration all initial steps are repeated:

- Check of flow rates, DMA high voltage and particle sizing.
- Intercomparison run of the candidate MPSS and the reference MPSS against the reference CPC for the total particle number concentration for at least 8 hours.
- Intercomparison of the PNSDs (candidate MPSS vs reference MPSS) and PNC (integrated candidate MPSS vs reference CPC).

If all quality criteria are fulfilled the MPSS passes the quality assurance. All steps and results are summarized in a written report:



Example of intercomparison of Mobility Particle Size Spectrometers (project No.: MPSS-2019-2-1, Participant: X, Made by: TROPOS Counter (SN): 70711Y; Location of the quality assurance: TROPOS Leipzig, lab 118; comparison period: May 20, 2019 – May 29, 2019)

Summary of Intercomparison. The candidate from X MPSS participated in the ACTRIS workshop from May 20, 2019 to May 24, 2019 with the participant. The setup of the candidate was done on Monday, May 20th, afternoon. During the Pre-Status the candidate was running under the same settings, with their own TSI Kr.85 source, like on the Institute. The performance of the candidate showed a concentration 9% lower than the TROPOS Reference Instrument No.1. On Tuesday, May 21st, after the CPC-Workshop the MPSS was checked and the first part of maintenance was done. The performance of the CPC is shown in the report of the CPC-Workshop. The TSI CPC 3772 passed the CPC Workshop after maintenance. For more information, please look at the CPC-workshop report. During the workshop week, the whole candidate was checked and trained how to optimize his instrument. In addition, the station setup and quality assurance procedures were discussed.

Within the AEROMET, ACTRIS, and GAW community, the following institutions have been identified to serve for the atmospheric aerosol community as calibration facility for CPCs:

Leibniz Institute for Tropospheric Research (TROPOS), Germany

TROPOS hosts the WCCAP (World Calibration Center for Aerosol Physics) since 2002 in the frame of the WMO-GAW network. The WCCAP is part of the ACTRIS-ECAC (European center for Aerosol Calibration) since 2015 and provides since then regular calibrations for MPSS of the atmospheric aerosol community, following the CEN standard FprCEN/TS 16976 and the standard ISO 27891. They will continue also in the future as part of a central facility in the European Research Infrastructure ACTRIS.

National Physical Laboratory (NPL), United Kingdom

NPL has an ISO 17025-accredited calibration service for CPCs using soot particles. This service is regularly used this to determine the "plateau detection efficiency" of CPCs for the United Kingdom Particle Counting Network, and commercial customers. This role will continue until at least 2024. As part of AEROMET, NPL has set up a silver nanoparticle generation facility, following the CEN standard FprCEN/TS 16976 and the standard ISO 27891. This service is expected to be available before the end of the AEROMET project.

Laboratory of Aerosol Chemistry and Physics of Institute of Chemical Process Fundamentals (LACP), Czech Republic

LACP is currently having most of the equipment needed for performing CPC. Currently, the new calibration lab in the frame of the ACTRIS-ECAC (European center for Aerosol Calibration) will be set up until end of 2020 in cooperation with WCCAP (World Calibration Center for Aerosol Physics). The calibrations will follow the standard ISO 27891 and the CEN standard FprCEN/TS 16976.

Bundesanstalt für Materialforschung und Materialprüfung (BAM), Germany

BAM provides CPC calibration with different test aerosols for outdoor and indoor aerosol measurements, following ISO 15900:2005 and ISO 27891:2012. For the latter BAM has set up a silver nanoparticle generation facility. BAM's activities focus on development of future standards and on scientific support of manufacturers in instrument development (CPC, MPSS, Chargers, FCAE).

Key outputs and conclusions (Objective 3)

This objective has been fully achieved. The final run took place from May 23 to May 24, 2019. Running the candidate using the new source Ni.63-DWD and the TROPOS Reference CPC No.4 the performance showed a concentration 9% lower than the TROPOS Reference Instrument No.1. The candidate passed the standards of ACTRIS and GAW conditions.

The second key results regarding the objective 3 was on the implementation and the provision of calibration facilities for condensation particle counters (CPCs) following the standards ISO 27891 and FprCEN/TS 16976. The aim of the related work was to provide and implement calibration facilities to certificate the performance of CPCs (Condensation Particle Counter), following the CEN standard FprCEN/TS 16976 and the standard ISO 27891. There is a need to identify such calibration facility, because the current CEN standard FprCEN/TS 16976 will become an EU norm in near future.



Objective 4: Quantifying airborne particle compositions in the field and development of traceable and reliable x-ray analytical techniques for chemical analysis of airborne particle.

Most prominent results related to this objective involve the comparison between field campaign results and laboratory analytical results on the measurement of mass concentrations of regulated elements in ambient airborne particles, including improvements in measurement uncertainties.

The main work was to apply mobile XRF to quantify particle compositions in the field and to compare the results with lab-based techniques. In particular, the aim was to demonstrate the field capability of mobile, timeresolved and quantitative in-situ (in-field) devices, i.e. cascade impactors and mobile TXRF, for quantifying the mass concentration of regulated elements in aerosol samples collected in the field. To this end, two experimental campaigns were designed and carried out: a) at the Csillebérc Campus of the Hungarian Academy of Sciences (Budapest, Hungary), and b) at the Department of Civil and Mechanical Engineering of the University of Cassino (Cassino, Italy). While the Budapest campaign mainly focused on training and testing of the technical procedures, the Cassino campaign produced a sufficient number of comparable samples from cascade impactor sampling and PM10 filter sampling. Therefore, this report focusses mainly on the quantitative results from the Cassino field campaign. The aim was to demonstrate at least equivalent uncertainty of the combination of cascade impactor sampling and TXRF compared to PM10 filter sampling and ICP-MS and secondly, substantially improved sensitivity of the innovative TXRF-and related methods used in Task 4.1 in the quantitative chemical analysis of regulated elements. To do this, the samples generated in the experimental campaigns were reanalyzed with conventional lab-based techniques (ICP-MS, particle-induced X-ray emission - PIXE) and stationary TXRF-measuring facilities at the BESSY II synchrotron radiation facility (Berlin, Germany), EK (Budapest, Hungary) and Bruker (Berlin, Germany).

