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1. INTRODUCTION

This deliverable is prepared in the context of the ITINERIS project, within the Work Package 4, Atmosphere, that deals with the integration of Research infrastructures working in the atmospheric domain through synergistic approaches and cross boundaries developments.

The aim of this document is to describe the implementation plan for the specific task of the WP 4 Atmosphere about the improved analytical performances at LABEC for laboratory and near real-time in situ aerosol analysis using new instrumentation purchased under the ITINERIS project. This is in the context of 100% digital outcome of the ITINERIS project.

The document is structured in five (5) different sections. After this introduction, an overview of the LABEC laboratory at INFN Firenze and its role in ACTRIS ERIC, the European Aerosol, Clouds, and Trace Gases Research Infrastructure Consortium, is reported in section 2. Section 3 reports the gaps and the needs for the improved analytical performances at LABEC. Finally, section 4 and 5 report the procedures for recruiting personnel and procuring equipment, respectively, for the achievement of the improved analytical performances at LABEC for laboratory and near real-time in situ aerosol analysis. Annexes and references are reported at the end of the document.

2. INFN FIRENZE LABEC LABORATORY AND ITS ROLE IN ATMOSPHERIC RIS

The INFN Firenze LABEC laboratory ("Laboratorio di Tecniche Nucleari per l'Ambiente e i Beni Culturali", Laboratory of nuclear techniques for the Environment and the Cultural Heritage) is located in the scientific campus of the University of Florence (Italy). LABEC is a high-qualified centre for the development of new technologies based on particle accelerators and ionizing radiations, and for their applications in environmental contexts and in heritage science [1]. The LABEC laboratory was born in 2003 with the installation of a "small" particle accelerator, namely a 3.0 MV Tandetron produced by High Voltage Engineering Europe, HVEE, and stems from more than thirty years of experience of the research group members with accelerator-related analytical techniques. Accelerated particles are used to characterize the elemental composition of aerosol samples collected on filters by Ion Beam Analysis (IBA) techniques. IBA are a suite of analytical techniques that exploits the detection (and analysis) of radiation such as X-rays and gamma-rays, or charged particles, as emitted in the interactions obtained by the bombardment of the sample with an accelerated particle (usually proton) beam. Among IBA, the particle-induced X-ray emission (PIXE) technique has been widely used for the study of the aerosol composition [2], since up to 20 key elements (from Na to Pb) including important anthropogenic elements (S, V, Ni, Cu, Zn, As and Pb) and all the crustal elements (Al, Si, K, Ca, Ti, Mn and Fe) can be detected in only few minutes of measurement. Moreover, PIXE is sensitive to concentrations down to μg/g, it is highly quantitative (few %) and traceable, and it is a non-destructive technique, so further measurements with other complementary techniques can be carried out on the same samples. The analysis of the elemental composition of aerosol samples gives important information on several markers that may help in disentangling the contributions of different atmospheric aerosol sources.

Typically, aerosol sampling and analysis are carried out using 24-h averaged data, in order to have sufficient quantities of material to perform a chemical characterization as complete as possible, and thus to obtain indications on the predominant sources of atmospheric

aerosol. However, most aerosol emissions as well as atmospheric dilution processes change within a few hours thus daily sampling cannot track these rapid changes. High-time resolution resolved measurements (i.e. less than few hours) require suitable techniques both for particle sampling and analysis. For time-resolved sampling one of the most suitable solutions is to use a system that automatically switches the particle collection substrate, for example every hour, to obtain a sequence of high-time resolution collected aerosol spots/deposits. However, this leads to a large number of "small" (as for mass and deposit area) collected samples to be analyzed. In this framework, PIXE technique is an optimal solution for offline, laboratory-based-measurements.

LABEC hosts the ECAC-CAIS unit Elemental Mass Calibration Centre (EMC2) of the CAIS-ECAC (Center for Aerosol In-Situ - European Center for Aerosol Calibration and Characterization) of ACTRIS ERIC [3]. The main goal of EMC2 in ACTRIS ERIC is: providing proficiency tests of individual laboratory analysis through the organization of inter-comparison and round-robin exercises; operation support for quality assurance and quality control for the measurement of mass concentration of particulate heavy metals and inorganic elements by both offline laboratory measurements (filter-based) and online, near-real time, in-situ measurements; hands-on training of operators and scientists from ACTRIS user community. EMC2 will work with the aim of harmonizing the analyses of the elemental composition of atmospheric aerosol samples, in order to make data from different atmospheric observatories fully comparable.

IBA techniques provide important information about the elemental composition of aerosol samples, but they do not fully capture the chemical composition and must be supplemented, for example, with measurements of the various chemical forms of the carbonaceous component present in the particulate matter, which often constitutes the majority fraction (up to 50% by mass) in urban environments. In this regard, a key distinction is between so-called "elemental" carbon and "organic" carbon. The production mechanisms and atmospheric emission sources of these two fractions differ: elemental carbon is essentially carbon in a graphitic form, refractory to combustion, and dark-black in color, whereas organic carbon refers to all organic components, typically lighter in color, consisting of compounds where carbon is bonded to hydrogen, oxygen, nitrogen, etc. Thermal-optical analysis [4] is a standard method for determining the carbon concentration in aerosols collected on quartz fibre filters and discriminating the total carbon into the two OC and EC components. This methodology is recommended in the CEN standard - EN 16909:2017: "Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters", and it is recommended by ACTRIS ERIC too.