Sampling scenario in Cassino. The experimental campaign in Cassino - a middle town in Central Italy at 30 km distance from the Tyrrhenian Sea - was held at the Department of Civil and Mechanical Engineering of the University of Cassino from 17.09.2018 to 28.09.2018. The sampling site was a covered balcony (floor surface 3.9 m x 7.5 m) on the second floor of a university building and 20 m away from the nearby street. The building is in the urban area of Cassino and flanks a two-ways single lane street with free flow traffic conditions characterized by a traffic density of approx. 24 vehicles/min with a mean velocity of about 30-40 km/h. The street can be considered as a wide canyon characterized by large openings on the walls. The weather conditions during the campaign in September 2018 were stable with negligible precipitation. In the first half of the campaign the average temperature was 24.9 °C at 72.2 % relative humidity with prevalently southerly low winds. In the second half a cold front was causing a lower average temperature of 19.5 °C at 47.1 % relative humidity and with slightly stronger shifting winds from S, NW and E. Referring to data from the nearby Environmental Protection Agency measuring station the 24-h average PM10 dropped from approximately 22 µg/m3 at the beginning of the first week to 12 µg/m3 afterwards. UNICAS offered the sampling site and the sampling was executed by EK, UNICAS and BAM. The labelling and storage of the samples was executed by BAM. The on-site XRF analysis was performed by Bruker. The dust monitoring was executed by UNICAS, JSI and EK. In order to compare on-site XRF analysis with lab-based ICP-MS, synchronous samples were obtained with several instruments. Four Cascade impactors were employed for size-resolved aerosol sampling at high temporal resolution (\geq 1 h) and the samples of two cascade impactors were analysed on site by XRF. Four PM10 samplers were employed to sample aerosol particles at a lower temporal resolution (\geq 3 h) and the samples were stored for lab-based ICP-MS analysis. The lower temporal resolution was required to provide enough particle mass on the filters for ICP-MS analysis. The atmospheric dust concentration, size and black carbon content was monitored continuously during the campaign by GRIMM OPC, Dust-Track, SMPS, APS, TEOM and Aethalometer. A sampling time of minimum 1 hour was enough for subsequent on site XRF analysis. Samples were also taken each night and over the weekend. The strategy during the campaign was to take several samples with different instruments in concurrent sampling blocks. Four cascade impactors were used to sample at a high temporal resolution (\geq 1 h) and at different size classes. The samples of two cascade impactor were analyzed on site with the mobile XRF device provided by Bruker Nano GmbH. Four PM10 samplers were used to sample at a lower temporal resolution (\geq 3 h) in order to collect enough particle mass for lab-based ICP-MS analysis. The PM10 sampling was interrupted during time intervals when cascade impactor samples were taken. Therefore, the PM10 samples are comparable to the cascade impactor samples.

Sampling and Instrumentation. The following aerosol samplers were used during the experimental campaign:

two PM10 samplers working at a nominal fixed flow rate of 1.0 m³/h (according to the US standard US-EPA 40 CFR) to collect PM10 through low porosity cellulose nitrate filters with a diameter of 47 mm and a pore size of 0.45 µm for further ICP-MS analyses;



- two PM10 samplers working at a nominal fixed flow rate of 2.3 m³/h (according to the standard EN 12341:2014) to collect PM10 through low porosity polycarbonate or cellulose filters with a diameter of 47 mm and a pore size of 3 µm for further ICP-MS analyses;
- one commercial Dekati DLPI 10® low-pressure cascade impactor which samples at a fixed rate of 10 L/min on 13 stages. Each stage generates, by its circular jets, rotationally symmetric deposition patterns on the carriers which consist of dots, arranged in up to four concentric rings. The stages' carrier holders were redesigned by BAM to hold acrylic discs as carriers. The discs are for single use and come with adhesive protection, which makes avoiding of contaminations during mounting easier. In the case of operation in a lightweight tent or in a mobile measuring station dismounting of loaded carriers and mounting of fresh ones takes altogether 0.5 1 h.
- one May impactor, which was extended by EK to 9 stages. Its sampling rate is 16.7 L/min. Each stage establishes a jet through a slit nozzle of 50 mm length. The slit width is decreasing with the stage cut point. The deposition pattern on each of the carriers is a thin centric stripe with varying widths of 0.1 mm (stage 9) to 1 mm (stage 3). Different types of carriers are applicable: round or square Si-wafers have a very smooth surface, which is preferable for TXRF. They are cleanable, reusable and a quick manual change of carriers at the sampling site is possible. Quartz or acrylic disc with 30 mm diameter and 3 mm thickness can e.g. also be applied and carrier holders can be designed with high adaptability.

For the on-site analysis of samples from the impactors a commercial mobile TXRF instrument (Bruker S2 Picofox®) was used which by its lack of cooling media, its low weight and its robustness allows for a manual transport to the site and on-site operation. The S2 operates in air and has an air-cooled Mo X-ray tube (max. 50 kV, 1 mA), a multilayer monochromator, and a Peltier-cooled XFlash® Silicon Drift detector with 60 mm2 detector area and energy resolution <149 eV at 100 kcps (Mo-Ka). The spectrometer comes in a 300 mm x 590 mm x 450 mm (height x width x depth) box and the weight is 39 kg. It automatically operates a cassette with up to 25 manually fed carriers which consist of either quartz or acrylic glass discs (round, 300 mm diameter, 3 mm thickness) with smooth surfaces.

The Dekati acrylic carriers have been pipetted in the center with 50 ng yttrium in an aqueous solution, which was dried up under clean air over night. Yttrium served as an internal standard for in-situ TXRF analysis. For minimization of particle re-entrainment or rebouncing the Dekati acrylic carriers have been coated with sprayable Apiezon® vacuum grease, following the procedure recommended in the manufacturer's manual.

Each stage has its characteristic pattern whose maximum lateral extension of 9 mm fits to the excitation zone width of the Bruker S2 TXRF spectrometer. A standard counting time of 1000 s per carrier using the Bruker S2 TXRF spectrometer sums up to 3.6 h for a complete measurement of a set of 13 carriers. While in principle a first come first served analysis is feasible, carriers loaded in shorter periods can easily be stored temporally before analysis at the same day or overnight.

The particulate matter load of samples for quantitative TXRF analysis is limited by self-absorption in the sampled material, which may impair the absolute quantification of elements. Therefore, the maximum collection time for TXRF was several hours at a moderate average air pollution, i.e. PM10 below 20 μ g/m³. On the other hand, PM10 sampling on filters requires under the same conditions at longer sampling more than several hours. For comparison ten sampling periods (below named RUN 1 to RUN 9), with a duration between 3 to about 60 hours, were planned and performed. In each run sampling periods of the cascade impactors precisely match the respective sampling period of the PM10 samplers. This allows for a direct comparison of PM10 and cascade impactor results.

In runs 5, 7 and 8 several TXRF-sampling periods have been lined up without gaps in between to cover the respective period for PM10 filter sampling. Besides sampling of particulate matter for ICP-MS and TXRF analyses, monitoring of airborne particle concentrations during the campaign were performed using particle counters, scanning mobility particle sizers, photometers, optical counters to provide auxiliary information. Details on the instrumentation, methodology, and preliminary results were provided in the deliverable D6 and is not replicated here for the sake of brevity.

<u>Post-hoc ICP-MS analyses</u>. All the filters used for PM10 samplings were pre-conditioned and pre-weighed under controlled conditions, as well as they were post-conditioned and post-weighed to calculate the PM10 concentration according to the standard EN 12341:2014. The ICP-MS analyses were independently performed by the project partners NPL, LNE, NTUA and NILU. Prior to the ICP-MS analyses, the filters underwent a filter preparation and digestion protocol. NPL and LNE digested the entire filters as supplied without taking any sub-sampled portions. NTUA cut the filters into quarters and digested 2 quarters from each filter in most cases (in



a few cases only 1 quarter was digested). NILU cut the filters into halves and digested 1 half portion from each filter. NILU and NTUA corrected their results for the portions analyzed. NPL, NTUA and LNE adopted very similar digestion protocols based on the standard EN 14902:2005. Filters were digested in hydrogen peroxide (~30%) and suprapure nitric acid (~70%). Microwave programs achieved temperatures up to 220 °C held for 25/30 min. Digested filter solutions were diluted to 50 mL with ultrapure water. NILU extracted each filter portion in a mixture of 1 mL supra pure nitric acid and 2 mL deionized water. Digestion of the filter samples was performed with a microwave high pressure reactor, highest temperature was 250 °C, held for 15 min. After cooling, the samples were diluted to 10 mL by deionized water.

The ICP-MS analyses were carried out as follows:

- NPL performed the ICP-MS analysis on an Agilent 8800 ICP-QQQ-MS. Calibration utilized up to 6 gravimetrically prepared calibration standards (acid matrix-matched to the samples). Analyte responses were normalised against an appropriate internal standard element (Sc for V, Cr; In for Mn, Fe, Cu, Zn, Cd; Y for Ni, As; Bi for Pb). The single quad method used He mode for Fe, No Gas (no interference removal) for all other analytes.
- LNE performed an initial analysis on a Thermo Element HR-ICP-MS to verify the absence of interferences in medium (MR) and high (HR) resolution modes. The reported results were obtained using a Thermo iCAPQ ICP-MS in Kinetic Energy Discrimination (KED) He mode. Calibration utilised up to 5 gravimetrically prepared calibration standards.
- NTUA analysis was performed on an Agilent 7700 ICP-MS and a Thermo iCAP ICP-MS. A calibration curve was generated for all analytes. Internal standardisation was applied (Sc for V, Mn; Ge for Cr, Ni, Cu, As; Ir for Pb). The method used He mode for all analytes.
- NILU determined the metal concentrations with an Agilent 7700x spectrometer. Indium was used as internal standard and was added to all samples, standards, CRMs and blank samples prior to analysis. The calibration curves were verified by analysing control samples before the filter samples. The method used He mode for all analytes except lead (No Gas mode).

<u>Uncertainty budget from ICP-MS analyses.</u> LNE and NPL supplied full expanded uncertainties (k=2) calculated in accordance with the Guide to the expression of uncertainty in measurement (GUM) (JCGM, 2008). The standard deviation of 3 repeated measurements of the samples was combined with the uncertainty associated with the preparation of the calibration standards, sample dilutions and the calibration curve regression model to give the standard uncertainty (k=1) for the sample result. This was doubled to give the expanded uncertainty (k=2). NTUA provided uncertainties calculated from the standard deviation of their sample results. NILU provided uncertainties calculated from the standard deviation of SRM measurements. The analytical uncertainties supplied were then combined with an estimated sampling uncertainty of 15 % to give the uncertainty associated with the final concentration in ambient air (ng/m³).

TXRF analyses. In-field elemental analysis of aerosol samples obtained from the Dekati impactor were carried out with the S2 PICOFOX portable TXRF spectrometer with Control software Spectra 7.8 (Bruker Nano GmbH, Berlin, Germany). Since quantitative TXRF analysis with the S2 requires the addition of an internal standard element to the sample, a key aspect of the methodology was the preparation of such an internal standard. The Dekati acrylic carriers have been pipetted in the center with 50 ng of an aqueous yttrium solution, which was dried up under clean air over night. The Y fluorescence peak areas of the prepared carriers have been premeasured before use and carriers showing more than 10% deviation from the mean have been rejected. Particles in an impactor may, due to their high kinetic energy, bounce off when they impact on the carriers surfaces before they eventually be deposited in stages downstream. While the total deposited mass is hardly affected the effect leads to a bias in the particle mass size distribution in the impactor. A standard measure to minimize re-entrainment from the carrier surface is the application of an adhesive. During the field campaigns the acrylic carriers used in the Dekati impactor have been coated with sprayable Apiezon® vacuum grease. following the procedure recommended in the Dekati manual. In the May-impactor, acrylic substrates at stages 1 and 2 (aerodynamic cut-points 17.9 and 8.9 µm) were coated in order to minimize bounce-off of large particles. After sampling, the carriers underwent the TXRF analysis. In particular, they were transferred directly from the aerosol sampling device (impactor) to the sample cassette of the TXRF spectrometer. TXRF measurements were carried out adopting the following operating conditions: Mo-Ka (17.44 keV) excitation, 50 kV, 1000 µA and spectral acquisition time of 1000 s per sample. To quantify the measured TXRF spectra, a peak deconvolution procedure was carried out to provide net counts of detected element peaks. The quantification routine was applied based on the internal standard and results are given as absolute element mass in ng. Then, based on the sampled air volume, the results for each element were converted to mass



concentrations in ng/m3. A comparison of the mobile TXRF data was performed against laboratory-based measurements of field samples collected with the May-type impactor. The analysis was carried out at EK with a compact lab based TXRF system consisting of a 50-W microfocus Mo-anode X-ray tube (Petrick, Bad Blankenburg, Germany), a Mo/Si multilayer monochromator (AXO, Dresden, Germany) for Mo-Kα excitation. The system was operated in air, at 50 kV and 1 mA, with a typical spectral counting time of 3000 s for the individual stages. The AXIL software was used to evaluate X-ray spectra. Calibration of the system was based on dried residues of liquid standards (Merck IV, 23 elements). Typically, 3000 s counting time was used for a Si wafer carrier with moderate load of aerosol particles.

<u>Reference-free GIXRF</u>. The setup for reference-free GIXRF at PTB employs radiometrically calibrated instrumentation and an atomic fundamental parameter (FP) based reference-free quantification approach. An ultrahigh-vacuum (UHV) chamber equipped with a 9-axis manipulator was employed used for the measurements allowing for very precise sample alignments in all relevant degrees of freedom. The incident angle θ between X-ray beam and sample surface can be varied from -5° to up to 110° with a resolution of 0.0005°, which is sufficient for the GIXRF and X-rays reflectometry (XRR) experiments. Additional photodiodes on a 2 θ axis allow for XRR simultaneously with the GIXRF measurements. For the detection of the emitted fluorescence radiation, a silicon drift detector (SDD), calibrated with respect to its detector response functions and detection efficiency was used. The incident photon flux was monitored by calibrated photodiodes. The PTB GIXRF setup can be installed at two different beamlines of PTB at the synchrotron radiation facility BESSY II covering an incident photon energy range of 78 eV up to 10.5 keV. The plane grating monochromator (PGM) beamline for undulator radiation provides soft X-ray radiation of high spectral purity in the photon energy range of 78 eV to 1860 eV. Hard X-ray radiation between 1.75 keV and 10.5 keV is available at the four-crystal monochromator (FCM) beamline for bending magnet radiation.