The list of current available instruments (including status, repository where data are stored, link to data and metadata example) is included in the ANNEX 1.

3. IDENTIFIED GAPS AND NEEDS FOR INTEGRATION

The activity of INFN Firenze will be focused to increase the availability of digital datasets concerning elemental composition of particulate matter samples with enhanced propensity for reuse according to the FAIR principles. This aim will be reached through an upgrade of the analytical performances of the LABEC accelerator laboratory for elemental in-situ analysis of atmospheric aerosol sample for ITINERIS and, in general, for the atmospheric aerosol community. This will be accomplished by improving the automatization of both the

offline, laboratory-based measurements for EC/OC analysis and the online, near-real time measurements for elemental analysis.

The high-time resolution measurements of elements are currently carried out sampling the aerosol with special high time-resolution samplers (Size and Time Resolved Aerosol Sampler, STRAS [5]) designed by INFN, followed by offline PIXE analysis at LABEC of the aerosol deposits on a collecting polycarbonate membrane [6].

The Elemental Carbon/Organic Carbon (EC/OC) measurements are currently carried out using a first-generation Laboratory ECOC thermo-optical analyser by Sunset Lab Inc., where samples are manually inserted in an oven and they are thermally desorbed from the filter medium, typically a quartz fibre filter, under an inert helium atmosphere followed by an oxidizing atmosphere using carefully controlled heating ramps. A flame ionization detector (FID), requiring the use of H2 gas, is used to monitor the analysis while pyrolysis correction is accomplished by a standard laser transmittance-based method.

For online, near-real time measurements of elements, the main activity will involve the procurement of a XACT 625i Ambient Metal Monitor; this instrument uses reel-to-reel filter tape sampling and non-destructive Energy Dispersive X-ray fluorescence (EDXRF) analysis. The air is sampled through a low volume particulate matter (PM) inlet and drawn through a filter tape. The resulting aerosol deposit is then advanced into the analysis area where the sample is analyzed by EDXRF for up to 67 elements with Z>12 (Al) while the next sample is collected, allowing automatic sampling, analysis, and near real-time reporting with time resolution between 15 and 240 minutes.

For laboratory-based measurements of EC/OC, the main activity will involve the procurement of a second and new Laboratory ECOC thermo-optical analyser with concurrent laser transmittance/reflectance optics with superior temperature controlled laser system, nondispersive infrared (NDIR) sensor for CO_2 detection (thus the use of H_2 gas in not needed anymore) and autoloader for full automation of the repetitive OCEC analysis procedures for up to 36 sequential samples. Both the old and the new Laboratory ECOC thermo-optical analysers will be installed in a new laboratory, with the costs of the design and the construction of the new laboratory technical gas pipelines paid by other funds.

List of instruments/goods to be acquired within ITINERIS:

- XACT 625i Ambient Metal Monitor (SaliBri Cooper, formerly Cooper Environmental) for automatic in-situ sampling and XRF analysis of particulate elemental matter.
- Laboratory ECOC thermo-optical analyser (Sunset Lab Inc.) with dual mode optics, NDIR CO_2 detector and autoloader for high-throughput automatic filter-based measurements of the Elemental and Organic carbonaceous fractions in atmospheric aerosol samples.

4. PROCEDURES FOR THE PERSONNEL

No personnel have been hired specifically for this activity of attaining improved analytical performances at LABEC for laboratory and near real-time in situ aerosol analysis under the ITINERIS budget.

The activity of setting-up and using the XACT 625i Ambient Metal Monitor is part of the PNRR PhD project of a student (Cosimo Fratticioli) funded by ITINERIS.

5. EQUIPMENT PROCEDURES

Purchase of XACT 625i Ambient Metal Monitor (SaliBri Cooper, formerly Cooper Environmental) for automatic in-situ sampling and XRF analysis of particulate elemental matter:

- Single supplier (*Fornitore unico*), above-threshold procedure (*procedura sopra soglia*)
- Classification by main CPV: 38947000-7 X-Ray microanalisers (*Microanalizzatori di raggi X*)
- Order issued in July 2023.
- Instrumentation delivered in December 2023

The purchase of this piece of equipment has been in line with ITINERIS timeline; the purchase procedure was concluded in December 2023 after the delivery and the verification of the instrumentation.

The XACT 625i Ambient Metal Monitor is now operational and working. The formal procedures for moving the XACT 625i and deploying it on the field (it is has a 50 kV X-ray tube) according to the Italian regulation, D.Lgs.101/2020, are under way.