Results of ICP-MS analyses. The results of ambient mass concentrations of V, Cr, Mn, Fe, Cu, Ni, Zn, As, Cd, Pb (expressed as average value and relative standard deviation) for the different runs are reported. There was generally good agreement between the partners for most of the elements analysed. However, there were some clear instances of discrepancy. The main reason of discrepancy could be due to the blank levels (filter contamination). Both filter materials showed very high levels of Cr, Mn, Fe, Cu, Zn and in some cases Pb. While there was significant variation between the results from the different laboratories, it is fair to conclude that the levels present were much higher than would be suitable for trace metal analysis for these metals. It also seems likely that variation in the blank levels could have contributed to the discrepancies between the sample results. Further reasons of discrepancy could be addressed to the sampling times, sampling rates, and air volumes. Indeed, samples sent to LNE and NTUA were sampled at a flow rate of 1 m3/h but samples sent to NPL and NILU were sampled at 2.3 m3/h, resulting in a higher volume of air being sampled and a larger PM deposit. While the average measured concentration should still be the same, the samples with the larger deposits provide (i) a greater chance of collecting analyte quantities above the ICP-MS detection limit and (ii) a more accurate average, because a larger air volume was sampled. Indeed, better agreement between results was seen when larger air volumes were sampled (Runs 6, 7, 8 and 10). This difference in sampling rate also suggests that a different type of sampler was used, which would introduce another source of potential discrepancy of the results, if the aerosol particle size selection was slightly different, for example. Finally, the different sample preparation and the ICP-MS method adopted by the partners are expected to slightly contribute to the discrepancies of the results. Indeed, there was little variation in the digestion methods used at NPL, LNE and NTUA, which were all based on the methods described in EN14902 (CEN, 2005). The method used by NILU was slightly different, using a smaller volume of nitric acid and a higher digestion temperature, but generally the NILU results were consistent with the other partners. There was no evidence of consistently lower or higher recoveries than the other laboratories, which would be the expected outcome of a significantly different digestion efficiency. The main variation in ICP-MS methods was the application of interference removal techniques. For the reported results, both LNE and NTUA used He KED mode for all elements and NILU used He for all elements except lead. NPL utilised He mode for Fe analysis only, and No Gas mode (no interference removal) for all other analytes. Helium mode is used to filter out any potential polyatomic interferences that could form in the ICP-MS plasma. The potential negative impact of using He mode is analyte signal loss. In either case, whether removing an interference or causing signal loss, a result produced with He mode is most likely to be the same or lower than a result produced with No Gas mode. Therefore, if discrepancies in the sample results were introduced from the use of He mode, the results from NPL should be consistently higher than the results from LNE, NTUA and NILU for all analytes (aside from Fe, and Pb for NILU) and this was not observed.

<u>Results from TXRF analyses</u>. The mass concentrations of elements measured by means of TXRF for carriers (RUN 9) collected with the Dekati impactor (mobile TXRF) and May-type impactor (lab-based TXRF) are



reported and compared. The comparison was carried out considering the PM10 fraction (summing elemental mass concentrations for all stages excluding stages above that size range, i.e. sum of stages 1–12 for Dekati and sum of stages 3–9 for May impactor). This illustrative example clearly shows a good agreement between the two combinations of samplers and TXRF systems for most of the elements. In particular, a good comparability was detected for the highly concentrated crustal elements K and Ca as well as for sulphur and chlorine and fairly good for some metals, while Ni was only detectable on the Dekati sample set. Significant differences were measured for Sr and Pb. The good agreement between the two samplers was also confirmed by the size resolved mass concentrations for the elements obtained from the collection at different stages (cut-off diameters) of the samplers: as an example, the size resolved element mass concentrations measured by means of TXRF for carriers (RUN 9) collected with Dekati impactor and May-type impactor are reported. The distributions showed a good agreement size by size for most of the elements (with the exception, once again, of Sr and Pb). A similar agreement was recognized also for the other runs. Results including all the runs performed are reported. As observed, most of the data are within ±40% deviation from the mean. Here, the comparability improves with signal strengths, i.e. at higher element concentrations.

The comparison between TXRF analysis (including both Dekati and May-type impactor data reported and ICP-MS analysis in determination of mass concentrations of elements is reported for RUN9. The ICP-MS data (unless otherwise specified) represent the average data amongst the four backup laboratories. The data show a general good agreement for most of the elements analyzed for the run discussed. DFM and FORCE provided consultation on the standard operation procedures for chemical analysis of airborne particles originating from field campaigns based on their aerosol expertise.

Elemental mass concentrations of selected metals in ambient aerosols as determined by ICP-MS, could be reproduced within approximately 50% after recalibration of the S2 spectrometer and correction of the results. For recalibration of the S2 spectrometer artificial Ni test aerosols have been collected on Dekati impactor substrates and measured with the S2. Secondly, on the same set of samples a reference-free XRF mapping, i.e. a lateral scanning using a small beam profile was performed at a PTB beamline at the third-generation synchrotron radiation facility BESSY II using a UHV compatible TXRF chamber. This measurement served for a traceability to a reference. A calibration function could be derived from the comparison of the S2- and mapping data and was applied for a stage-selective calibration of the S2 TXRF spectrometer. The corrected results were used for the comparison to the ICP-MS data.

The quality of this comparison is, however, affected by the beforementioned filter contamination issue. Nonetheless, the good agreement between the two analytical techniques can be demonstrated by considering the ICP-MS-data sets with the lowest measurement uncertainty, i.e. Runs 6,7 and 8, for which obviously no filter contamination problem existed. The relative deviation of the Dekati impactor-TXRF results to the ICP-MS data are reported for the elements analyzed. The TXRF data under- or overestimated the ICP-MS data for the elements V, Cr, Mn, Fe, Ni, Cu and Zn by 50% at maximum. A much larger deviation is observable for Pb, which is in general overestimated by TXRF. The most likely explanation for this is an incorrect deconvolution of the Pb- fluorescence raw signals by the XRF analysis software due to the fact that any element which shares an fluorescence emission line with Pb has the potential to bias the calculated Pb quantity: For example, As Kα emission is at 10.54 keV, and Pb Lα emission is almost identical at 10.55 keV. Element sum peaks can overlap with emission lines of other elements, e.g. the Fe sum peak (12.8 keV) and the Pb L β (12.61 keV) emission line.

Summary of the Cassino field campaign. The results of the above activities lead to the following conclusions:

- an overall good quantitative agreement was found between the partners in their ICP-MS analyses. Nonetheless, high, variable levels of several metals were measured in some of the blank filters, indicating also unexpected and unaccountable high background contaminations on at least parts of the sampled filters. This made a proper background correction problematic and provides the most likely source of disagreement between the reported results. Minor sources of discrepancies such as slightly different sampling times and air volumes, and calibration of ICP-MS instruments in the laboratories are not expected to have contributed significantly to the discrepancies observed;
- the attempt to use cascade impactors and mobile TXRF for a measurement of element concentrations in ambient aerosols revealed that operating of the impactors and manipulation of carriers and samples as well as TXRF spectroscopy is technically workable on site within the framework of field campaigns even at very short sampling intervals below 6 h. TXRF proved to be sufficiently sensitive for the detection of element mass concentrations as low as 1 ng/m³. By this, the ability of the cascade impactor/TXRF method to deliver results at higher time resolution than the traditional PM10-filter/ICP-MS method could be demonstrated.



- the combination of cascade impactor sampling and TXRF analysis is comparable to the traditional method of PM10 filter sampling and ICP-MS for the determination of element mass concentrations in ambient aerosols. TXRF spectrometers need a careful recalibration with an independent reference which should consider the characteristics of the cascade impactor used. It could be demonstrated that deviations between the methods can be kept within 50% at maximum for most of the elements investigated here. The regulated element As could not been considered for comparison due to its occurrence at the Cassino field campaign site below or at the LLODs of the methods.
- the total element mass concentrations measured by TXRF on samples collected with the Dekati impactor (mobile TXRF) and the May-type impactor (lab-based TXRF) agreed quite well within 40% for most of the elements analyzed. Deviations were higher at low concentrations of Pb. The size distributions of elements compared quite well with the exception of Sr. In this example Ni was below detection limit for the TXRF spectrometer at EK.

A selection of the samples collected and monitored during the field campaigns has been investigated using reference-free X-ray spectrometry by PTB. A difficulty when transferring results from reference-free GIXRF to laboratory-based XRF is the disparity between the sample area of the DEKATI pattern and the incident X-ray beam which requires mapping the sample. While the laboratory X-ray sources offers a wide illumination cone which approximately matches the area where aerosols are collected. The use of synchrotron radiation requires mapping the sample area. Indeed, the spot size at the synchrotron beamlines used is a few hundred micrometers wide whereas the area covered by the deposition pattern is about 9 mm in diameter. Hence, a mapping of the collected samples was required. To do so, two different incidence angles were used. A shallow incidence angle of 1° allowed dispersing the incident beam on a sufficiently wide area along the incidence (horizontal) direction to allow for a line scan in the vertical direction. Also, the background contributions from the substrate were still considerably attenuated. A steeper incidence angle of 10° allowed achieving excitation conditions closer to standard XRF conditions but required a two-dimensional mapping scan to cover the full area where the aerosols are collected. The goal of doing two measurements was to enable a cross-check between the results obtained. Finally, when considering the Gaussian beam shape and the step size in the mapping which was chosen, there will be an overlap between neighboring measurement positions which needs to be considered before the total mass of the deposit can be calculated. The incident photon energy was 10 keV.

Table 2:	Quantitative	elemental	analysis by	reference-free	GIXRF	and the r	respective	uncertainties	(k=1)

Stage	m(K) / ng		m(Ca) / ng)	m(Fe) / ng		m(Zn) / ng		m(Al) / ng		m(Si) / ng		m(S) / ng		m(Ti) / ng		m(Mn / ng)
#4	49 ± 5		23 ± 2		21 ± 2		1.2 0.1	±	300 30	±	21 ± 2		2400 200	±	0		3.1 0.3	±
#5	110 11	±	56 ± 6	i	63 ± 6	i	5.5 0.5	±	86 ± 9)	210 20	±	3000 300	±	6.5 0.6	±	1.4 0.1	±
#6	190 20	±	54 ± 4		88 ± 9)	12.7 1.3	±	200 20	±	100 10	±	2900 300	±	2.2 0.2	±	4.3 0.4	±
#8	72 ± 7		141 14	±	161 16	±	6.7 0.7	±	330 30	±	380 40	±	2000 200	±	6.2 0.6	±	4.5 0.4	±
#9	92 ± 9		250 30	±	250 30	±	4.4 0.4	±	620 60	±	650 70	±	1700 170	±	18 ± 2		9.1 0.9	±
#10	180 18	±	510 50	±	430 40	±	1.7 0.2	±	830 80	±	1500 150	±	2500 300	±	28 ± 3		11.2 1.1	±
#12	110 11	±	420 40	±	250 30	±	0.6 0.1	±	300 30	±	1180 120	±	1400 140	±	21 ± 2		4.9 0.5	±
Blank	11		9		7		0		96		113		831		4		1	

The position-resolved measurements using reference-free XRF are of importance to enable a reliable and accurate interpretation of the quantitative results. Indeed, among the detected elements different behaviors could be observed. The knowledge on the lateral distribution of the collected elements is essential for a reliable and accurate determination of the particle masses collected with a cascade impactor. These distribution



patterns cannot be assessed with the large illumination cone provided by the X-ray tube installed in the laboratory based TXRF instrument. Thus, it is required to perform independent investigations in order to validate that the samples which are collected during the field campaigns can be analyzed in a straightforward manner. Here the reference-free GIXRF scheme implemented in the PTB laboratory at the BESSY II synchrotron radiation facility is essential to validate the samples and provide an independent cross-validation of the samples from the field campaigns (see Table 2). The benefit is that the validated samples for the different stages are representative for all samples collected and that this allows establishing possible correction factors to the measurements realized during the field campaigns and even to identify and hence reject erroneous assumptions.

Summary and conclusion. With the use of PTB's reference-free GIXRF technique, a traceable quantitative characterization of different nanoscale samples was performed. This approach allows qualifying the samples investigated as calibration samples for laboratory X-ray instrumentation and approaching the goal of introducing physical traceability for TXRF experiments realized at the laboratory scale rather than large-scale research infrastructures. In this sense the calibration of benchtop instruments, which are used for time-resolved measurements in outdoor field campaigns, with adequate and experimentally characterized, hence validated, samples is essential.

Another set of relevant results regarding objective 4 has been the traceable calibration of benchtop GIXRF devices and sampling devices for the measurement of elemental mass concentrations in ambient airborne particles ranging from the micron (PM10, PM2.5) to the nanoscale. This involves the outcome of the investigations concerning the development of traceable X-rays analytical techniques to perform chemical analysis of airborne particles. Particularly, the aim of this task is to develop artificial micro and nanostructures as reference for TXRF and GIXRF techniques and to use these to measure the elemental composition and mass deposition of airborne particles. Different micro- and nanostructures were fabricated by INRiM and UPO. CMI worked on the modeling of the X-ray standing wave field. These nanostructures were characterised by GIXRF by PTB.

At PTB, the physically traceable characterisation technique of reference-free Grazing Incidence X-Ray Fluorescence (GIXRF) spectrometry is available to measure mass depositions and elemental depth profiles of nanolayered materials. In Grazing Incidence XRF (GIXRF), the incident angle between the X-ray beam and the sample surface is varied around the critical angle for total external reflection. On flat samples, the interference between the incoming and the reflected beam results in the so-called X-ray Standing Wave (XSW) field. The intensity distribution inside the XSW strongly depends on the incident angle and can significantly enhance the emitted fluorescence intensity of an atom inside the XSW as well as reduce the substrate contribution simultaneously. In contrast to conventional Total reflection XRF (TXRF) at an angle of incidence fixed usually at 70 % of the critical angle, the GIXRF technique can take advantage of the XSW effect. Performing angular scans around the critical angle provides additional information about the depth distribution of the mass deposited on the substrate. The fluorescence signal of nanoparticles, thin layers and implantation profiles shows different angular dependencies, which enables elemental depth profiling by GIXRF.