Purchase of Laboratory ECOC thermo-optical analyser (Sunset Lab Inc.) with dual mode optics, NDIR CO_2 detector and autoloader for high-throughput automatic filter-based measurements of the Elemental and Organic carbonaceous fractions in atmospheric aerosol samples:

- Direct assignment (*Affidamento diretto*), below-threshold procedure (*procedura sotto soglia*)
- Classification by main CPV: 38413000-3 Pyrometers (*Pirometri*)
- Order issued in March 2023.
- Instrumentation delivered in March 2024

The purchase of this piece of equipment has been in line with ITINERIS timeline; the purchase procedure was concluded in March 2024 after the delivery and the verification of the instrumentation.

The Laboratory ECOC thermo-optical analyser (Sunset Lab Inc.) with dual mode optics, NDIR CO_2 detector and autoloader is now operation and working.

The ITINERIS scientific team working on both these instruments is composed by Massimo Chiari, Giulia Calzolai, Cosimo Fratticioli, Fabio Giardi, Franco Lucarelli and Silvia Nava.

ANNEX 1 –AVAILABLE INSTRUMENTS AT INFN FIRENZE LABEC LABORATORY

- Tandem accelerator (3.0 MV terminal voltage HVEE Tandetron) with 5 IBA beamlines and 5 measuring end stations. The accelerator is equipped with three independent ion sources, two of which (a single-sample Cs-sputtering and a Duoplasmatron) are used to produce all kind of beams (from protons to heavy ions), mainly for applications of Ion Beam Analysis.
- External proton milli-beam set-up high-current/high-throughput PIXE and PIGE analysis of atmospheric aerosol samples (PMx samples, size-segregated samples, high time-resolution samples) collected on any type of substrate (Teflon, Nuclepore, Quartz fibre...) and by a large variety of commercial samplers.
- External scanning proton microprobe set-up with detectors for PIXE, PIGE and RBS/EBS analysis; the focusing system is an Oxford Microbeam quadrupole doublet and the scanning is achieved by magnetic and mechanical scanning.
- Pulsed beam facility for irradiation of devices in-vacuum or in-air with bunches of ions (ranging from proton to oxygen), counting from 1 ion to a few thousand ions per bunch, at a repetition rate of the bunches from single shot to a few kHz.
- Multi-purpose in-vacuum scattering chamber equipped for PIXE, PIGE and RBS/EBS analysis.
- External proton sub-milli-beam set-up for low-current PIXE, PIGE and RBS/EBS analysis of thick and bulk samples, such as cultural heritage objects.
- Analytical grade micro-balance with automated filter weighing (Sartorius) installed in a controlled environment laboratory for gravimetric analysis of atmospheric aerosols.
- Laboratory ECOC thermo-optical analyser (Sunset Lab Inc.) for filter-based measurements of the Elemental and Organic carbonaceous fractions in atmospheric aerosol samples;
- Laboratory ECOC thermo-optical analyser (Sunset Lab Inc.) with dual mode optics, NDIR CO_2 detector and autosampler for high-throughput filter-based measurements of the Elemental and Organic carbonaceous fractions in atmospheric aerosol samples.
- Field ECOC thermo-optical analyser (Sunset Lab Inc.) for near-real time measurements of the Elemental and Organic carbonaceous fractions in atmospheric aerosol samples with a time resolution down to 1 hour.
- Commercial “Epsilon 5” ED-XRF spectrometer (Panalytical) in polarizing geometry for elemental analysis of aerosol (the spectrometer is currently not operational and needs refurbishing, and software and hardware upgrades).
- XACT 625i Ambient Metal Monitor (SaliBri Cooper, formerly Cooper Environmental) for automatic in-situ sampling and XRF analysis of particulate elemental matter, such as metals and dust.
- Two (2) double channels sequential samplers for PM10, PM2.5 or PM1 (Dado Lab Gemini).

- Two (2) single channels sequential samplers for PM10, PM2.5 or PM1 (TCR Tecora Skypost).
- Three (3) Streaker high-time resolution aerosol samplers (PIXE International) for collection of the fine and coarse aerosol fractions with hourly resolution (instrument out of production).
- Two (2) STRAS (Size and Time Resolved Aerosol Sampler) high-time resolution aerosol samplers (designed by INFN) for collection of the fine and coarse aerosol fractions with hourly resolution.
- Multi-stage cascade impactor (Dekati SDI, Small Deposit Impactor) for the collection of aerosols in 12 dimensional classes from 40 to 8 μm (from nanoparticles to PM10).

Datasets produced by analysis of aerosol particle samples by PIXE and other IBA techniques, as well by other complementary techniques at LABEC (Thermo-Optical, XRF…) are stored in the INFN Open Access Repository (INFN OAR):

- https://www.openaccessrepository.it/

under the Creative Commons Attribution 4.0 license. The datasets are accessible and reusable.

Stored datasets include, at least:

- Experiment title
- Contributing authors (external and local)
- Description of the experiment
- Funding institution (grant)
- Scientific community of reference
- Raw data file (measured samples and reference standards)
- Scanned copy of the logbook (pdf)
- Spectra files converted for the dedicated IBA analysis codes
- Photos of the measured samples (if any)
- Plot of the temperature in the accelerator hall during the measurements

An example can be found, amongst others, at the repository link https://www.openaccessrepository.it/record/77163 (DOI 10.15161/oar.it/77163)

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