However, the standard quantification methods of XRF rely on reference materials or calibration standards in order to compensate for missing instrumental information. As the spatial matrix elemental distribution of the calibration samples has to be as similar as possible to the specimens to be analyzed, their availability is very limited compared to the quickly growing amount of scientifically and technologically relevant material systems at the nanoscale. This aspect is even more true for samples from the aerosol phase where the composition cannot be known beforehand. Thus, using quantification schemes based on internal or external standards is error-prone since the matrix investigated and more importantly the spatial distribution of the collected aerosols on the top of the substrate can severely affect the count rates measured. Some cascade impactors as used during the outdoor campaigns generate different spatial distribution patterns on the top of the surface for each impactor stage. This discrepancy between using internal calibration standards (e.g., droplets with known mass concentration and volume added to the specimen investigated) which are based on assuming laterally homogeneous distributions and distribution patterns with pronounced localized depositions with pronounced lateral gradients requires calibrated instrumentation to be addressed. The reference-free X-ray fluorescence spectrometry methodologies of the PTB, Germany's national metrology institute allows characterizing different sample types which can thereafter be used in laboratory instrumentation as representative calibration samples. By relying on radiometrically calibrated instrumentation and knowledge of the atomic fundamental parameters, no reference or calibration standards are needed for a quantitative analysis of the mass deposition of an element of interest. The quantitative analysis in reference-free GIXRF is based on the Sherman equation, which provides the connection between the present mass deposition per unit area mi/Fi of an element with the measured fluorescence intensities Pi,j in detected counts per second for that element.



One of the candidate nanostructured sample systems consisted of aluminum nanodisks spread on a silicon wafer. The reference sample was fabricated in a three-step process. After cleaning the silicon wafer, we deposited 20 nm of Al by DC sputtering and we deposited a monolayer of polystyrene nanospheres with diameter of 200 nm. The concentration of the nanospheres was tuned so to obtain a spread distribution on the surface. The polymeric nanoparticles were used as a mask in the following ion milling process to etch the Al layer in the uncovered areas and to leave Al disks on the Si substrate. After the ion milling process, the residual polymeric mask was removed in an ultrasonic bath of ethanol. The resulting nanodisks constitute a reference material for TXRF and GIXRF measurements.

The dimensional characterisation of the afore-mentioned nanostructures was carried out by scanning electron microscopy (SEM) analysis. The evaluation of the uncertainty budget in length measurements is required and, in this framework, the calibration of the SEM magnification is of utmost importance. The standard procedure for the SEM calibration requires using a reference sample with proper feature size, depending on the selected magnification. The selected length standard was developed and patented by INRiM in the framework of the EMRP project CRYSTAL (SIB61) and it is constituted of an array of vertically-aligned cylinders obtained through the self-assembly of PS-b-PMMA block copolymers (BCPs). The molecular weight of the polymeric chains determines the values of the diameter and centre-to-centre distance of the nanostructures. The centre-to-centre distance L0 was measured by means of a metrological AFM (L0calib = (28.1 ± 0.5) nm) so that using such length standard for SEM calibration guarantees the traceability to the SI unit of length. The calibration of the SEM magnification to 160 000. The length scale can change at different magnification and working distance and it can shift over time. The measurement of the characteristic feature F is corrected by means of the measured and calibrated value of L0 as follows:

$F_{calib} = F_{meas} \cdot (L0_{calib} / L0_{meas})$

where F_{calib} is the calibrated value of the feature size, F_{meas} is the measured value prior to calibration, $L0_{meas}$ is the value of the centre-to-centre distance L0 measured by SEM and $L0_{calib}$ is measured by AFM. The dimensional SEM measurements bring a relative uncertainty of 9.9 %. The AI nanodisks had a diameter of $(0.19 \pm 0.02) \ \mu m$.

Another candidate calibration sample consisted of artificial nanoparticles spread on a solid substrate. The nanoparticles were synthesized by UPO and the samples were fabricated by depositing the nanoparticles on a germanium substrate through simple drop casting or spin coating procedures. The particles system consisted of magnetite (Fe₃O₄) seeds. Due to their magnetic properties, the nanoparticles formed aggregates with average size of (96 \pm 9) nm. Moreover, these behaviour made it difficult to obtain a uniform nanoparticles distribution on the substrate.

A third candidate reference samples is constituted of different polymeric layers infiltrated with Al2O3 by means of atomic layer deposition (ALD) treatment. These reference samples were fabricated by a two-steps process. After rinsing the silicon substrates with isopropyl alcohol, these were treated with O_2 plasma cleaning and deposited with the polymeric films. Three different polymeric solutions were spin coated over the cleaned samples. In the first case a commercial PMMA positive resist for EBL (Microchem 950 PMMA Mn = 950 kg·mol-1) was spin-coated at 4000 rpm for 60 s, obtaining a ~ 200 nm thick layer. Random copolymer samples were prepared by spinning a solution with 18 mg of P(S-r-MMA) in 2 ml of toluene over the cleaned substrates. The spin coating was carried out at 3000 rpm for 30 s obtaining a ~ 30 nm thick film. Block copolymers samples were prepared from the asymmetric PS-b-PMMA BCP with a styrene fraction of 0.71, Mn = 67 kg·mol-1 and PDI = 1.09, purchased from Polymer Source Inc. and used without further purification. A solution with PS-b-PMMA in toluene was prepared. The BCP self-assembly process was promoted by annealing the samples at 260 °C for 120 s. The resulting layer was constituted of PMMA cylindrical nanodomains with nominal diameter of d = (13 ± 1) nm and centre-to-centre distance L0 = (29 ± 3) nm oriented parallel to the substrate and embedded in a PS matrix of thickness equal to 23 nm.

The infiltration of Al2O3 inside the polymeric films was performed by ALD with TMA and H2O as precursors. The polymeric layer samples and bare Si/SiO2 substrate samples were introduced in the chamber. One cycle of ALD consists of the injection of the TMA and a nitrogen purging step, followed by the injection of H2O for the oxidation of aluminum and another N₂ purging step. Each step of the process was carried out at 80 °C for 30 s. All the samples were treated with 1, 3, 5 or 10 ALD cycles.

The thickness measurements on the polymeric layers were carried out by spectroscopic ellipsometry and the morphological characterisation of the BCP layer was performed by scanning electron microscopy (SEM) and image processing. To this goal, the PS phase was removed after the SIS process exposing the fingerprint-like



cylinders. The reported geometrical parameters of the nanostructures, i.e. diameter d and center-to-center distance L_0 , were determined at different cycles by scanning electron microscopy (SEM).

The realization of this work included a RMG between INRiM and PTB during which a PhD from INRiM conducted XRF measurements on nanostructured and fully characterised reference samples with the support of PTB staff at BESSY II synchrotron radiation facility. In particular, the block copolymer layers infiltrated with Al2O3 were characterised by means of GIXRF with calibrated instrumentation to allow a reference-free quantification of the Al mass deposition and depth-dependent reconstruction. In parallel, ordered arrays of Aucoated nanowires were characterised with XRF and complementary surface-enhanced infrared absorption (SEIRA) spectroscopy measurements were performed at MLS.

Data interpretation in techniques employing X-ray standing wave fields (XSW) is often based on fitting a numerical model on experimental data. This can be done using simple analytical solutions if the objects are ideal (e.g. spheres randomly distributed with large distances), however such approach fails when the objects are more complex – rough, agglomerated or somehow ordered.

To be able to work with more complex sample types CMI has adapted and further developed the Xray trace software which development started years ago within another EMPIR project (3DMetChemIT). It is formed by a set of numerical methods that can form the XSW in material and evaluate its distribution, using either simpler analytical approaches or using raytracing. A key feature of the software is that the sample is represented by a general voxel model. The computational domain in the calculation is defined by a parallelepipedon mesh divided into individual voxels, with an equal voxel spacing (that can differ in x, y and z). Each voxel can be assigned to have some material properties (complex refractive index and attenuation). This means that the material distribution can be in principle almost any. The voxel data can be input either by defining some basic geometrical primitives (spheres, cylinders, etc) or their combination, by loading the surface geometry data obtained using some microscopic technique as Gwyddion arrays or by using a tetrahedral mesh obtained from some 3D modeling software. In most general case thee voxel by voxel distribution can be generated using some scripting language. As an example, based on Gwyddion open source libraries we created a numerical approach to simulate the aerosol particles settlement on the surface and their potential applomeration. In contrast to using only geometric primitives, the voxel mesh is very universal and there are many further treatment possibilities. A basic example is adding a roughness to virtually any object. Surface roughness is almost omnipresent phenomenon and the smaller the objects we are treating are, the higher is its impact. The roughness addition method is based on constructing a vector displacement arrays that are then used for modifying object boundaries, by a slight alteration of the voxel positions.

The Xray trace software was benchmarked against to different reference models on simple systems where solutions are known. As part of the benchmarking a special 2D version of the code was implemented and better conformal handling of interfaces was introduced. The code is available through CMI's website.

Key outputs and conclusions (Objective 4)

This objective has been fully achieved. Mobile x-ray total-reflection spectroscopy techniques combined within size-fractionating particle sampling techniques have been successfully employed for quantifying elemental particle compositions in the field for real time analysis. ICP-MS and physically traceable, SR based TXRF analyses have been used for complementary analysis of the field samples for validation purposes. To account for drastically varying mass depositions and elemental compositions of different particle size fractions a SR based GIXRF setup has served to provide reliable results over a large dynamic range of the elemental mass depositions. A-priori knowledge on calibration samples has been achieved by the use of artificial micro- and nano-scaled structures.

5 Impact

The project partners have given 40 presentations and exhibited 17 posters, at European and International conferences. The consortium prepared 17 publications, 13 of these have been published and the rest have been drafted and/are submitted to peer-reviewed journals. In 2017 and 2019, the project organised 5 workshops on key project outputs (such as i) the Operational use of Mobility Particle Size Spectrometers, ii) the Comparison of FCAEs and the determination of diffusion losses at small particle sizes). The project results were also mentioned in 8 trade journals in various countries (such as Greece, Denmark, Hungary, France, Spain and the United States). During its lifetime the project gained 12 collaborators and stakeholders, moreover, the consortium regularly updated the project website to disseminate results and maximise impact.

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Impact on relevant standards

Partners have been contributing to many European and international standard committees. Metrological advice relating to PM, EC/OC, anions and cations, metals, and particle number concentration and sizing for regulatory purposes has already been disseminated to CEN Working groups and other relevant bodies. For example, advice on total carbon (TC) calibration was passed on at the AQUILA (Association of European Air Quality Reference laboratories) meeting in February-March 2018. Advice on more general aspects of aerosol particle number concentration and sizing measurements is being provided through ISO TC 24. After a brief introduction of the AEROMET project during the ISO meeting in Oct. 2018, members of two working groups on aerosol metrology (WGs 9 "Single Particle Light Interaction" and 12 "Electrical mobility and number concentration analysis for aerosol particles") of ISO TC 24/SC 4 "Particle Characterization" have expressed their deeper interest in the AEROMET project methods and results. The outcomes of the work on the generation of reference aerosols has been seen to directly correspond to future work items of WG9 while WG12 is interested in the calibration procedures for MPSS including the calibration facilities of CPCs and quantitative in field analysis. An update on the AEROMET project with emphasis on this work was presented to TC24/SC4, WGs 9 and 12 during the ISO meeting in Graz, Austria, in April 2019. Within the research in WP3 a knowledge gap concerning the quantification of sub 30 nm particle losses in inlets of Faraday Cup Aerosol Electrometers could be closed. The result will be presented to the ISO working group and considered for the next revision of the respective ISO standard (ISO27891) for the calibration of Condensation Particle Counters (CPC). The x-ray analytical results of the project had been presented to ISO TC201 SC10.

Impact on industrial and other user communities

Broad stakeholder interests were addressed in the regular project meetings (June 2017, February 2018, November 2018, September 2019) by means of dedicated presentations and related Q&A sessions. A stakeholder committee was formed during the first stakeholder meeting. The developed and successfully demonstrated methodology for aerosol sampling and TXRF analysis has initiated development activities at least by one manufacturer for XRF instrumentation towards automated particle collection and analysis devices. The MPSS of the participating institutes, such as the national metrology institutes from Europe, Russia, Korea, China, India, and Japan, University Lund and Aarhus have been upgraded and the representatives have been trained to evaluate the data. Feedback of the calibration workshop has been given to the manufacturers, as TSI Inc. and GRIMM Aerosol Technik Ainring GmbH & Co. KG. The harmonised decisions about the MPSS calibration among AEROMET, WMO-GAW, ACTRIS, ISO and CEN working groups are beneficial for the manufacturers as well for the community so that there is more consistent and comparable data available in the future.

Impact on the metrology and scientific communities

Aerosol metrology is included in the CIPM Consultative Committee framework through CCQM's Gas Analysis Working Group (GAWG). The early focus within GAWG has been on particle number concentration and particle charge concentration, as covered in the project, and discussed at GAWG meetings in BIPM (April 2018), in Mexico (October 2018), and Paris (April 2019). 39 presentations have been made to predominantly scientific audiences since the start of the project, including at the International Aerosol Conference in St Louis in September 2018 and the European Aerosol Conference in Gothenburg in September 2019. In order to enhance the dissemination of the AEROMET project in Europe the consortium has decided to arrange for four dedicated project sessions at the European Aerosol Conference (EAC) 2019, the 11th International Conference on "Instrumental Methods of Analysis" IMA 2019 in Ioannina, Greece, as well as at the RSC 2019 meeting in London and the E-MRS 2020 spring meeting symposium ALTECH. The dedicated sessions at EAC 2019 and IMA 2019 received about 150 attendees each.

Two dedicated workshops presenting the AEROMET project with emphasis on work on the quantification of airborne particles in the field were held at the University of Cassino (02-28-2018) and the Hungarian Academy of Sciences (05-25-2018). The workshops were attended respectively by local air quality experts of the Italian environmental agency "ARPA Lazio" and the Hungarian Meteorological Service, operator of the Hungarian Air Quality Network. Other representatives such as the head of the Department of Civil and Mechanical Engineering of the University of Cassino and the president of the Hungarian Aerosol Society as well as scientists from the departments of University of Cassino and research centres of Hungarian Academy of Sciences also attended and expressed their interest.

Longer-term economic, social and environmental impacts

The project results will provide relevant methodological improvements and innovations in ambient aerosol monitoring in order to overcome existing deficiencies in the analysis of PM, (i.e. the quantification of aerosols



and other air pollutants, sizing and quantitative chemical analysis of airborne particles). More accurate, standardised and traceable routine measurement techniques, which are flexible in time and space, will also bring a better understanding to the formation, evolution and removal of PM and gaseous pollutants in the environment. This will have an important impact on the design of targeted actions to minimise adverse effect on human health and climate change. Various stakeholder communities are directly involved in the mitigation of environmental problems related to air pollution and they will directly benefit. Additionally, a wider environmental impact has also been generated for relevant CEN standardisation and ISO projects. The main economic impact of the project results is its contribution to the prevention, or at least the reduction, of future costs for the compensation of environmental damages. Further economic impacts will be achieved through the availability of relevant new information for upcoming applications with regard to ambient air quality e.g. automotive brake dust tests, friction and wear tests, filter performance tests, particle emission from consumer products, additive manufacturing and other industrial processes. Social impact in this project has been generated by analysing adverse effects on human health and climate change using accurate and traceable measurement techniques that can bring quantitative understanding to the formation, evolution and removal of particulate matter from the atmosphere. Typical uncertainties are expected to reduce from 25 % to 15 % for PM_{2.5} and from 40 % to 25 % for metals. This project has supported the improvement of EU environmental measures by creating awareness to revise existing EU directives.

6 List of publications

- Mobility Particle Size Spectrometers: Calibration Procedures and Measurement Uncertainties; A. Wiedensohler, A. Wiesner, K. Weinhold, W. Birmili, M. Hermann, M. Merkel, T. Müller, S. Pfeifer, A. Schmidt, T. Tuch, F. Velarde, P. Quincey, S. Seeger and A. Nowak; Aerosol Science and Technology 55(2), 146-164 (2018); https://doi.org/10.1080/02786826.2017.1387229
- Facility for calibration of optical and condensation particle counters based on a turbulent aerosol mixing tube and a reference optical particle counter; S. Horender, K. Auderset, and K. Vasilatou; Review of Scientific Instruments 90, 075111 (2019); <u>https://doi.org/10.1063/1.5095853</u>
- Calibration of optical particle counters: first comprehensive inter-comparison for particle sizes up to 5 μm and number concentrations up to 2 cm-3; Konstantina Vasilatou, Kai Dirscherl, Kenjiro lida, Hiromu Sakurai, Stefan Horender and Kevin Auderset, (2020) Metrologia 57 025005, https://iopscience.iop.org/article/10.1088/1681-7575/ab5c84/pdf
- Real-time pollen monitoring using digital holography, Eric Sauvageat, Yanick Zeder, Kevin Auderset, Bertrand Calpini, Bernard Clot, Benoît Crouzy, Thomas Konzelmann, Gian Lieberherr, Fiona Tummon, and Konstantina Vasilatou; Atmos. Meas. Tech., 13, 1539–1550, (2020); <u>https://doi.org/10.5194/amt-13-1539-2020</u>
- Directed self-assembly of polystyrene nanospheres by direct laser-writing lithography; E. Cara, F. Ferrarese Lupi, M. Fretto, N. De Leo, M. Tortello, R. Gonnelli, K. Sparnacci, L. Boarino; Nanomaterials 10(2), 280, (2020); <u>https://doi.org/10.3390/nano10020280</u>
- Towards a traceable enhancement factor in surface-enhanced Raman spectroscopy; E. Cara, L. Mandrile, A. Sacco, A.M. Giovannozzi, A. M. Rossi, F. Celegato, L. De Leo, P. Hönicke, Y. Kayser, B. Beckhoff, D. Marchi, A. Zoccante, M. Cossi, M. Laus, L. Boarino, F. Ferrarese Lupi; Journal of Materials Chemistry C (2020); https://doi.org/10.1039/D0TC04364H
- Facility for production of ambient-like model aerosols (PALMA) in the laboratory: application in the intercomparison of automated PM monitors with the reference gravimetric method; Horender, S., Auderset, K., Quincey, P., Seeger, S., Skov, S. N., Dirscherl, K., Smith, T. O. M., Williams, K., Aegerter, C. C., Kalbermatter, D. M., Gaie-Levrel, F., and Vasilatou, K; Atmos. Meas. Tech.;14, 1225– 1238; https://doi.org/10.5194/amt-14-1225-2021
- Direct approach to determine the size setting error and size resolution of an optical particle counter; Mathias Geisler, Kai Dirscherl, 91, 045105 (2020); <u>https://doi.org/10.1063/1.5142907</u>
- Interaction of nanoparticle properties and X-ray analytical techniques; Rainer Unterumsberger, Philipp Hönicke, Yves Kayser, Beatrix Pollakowski-Herrmann, Saeed Gholhaki, Quanmin Guo, Richard E. Palmer & Burkhard Beckhoff; J. Anal. At. Spectrom; (2020) 35, 1022-1033 <u>https://doi.org/10.1039/D0JA00049C; https://arxiv.org/abs/2004.02955</u>
- Reference-free grazing incidence x-ray fluorescence and reflectometry as a methodology for independent validation of x-ray reflectometry on ultrathin layer stacks and a depth-dependent characterization; Honicke, P., Kayser, Y., Mühle, U., Beckhoff, B., Pollakowski, B. and Detlefs, B.; Journal of Vacuum Science & Technology A 37, 041502 (2019); https://avs.scitation.org/doi/10.1116/1.5094891, https://arxiv.org/abs/1903.01196



- Experimental determination of line energies, line widths and relative transition probabilities of the Gadolinium L x-ray emission spectrum; Malte Wansleben et al (2019) Metrologia 56 065007; <u>http://dx.doi.org/10.1088/1681-7575/ab40d2</u>, <u>https://arxiv.org/abs/1903.08085</u>
- Experimental evaluation of the in-the-field capabilities of total-reflection X-ray fluorescence analysis to trace fine and ultrafine aerosol particles in populated areas; János Osán, Endre Börcsök, Ottó Czömpöly, Csenge Dian, Veronika Groma, Luca Stabile, Szabina Török,; Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 167 (2020),105852; <u>http://dx.doi.org/10.1016/j.sab.2020.105852</u>
- Statistics of a Sharp GP2Y low-cost aerosol PM sensor output signals; Bučar K, Malet J, Stabile L, Pražnikar J, Seeger S, Žitnik M.; Sensors (Basel). 2020;20(23):6707, (2020); <u>https://doi.org/10.3390/s20236707</u>

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